LITERATURE OF THE COMBUSTION OF PETROLEUM

A collection of papers presented at the
Symposium on the Literature of the Combustion
of Petroleum held by the Division of
Chemical Literature and the Division of
Petroleum Chemistry at the 129th national
meeting of the American Chemical Society
in Dallas, Texas, April 1956

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Introduction

This volume comprises the papers presented at a symposium held at Dallas, Tex., in April 1956, which was sponsored by the Division of Chemical Literature and the Division of Petroleum Chemistry of the AMERICAN CHEMICAL SOCIETY. We are especially grateful for the help provided by D. P. Barnard, research coordinator, Standard Oil Co. (Indiana), and Cecil E. Boord, professor emeritus of Ohio State University, who reviewed the program during its formative stages, presided over the sessions, and enriched the discussions. Their assistance was particularly valuable because we accepted the invitation to arrange the symposium on the basis of our experience in organizing technical information rather than because of any special competence in the field of combustion.

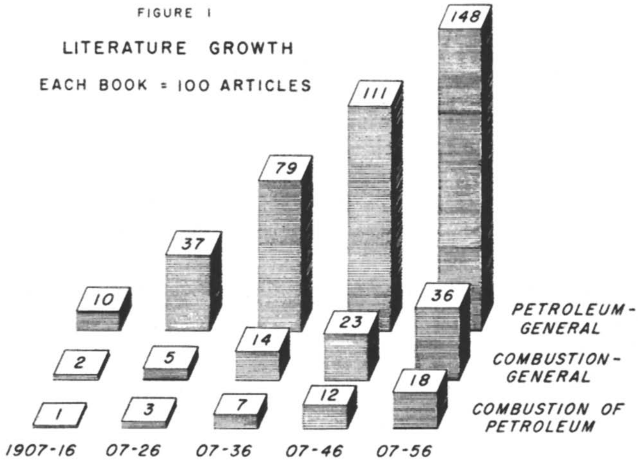
Historically significant progress in the technology of the combustion of petroleum had occurred in the first half of this century. This has gone hand in hand with the amazingly steady growth in the use of energy in the technically progressive areas of the world. The accelerative growth of combustion literature can be attributed in part to technological advances in the automotive and aviation industries, and in part to the impetus given to research on all aspects of combustion by World War II and the desire for security that followed.

D. P. Barnard put his finger on the special advantages enjoyed by petroleum as a fuel for engines, which led to its present position as our most important fuel. The very high rate of heat release possible with a liquid fuel makes it ideal for use in internal combustion engines, which are a relatively cheap apparatus made mostly from cast iron. In the internal combustion engine—with its high specific output, good efficiency, and low cost per unit of power—combustion takes place for only a brief period in the cycle. More recently, we have become vitally interested in engines that release heat at a high rate continuously. In the case of the aviation turbine and the turbo jet, heat release—although lower than the transient rate in the gas engine—is close to the limit that even exotic materials of construction can tolerate continuously. The rocket represents conditions even more drastic in which energy release for many seconds exceeds that of the transient rate of the gasoline engine.

The diesel engine, the turbine, and the rocket are less amenable to the rule of thumb and crude experimental approaches that were so successful in the case of the gasoline engine, hence there has been great interest in the basic phenomena involved in combustion. In these engines, the combustion of each individual droplet is extremely important; hence, basic research in the combustion of droplets of fuel has been most extensive and rewarding. Besides the fundamental work, many practical problems have been encountered and partially solved. With this broad attack on the problem—from both fundamental and practical points of view—there has been an explosive growth of knowledge in the last decade.

Much of this knowledge appears in the literature of both petroleum and combustion—which, like all literature, has become unwieldy. The rapid accumulation of chemical literature in areas of petroleum and combustion, as measured by entries in *Chemical Abstracts Decennial Indexes,* is shown in Figure 1. From 1907 to the end of this year, about 15,000 items will have been cited on petroleum and nearly 4000 on combustion. The literature common to these two major areas—the combustion of petroleum—is hard to handle because of its growth in several directions and the practice of groups of scientists to report their work in publications of limited circulation. There will be in this same period about 2000 citations specifically on the combustion of petroleum fuels.

FIGURE I



LITERATURE GROWTH

EACH BOOK = 100 ARTICLES

The chemical literature on the combustion of petroleum is only a fraction of the total, however, as combustion involves several sciences in a major way. Physicists, engineers, mathematicians, metallurgists, and others are active in this field and have provided important segments of relevant literature.

Those specializing in combustion studies have taken steps to co-ordinate their work and to provide a special literature. This has been done by setting up organizations designed to aid communication among the disciplines active in combustion research:

The National Advisory Committee for Aeronautics (NACA) was created by Congress in 1915 and has published well over 500 technical reports and memoranda dealing with various phases of combustion.

The Coordinating Research Council (CRC) organized in 1942 jointly by the American Petroleum Institute and the Society of Automotive Engineers, issues reports dealing with practical problems in combustion which are of concern to the petroleum and automotive industries.

Project Squid, a cooperative program for basic research in jet propulsion, supported jointly by the armed services, has issued reports dealing with the combustion of jet fuels.

AGARD, an advisory group for aeronautical research and devlopment, functions under the North Atlantic Treaty organization, and has issued books and reports on combustion.

The Combustion Institute, which deals exclusively with combustion, was formally organized on July 1, 1954, and has held six international symposia, all papers of which have been published. The sixth was held in August, 1956 at Yale University.

In addition, the Bureau of Mines and the Bureau of Standards have issued many reports and bibliographies through the years. The publications of these special organizations and regular government agencies contain a great amount of significant information on the combustion of petroleum which must be integrated with that from other sources.

Our aim in this symposium was to gather a selective and up-to-date interpretation of the literature on the combustion of petroleum to aid further progress. Our hope is that it will prove useful to petroleum scientists, younger researchers entering this important field, and the harried literature searchers who are called upon to bring to light facts and theories buried in the archives.

Whatever success we have had in attaining our objectives must be credited primarily to the authors who have contributed to this volume. These men, working in such a vital field, have been unusually busy. Their willingness to give time and talent to improving communications speaks well of their devotion to science and progress.

E. L. d'Ouville, *Chairman*
M. L. Kalinowski, *Cochairman*

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Cool Flames and the Organic Reaction Mechanisms Involved in Their Formation

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The initial step in the oxidation of a hydrocarbon is substitution. For saturated hydrocarbons such as open- and closed-chain paraffins and the alkyl groups of other hydrocarbons, the substitution reaction moves by a free radical mechanism, and sets up a chain reaction. This mechanism has been most fully explored in the field of photochemistry. The substitution product is an alkyl hydroperoxide. The degradation reaction, essentially a second stage in the oxidation, may be intra- or intermolecular, and the degradation may be mono- or bimolecular. The rate of degradation is a function of the temperature and is readily subject to catalysis. The "stabilized cool flame" tube of Barusch and Payne, as modified by Oberdorfer, and the motored engine are effective for separating the primary combustion products. Chromatography, polarography, and spectroscopy provide excellent techniques for the analysis of such products, and may make it possible to follow the combustion step by step, from the hydrocarbon to carbon dioxide and water.

The first recorded observation of cool flames was made by Davy (*15*). Perkin (*33*) further explored the phenomenon, developing what might be described as a lecture demonstration technique and noting that aldehydes and acids were produced. Leighton (*21*), at the suggestion of W. D. Bancroft, reinvestigated and confirmed Perkin's observations.

Midgley (*29*) and his coworkers, in America, and Ricardo (*36*) and his coworkers, in Great Britain, during the early 1920's independently discovered that different pure hydrocarbons behave differently when used as fuels in the spark ignition engine. Following the pioneer work of Midgley and Ricardo, other investigators have contributed much to our knowledge of the engine performance of individual hydrocarbons. Since 1938 an American Petroleum Institute Research Project (APIRP–45) has addressed itself systematically to the problem of which hydrocarbons give good engine performance and which perform poorly.

Callender (*12*) reporting on work done in the Air Ministry Laboratory by Mardles, Stern, and Fowler, under the direction of K. O. King, states that paraffins by slow oxidation yield aldehydes, carbon monoxide, and water. These authors believed the aldehydes were not the first products formed and it was argued that the addition of oxygen to paraffins should form peroxides, which naturally give rise to aldehydes.

Emelius (*17*), in 1926, describing the spectra produced by the phosphorescent flames

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of carbon disulfide and of ether, found the characteristic spectra of acetaldehyde among the low temperature combustion products of ether. Reporting further, in 1929, he stated that interest in this phenomenon was revived by the discovery that substances giving such a flame have a tendency to promote knocking when used as motor fuels, while many "antiknocks" inhibit the flames.

Reporting in detail on these and similar experiments, in 1928, Mardles (*28*) concluded that the active oxygen obtained during the slow oxidation of fuel-air mixtures is greatly diminished if the mixture is heated longer than required for the initial formation of the peroxide, showing that the primary peroxides because of their greater reactivity are very short lived.

The activity of the primary peroxides formed in hexane-air or ether-air mixtures is also demonstrated by the autoxidation of benzene and aniline, which occurs readily in the presence of hexane or ether, but cannot be induced at equally low temperatures in their absence.

The effects mentioned above have been attributed by others to hydrogen peroxide, but experiments lead to the conclusion that the hydrogen peroxide produced from combustion in heated tubes or in the engine during compression is a decomposition product arising from much more active and unstable peroxides previously formed.

The author believes the present experimental work confirms the view previously expressed, that the detonation in an engine using liquid fuel is due to the formation of organic peroxides, which become concentrated in the nuclear drops during compression and ignite them simultaneously where the detonation temperature is reached. The addition of detonation inducers such as nitro derivatives, amyl nitrite, and benzoyl peroxide to a variety of fuels shows that the temperature of spontaneous ignition is lowered in all cases and detonation preventors, such as organometallic compounds, have the opposite effect.

Pope, Dykstra, and Edgar (*34*), in 1929, published three papers on the mechanism of the vapor phase oxidation of isomeric octanes. The flow method was used. *n*-Octane was burned in a mixture of oxygen and nitrogen approximating the composition of air. A chemiluminescence filled the tube with occasional flashes from end to end. The principal products were aldehydes, water, and carbon monoxide. Some carbon dioxide was produced also.

The reaction mechanism was explained on the theory that the oxidative attack was through the methyl group, *n*-octane being converted to *n*-octaldehyde and this in turn to the next lower aldehyde, with the elimination of carbon monoxide. The degradative action was believed to be repeated step by step, through a "nonstop run," to formaldehyde as the final product. *n*-Heptaldehyde and *n*-butyraldehyde gave essentially the same products. It was believed the luminescence was due to the chain reaction by which each aldehyde was converted to the next lower aldehyde with the elimination of carbon monoxide.

$$\begin{array}{lclcllll}
CH_3\text{—}(CH_2)_6\text{—}CH_3 & + & O_2 & \rightarrow & CH_3\text{—}(CH_2)_6\text{—}CHO & + & H_2O & \\
CH_3\text{—}(CH_2)_6\text{—}CHO & + & O_2 & \rightarrow & CH_3\text{—}(CH_2)_5\text{—}CHO & + & CO & + \; H_2O \\
CH_3\text{—}(CH_2)_6\text{—}CHO & + & 1.5O_2 & \rightarrow & CH_3\text{—}(CH_2)_5\text{—}CHO & + & CO_2 & + \; H_2O
\end{array}$$

The second paper dealt with the oxidation of five isomeric octanes. The results in these cases were interpreted in an analogous manner, the oxidation starting with the methyl group of the longest free chain, and the degradation continuing stepwise down to the point of branching, where the reaction was remarkedly slowed down.

In the third paper it developed that the effect of tetraethyllead was chiefly that of slowing down the oxidation of aldehydes to the next lower aldehydes.

The authors were aware that Callender, Mardles, and their associates believed that peroxides were formed. They found some evidence that the reaction mixtures would reduce aqueous potassium iodide solution but were unable to concentrate any peroxides in the low temperature condensate of the reaction mixture. They rejected the hydroxylation theory on the basis of the findings of Layng and Youker (*20*) that *n*-heptyl alcohol proved more difficult to oxidize in the vapor phase than *n*-heptane.

Beatty and Edgar (*7*) studied the oxidation of *n*-heptane, 1-heptene, and 3-heptene. They observed that the olefins oxidize more slowly than *n*-heptane. Iso-octane was sluggish when oxidized alone. These hydrocarbons show a marked negative temperature coefficient in the region between 400° and 500° C. The chemiluminescence of *n*-heptane was studied but peroxides were not mentioned.

Bone (*9*), in a lecture before the Chemical Society on October 19, 1933, gave some consideration to the "peroxidation theory." He said in part:

> In recent years, there has been much talk about the initial association of the hydrocarbon and oxygen resulting in an alkyl "peroxide" rather than in an hydroxylated molecule, and ... we may profitably consider the suggestion in the light of the latest evidence available.
>
> Alkyl peroxides—e.g., $CH_3—O—O—H$ and $CH_3—O—O—CH_3$—which were first described by Baeyer and Villiger (*3*) and more recently have been reinvestigated by Reiche (*35*) and collaborators, are obtained upon acting a dialkyl sulfate with hydrogen peroxide in alkaline solution. They are unstable endothermic liquids which readily explode upon being suddenly heated or subjected to "shock," producing aldehydes and hydrogen together with hydrocarbons, alcohols, acids, and steam.
>
> It was the late Professor Callender (*12*), who as an outcome of experiments upon the slow combustion of hexane which resulted in the formation of valeraldehyde, acetaldehyde, and formaldehyde without any detectable initial hexyl alcohol, $C_6H_{13}OH$, first suggested that the initial oxidation of a hydrocarbon in air more probably involves the formation of an alkyl peroxide "by the direct incorporation of the oxygen molecule in the hydrocarbon molecule after the collision" which subsequently decomposes into aldehydes and water; thus
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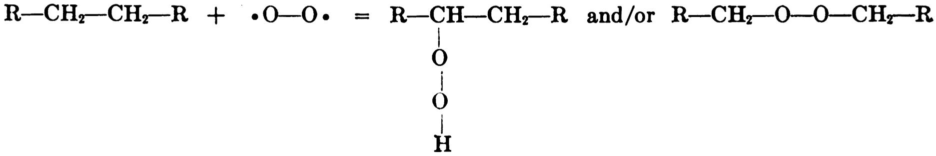
> 
>
> $$R—CH_2—CH_2—R + \cdot O—O\cdot = R—\underset{\substack{| \\ O \\ | \\ O \\ | \\ H}}{CH}—CH_2—R \text{ and/or } R—CH_2—O—O—CH_2—R$$
>
> The idea was then put forward to explain "knock" in petrol engines, though it is rather difficult to see how; if valid in such connection, it can at the same time be applied to the normal course of the combustion.
>
> Two years later Thompson and Hinshelwood (*40*) after studying the kinetics of the oxidation of ethylene in silica vessels at temperatures between 400° and 500° and finding that the rate is affected by the total pressure approximately in a reaction of the third order, the effects depending very much more on the partial pressure of the ethylenes than on that of oxygen, suggested as a *via media* that while "there is no doubt that Bone's interpretation of the course of the oxidation as a process of successive hydroxylations is essentially correct ... the first stage in the reaction is the formation of an unstable peroxide; if this reacts with more oxygen the chain ends but if it reacts with ethylene, unstable hydroxylated molecules are formed which continues the chain." It should be noted, however, that they adduced no experimental proof of the actual initial formation of the assumed peroxide.
>
> Although at first sight the notion may seem plausible enough, and obviates the difficulty which some feel of an initial termolecular reaction, I venture to think that it is not merely unsupported by any valid experimental evidence but contrary to much that has been established.

And so the issue was joined: "hydroxylation" versus "peroxidation." It is true that if all of the hydrogen atoms of a saturated hydrocarbon were replaced by hydroxyl groups and if all the carbon to carbon bonds were broken and the carbon atoms completely hydroxylated, the net result would be an equivalent amount of carbon dioxide and water. But this does not constitute proof that these were produced in the manner indicated. In truth, it generally is not clear by what mechanism the hydrogen atoms are converted to hydroxyl groups.

Within the past few years the experimental proof of the formation and degradation of organic peroxides which Bone felt so essential to the establishment of the peroxidation theory has been forthcoming in abundance. The problem is complex (*10*). The results vary not only with mixture ratio, temperature, flow rate, and pressure but also with the hydrocarbon structure and the size and shape of the reaction vessel.

Both the static and the flow methods of experimentation have been used. It is more difficult to obtain evidence for the formation of peroxides by the static method, because the high residence time at high temperatures accomplishes almost complete decomposition. This, perhaps, explains the failure of Harris and Edgerton (*18*) to find peroxides among the products of their static experiments. Recently Blosser (*8*) (with Verhoek) working on the oxidation of *n*-pentane (150 mm.) with oxygen (150 mm.) at 230° C. found measurable quantities of peroxides as determined by the polarographic method of MacNevin and Urone (*22*).

The flow method has proved to be better suited to the separation of the products of the combustion in the sequence of their formation. Pease (*32*), working with propane and higher hydrocarbons at 1 atm. in the temperature range of 300° to 400° C., found peroxides in low concentration. Harris and Edgerton (*18*), using a 1 to 1 mixture of propane and oxygen at 1 atm. and in the range of 325° to 355° C., found the peroxides concentrated chiefly in the residue from the distillation of the condensed reaction products.

Bailey and Norrish (*4*), using a conical quartz reaction chamber, studied the oxidation of *n*-hexane with oxygen in a mixture ratio of 1:1 to 1:2. Varying the mixture ratio as indicated, they were able to produce a cool flame at 300° and a blue flame at 310° C. Peroxides, which were obtained in easily measurable quantities, were analyzed by both the titration and the polarographic methods. The organic peroxides and the hydrogen peroxides were not separated, although both were indicated on the polarogram.

Barusch and Payne (*6*), in 1951, were successful in stabilizing a cool flame in a straight tube, and used this device to investigate the relationship between the octane number of the fuel and its tendency to form cool flames. Using a similar device Oberdorfer (*30*), working in the author's laboratory was able to study the cool flames of the isomeric hexanes. In this manner, *n*-hexane, 2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane were readily brought to cool-flame combustion. The fuel-air ratio

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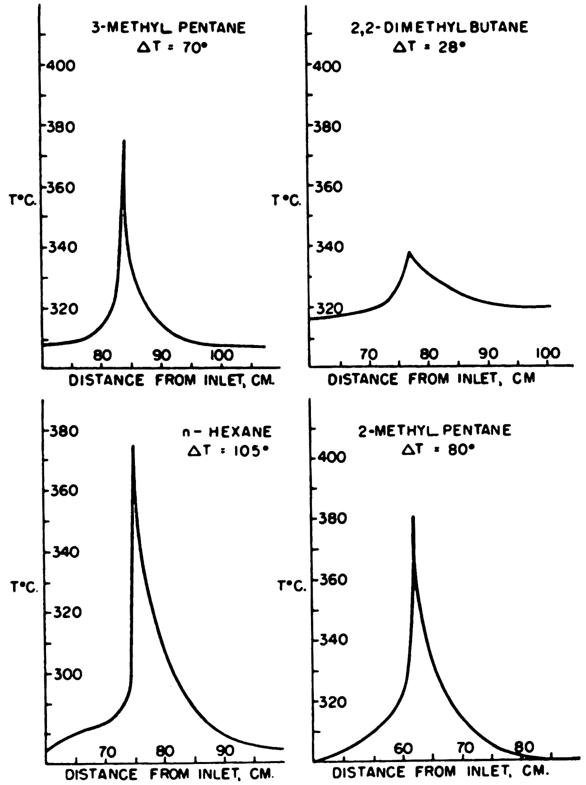

Figure 1. Cool flame temperature profiles

was stoichiometric, and the flow rate was 10 cm. per second. By means of a traveling thermocouple operating through the open end of the combustion tube it was possible to trace the temperature profiles of the four hexanes as shown in Figure 1. Each pure fuel was characterized by a minimum cool-flame temperature and a maximum or peak flame temperature. The difference between these two was designated as the temperature differential, Δt. The temperature differentials of the four hexanes are recorded in Table I, in comparison with their performance numbers as derived from the engine data tables of the American Petroleum Institute (*1*).

Table I. Temperature Differential

Fuel	Tube Temp., ° C.	Max. Flame Temp., ° C.	Temp. Differential, Δt° C.
n-Hexane	270	375	105
2-Me-Pentane	295	380	85
3-Me-Pentane	305	375	70
2,2-Me$_2$-Butane	310	338	28

Using a traveling capillary probe it was possible to remove samples for analysis from either the pre- or the post cool-flame regions. Alkyl hydroperoxides were characteristic of the pre-cool-flame region. They were present in highest concentration just ahead of the flame. These organic peroxides were largely decomposed in passing through the cool flame and hydrogen peroxide was characteristic of the post cool-flame region. The peroxide concentration patterns are shown in Figure 2. The concentration of hydrogen peroxide is from 10 to 15 times greater than that of the R—O—O—H. Both the chromatographic (*24*) and polarographic (*23*) methods of detection, identification, and estimation of the peroxides were used.

Formaldehyde, acetaldehyde, acetone, and carbon monoxide were common combustion products of the four hexanes. Propionaldehyde, *n*-butyraldehyde, acrylic aldehyde, crotonic aldehyde, and methyl ethyl ketone were all found as intermediates in the combustion of *n*-hexane. Acetaldehyde and acetone were prominent and propionaldehyde and acrylic aldehyde were present among the intermediates from 2-methylpentane. Acetaldehyde and methyl ethyl ketone were peculiarly characteristic of 3-methylpentane; and acetaldehyde, acetone, and pivalic aldehyde were characteristic of 2,2-dimethylbutane. In other words, the intermediate monocarbonyl combustion products

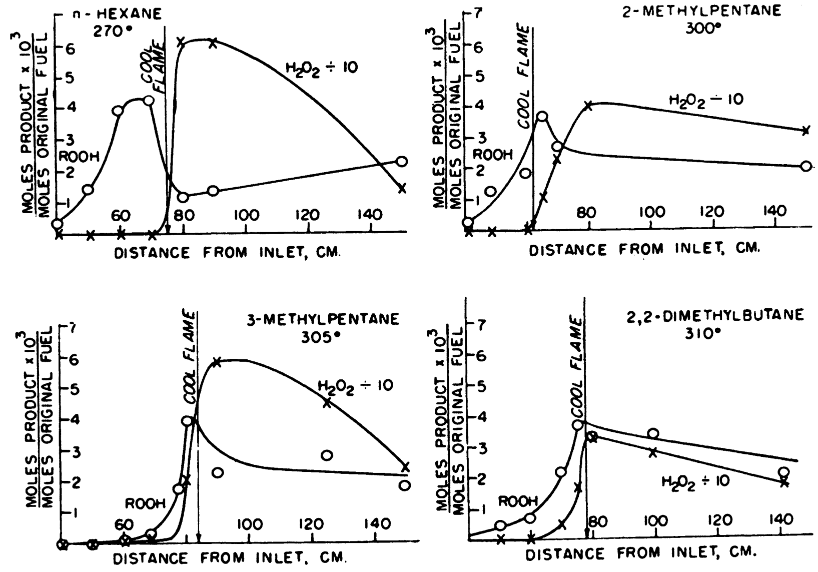

Figure 2. Alkyl and hydrogen peroxide production patterns

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of the simple paraffins are indicative of their structure. This fact becomes of utmost importance in tracing the contribution of each hydrocarbon when used as a component in a fuel blend.

In addition to the monocarbonyls, olefins appear as intermediate cool-flame combustion products. At first these were estimated simply as ethylene. Later Watters (*43*) and his associates found it possible, by the application of infrared techniques, to estimate the individual olefins in such mixtures. The data are shown in Table II.

Table II. Relative Percentage of Olefins

Fuel	C_2H_4	C_3H_6	C_4H_8
n-Hexane	90	10	—
2-Me-pentane	81	13	6
3-Me-pentane	60	23	17
2,2-Me₂-butane	23	46	31

The analytical data on monocarbonyls, olefins, and oxides of carbon were then used to strike a carbon balance for the purpose of finding what part of the cool-flame combustion products had been accounted for. The balance for *n*-hexane proved to be nearly quantitative. For the more highly branched isohexanes the carbon balance was much less complete.

Table III. Carbon Balance for n-Hexane

Monocarbonyls	60%
Olefins	16%
Oxides of carbon	20.6%
Undetermined	3.4%
Total	100.0%

Since the work described above was completed, 23 additional hydrocarbons have been brought to cool-flame combustion in the same apparatus (*19*). Any paraffin, cycloparaffin, or olefin having a research octane number not to exceed 90 may be brought to cool-flame combustion by such a procedure. Aromatic hydrocarbons for the most part do not fall within the indicated range, but *n*-butylbenzene yields a cool flame with much smoke and soot formation.

During the past several years much work has been done on the oxidation reactions which take place during the compression stroke of an Otto cycle engine (*13*, *14*, *16*, *31*). These reactions are very comparable to the cool-flame reactions and, in fact, the motored engine operating without ignition has proved an excellent tool for carrying preignition combustion into the higher octane range. Malmberg and Bobbitt (*25*) have found that some hydrocarbons, as in the case of *n*-heptane (Table IV) (*26*), yields the same products in very nearly the same relative proportions. Other hydrocarbons, as in the case of cyclohexane, yield the same products but in somewhat different proportions.

These facts prove that the same reactions are operating but at very different rates.

Table IV. Carbonyl Products from Cool-Flame Reactions

	DNPH. Weight %	
	n-Heptane	
Product	Tube	Engine
CH_2O	21.9	25.6
MeCHO	24.4	23.9
Me_2CO	7.5	1.3
Zone 2	17.3	19.3
MeCOEt and unknown	10.6	7.9
MeCOPr (*n*)	3.3	3.1
Unidentified product	1.6	2.4
(Zone 2 C_2H_5CHO, $CH_2{=}CHCHO$, $CH_3CH{=}CH{-}CHO$)		
	Cyclohexane	
CH_2O	9.4	29.3
MeCHO	15.9	6.1
Me_2CO	6.5	0.0
EtCHO and $CH_2{=}CH{-}CHO$	25.8	10.2
Unidentified product	13.3	16.8
n-C_4H_9CHO	9.2	6.6

Reaction Mechanism

The confusion among the theories relating to the oxidation of hydrocarbons is almost greater than the uncertainty of the facts. Almost every conceivable oxidation equation has been written into the literature, some of them many times. What is needed is not a new idea but a central theme around which existing ideas can be organized into a definite logical pattern.

The formation of organic peroxides as the primary intermediates in the oxidation of hydrocarbons has been definitely established. The degradation of these peroxides to aldehydes, ketones, carbon oxides, and olefins has also been experimentally proved. These facts bring the oxidation of hydrocarbons directly into line with the simpler and better known operations of chlorination, bromination, and nitration.

The initial step in the oxidation of a hydrocarbon is substitution. For saturated hydrocarbons such as open- and closed-chain paraffins and the alkyl groups of other hydrocarbons, the substitution reaction moves by a free radical mechanism, and sets up a chain reaction. Such a reaction is best illustrated by halogenation.

$$\begin{aligned} X_2 &+ hv &&\rightarrow X\cdot &&+ X\cdot \\ RH &+ X\cdot &&\rightarrow R\cdot &&+ HX \\ R\cdot &+ X_2 &&\rightarrow RX &&+ X\cdot \end{aligned}$$

This mechanism has been most fully explored in the field of photochemistry and is fully documented by Steacie (*39*).

In the oxidation of a hydrocarbon the substitution product is an alkyl hydroperoxide. The mechanism is rendered more complex by the fact that the oxygen molecule is diatomic and oxygen atom bivalent.

$$RH + \cdot O\text{—}O\cdot \rightarrow R\cdot + HOO\cdot \tag{1}$$

$$R\cdot + O_2 \rightarrow R\text{—}O\text{—}O\cdot \tag{2}$$

$$R\text{—}O\text{—}O\cdot + RH \rightarrow R\cdot + ROOH \tag{3}$$

There is said to be much evidence to support the view that the oxygen molecule is essentially a diradical, $\cdot O\text{—}O\cdot$. If this is true, one may be justified in writing Reaction 1. In support of this view one may also write:

$$RH + HOO\cdot \rightarrow R\cdot + H_2O_2 \quad \text{and} \quad R'CHO + HOO\cdot \rightarrow R'CO + H_2O_2$$

and cite the high yield of hydrogen peroxide in the immediate post-cool-flame region. Reactions 2 and 3 continue the reaction chain.

When the alkyl hydroperoxide has been fully formed, only one half of the oxidizing power of the oxygen has been utilized. Alkyl hydroperoxides are therefore unstable, the stability being dependent upon the structure. Tertiary hydroperoxides are the most, and primary hydroperoxides the least, stable. The degradation reaction, which is essentially a second stage in the oxidation, may be either inter- or intramolecular; the degradation may be either bi- or monomolecular. The rate of degradation is a function of the temperature and is easily subject to catalysis.

When the oxidation moves by the intermolecular path and the reaction is applied to *n*-hexane, the sequence of steps may be written as indicated below. This sequence, for steps 2 to 5, inclusive, is analogous to the sequence used by Walsh (*42*) for the oxidation of iso-octane. Step 1 is different, in that Walsh used the tertiary hydrogen atom as a preferred point of attack. This sequence is also analogous to the one used by Bailey and Norrish (*4*), except that these authors seemed to prefer to start with the methyl group. They were careful to point out that much, possibly more, of the oxidation would be initiated at methylene groups and that the alkylhydroperoxides involved in the repeating sequences of the decadent reaction chain would all be primary hydroperoxides.

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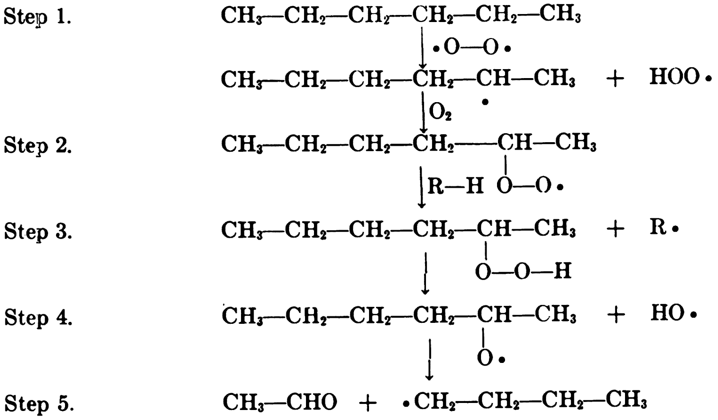
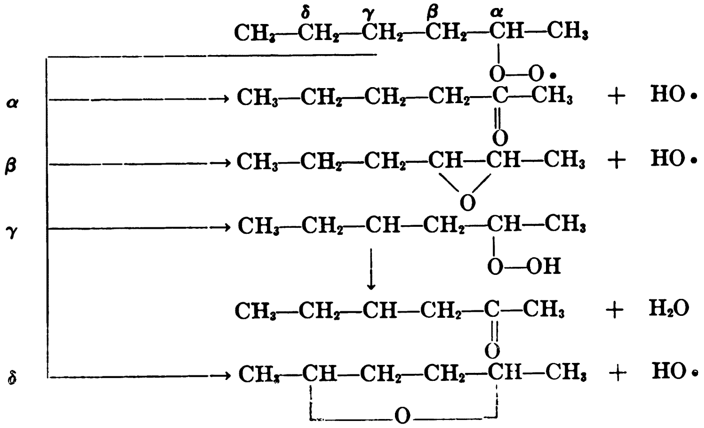


1. The implications involved in step 1 have been pointed out.
2. The 2-hexyl free radical at step 2 should be a powerful initiator.
3. The initiator in step 3 is portrayed as stripping hydrogen from a new molecule of *n*-hexane, producing a new hexyl radical, R•, which continues the principal chain. Additional proof of the formation of alkyl hydroperoxides has been presented; in the pre cool-flame region by Oberdorfer (*30*), in the low temperature oxidation of *n*-pentane by Blosser (*8*), and among the preignition combustion products of an engine by Malmberg, and others (*27*).
4. Step 4 presents the first real difficulty. While the oxygen-oxygen bond is admittedly the weaker bond in the alkylhydroperoxide, it is not a very weak bond. Kineticists are concerned to know where the energy to activate this bond for fission is to be found. A partial answer to this question may be found in the intramolecular reaction scheme which follows.
5. Step 5 provides a "higher aldehyde" as a source of hydrogen in the formation of hydrogen peroxide and a potential source for the carbon monoxide which appears as an accompanying combustion intermediate. The free butyl radical continues the decadent oxidation reaction chain.

Free radicals move in the direction of greater stability. Frequently this results in a dismutation reaction which stabilizes a portion of the molecule and produces a smaller free radical (*2*, *37*, *38*).

$$R{-}CH_2{-}CH_2{-}O\bullet \rightarrow R{-}CH_2\bullet + CH_2O$$
$$R{-}CH_2{-}CH_2\bullet \rightarrow R\bullet + CH_2 = CH_2$$
$$R{-}CO\bullet \rightarrow R\bullet + CO$$

The difficulty met at step 4 will in part be avoided if the further oxidizing power of the alkyl hydroperoxide is in part expended within its own molecule as indicated by the following reaction scheme.



Alpha (α). It is well known in organic chemistry that the hydrogen atoms attached to the same carbon atom to which oxygen is bound are easily removed: Primary carbinols oxidize to aldehydes, secondary carbinols to ketones, and aldehydes to acids. Blosser (*7*) found both acetone and pentanones among the low temperature oxidation products of *n*-pentane.

Beta (β). In work in progress Hoffman of this laboratory finds copious quantities of epoxides among the degradative products of certain organic hydroperoxides.

Gamma (γ). Barusch, Neu, Payne, and Thomas (*5*) found 1,3-diketones among the intermediate oxidation products of *n*-heptane.

Delta (δ). Ubbelohde (*41*) has reported the derivatives of tetrahydrofuran and tetrahydropyran among the low temperature oxidation products of *n*-pentane and *n*-hexane.

Intramolecular oxidation will, therefore, explain the presence of several previously observed products not heretofore tied in to reaction mechanism.

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Fundamental Principles of Flammability and Ignition

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No theoretical criterion for flammability limits is obtained from the steady-state equation of the combustion wave. On the basis of a model of the thermally propagating combustion wave it is shown that the limit is due to instability of the wave toward perturbation of the temperature profile. Such perturbation causes a transient increase of the volume of the medium reacting per unit wave area and decrease of the temperature levels throughout the wave. If the gain in over-all reaction rate due to this increase in volume exceeds the decrease in over-all reaction rate due to temperature decrease, the wave is stable; otherwise, it degenerates to a temperature wave. Above some critical dilution of the mixture, the latter condition is always fulfilled. It is concluded that the existence of excess enthalpy in the wave is a prerequisite of all aspects of combustion wave propagation.

Despite intensive theoretical and experimental research on the combustion wave over the past decade, a universally accepted concept of the phenomenon has not been achieved. This is particularly true with respect to the nonsteady state phenomena of limits of inflammability and ignition.

Frequently in theoretical work on the subject, whether dealing with the steady or nonsteady state, the mathematical development of an adopted model is followed by a descriptive summary of the results which is rarely traced back clearly to the assumptions inherent in the model. This has often resulted in extravagant identification of the model with the actual phenomenon and has been an obstacle in the task of reconciling conflicting views. There is need, therefore, of a purely descriptive exposition, stripped as completely as possible of mathematical language, to clarify the physical concepts of the combustion wave phenomenon.

General Description

A combustion wave is established in an explosive medium by application of a local source of ignition. As heat and, possibly, chain carriers of various kinds flow from the source into the adjacent medium, reaction is initiated in the layer next to the source which in turn becomes a source for igniting the next layer, and so on. Let us consider a mass element of the unburned mixture being overrun by the combustion wave. The reaction rate is virtually zero at the initial temperature but increases with temperature at

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a high order. Therefore, the mass element at first absorbs heat as a heat sink until at some point inside the wave it becomes a heat source by virtue of the chemical reaction initiated by the temperature rise. From this instant and until the temperature crest of the wave has passed, the mass element remains a heat source. Its source strength at first increases because the rising temperature accelerates the chemical reaction; but because the trend is reversed as the explosive reactant is exhausted, the source strength in time passes through a maximum and then decreases steadily even though the temperature is still rising. When heat liberation has substantially subsided, the mass element has arrived at the crest of the wave. During the period of heat liberation the element loses heat to the adjacent cooler regions of the medium upstream—that is, toward the unburned side—in an amount equal to that which it had received while it was a heat sink. In this way heat is continuously borrowed and repaid in the wave out of what may be called a revolving heat fund which travels with the wave and is referred to as the excess enthalpy (*6*, *10*), h, of the wave.

The above description is of a thermally propagating steady-state wave. It must be emphasized, however, that the basic feature of a thermal mechanism is not altered by the superposition of molecular diffusion onto the diffusional transport of heat. This applies not only to interdiffusion of reactants and products but also to the diffusion of chain carriers participating in the chemical reaction, provided that the chains are unbranched. The reason for this is that in a wave driven by a diffusion process, the source strength of an entering mass element must continue to grow despite the drain by the adjacent sink region. This growth can occur only if the reaction rate is increased by a product of the reaction, which may be temperature as well as a material product.

In the case of both nonchain and unbranched chain reactions, temperature is the only product that produces this result. Therefore, combustion waves depending on such reactions are all thermal in the sense that the temperature dependence of the reaction rate and thermal diffusivity control the propagation. A different class of waves is encountered in case of a branched-chain reaction. In this case the principal reaction product responsible for wave propagation is a chain carrier which diffuses into the sink region, and causes the growth of source strength (represented by its own concentration) as it multiplies. Because all such reactions are exothermic, this case is never entirely separated from the simultaneous rise of temperature. However, it appears that the so-called cool flames are driven principally by chain branching, examples of which are the cool flames in hydrocarbons and carbon disulfide. The flames normally encountered with flame temperatures exceeding about 1000° C. are thermally driven. This includes flames of hydrogen even though hydrogen and oxygen are capable of chain branching by the reaction

$$H + O_2 = OH + O$$

It is perhaps intuitively understandable that the steady state, characterized by the well known property of the combustion wave to propagate at constant velocity in a homogeneous explosive medium, results from the fact that there is a ceiling on the source strength imposed by exhaustion of the reactants. Mathematical treatments of the steady state, of which there are many, involve integration of the various wave parameters between suitably formulated boundaries representing the unburned and burned states, and yield the value of burning velocity as an eigen-value solution. Some perplexity connected with the formulation of the boundary conditions for the unburned state has arisen occasionally as a result of the assumption of an ideal steady state, in the sense that the wave was thought to travel *ad infinitum* in an infinite volume of explosive medium. Evidently, if such assumption is not supplemented by the further assumption that the reaction rate is absolutely zero throughout the medium untouched by the wave and becomes finite only as the wave approaches, the system mathematically "explodes." The relation of such boundary conditions to reality lies merely in the fact that an explosive medium is always so recently prepared that it has not reacted appreciably prior to the instant it is consumed by the wave.

Flammability Limits

It is found experimentally that limit mixtures, incapable of supporting combustion waves, nevertheless have theoretical thermodynamic flame temperatures of the order of 1000° C. or more. It is, therefore, not immediately clear why combustion waves, albeit slowly propagating, should not develop in mixtures possessing such substantial chemical enthalpy. The question arises whether the observed limits of flammability are true limits or whether such mixtures are actually capable of supporting combustion waves but are prevented from doing so by experimental limitations. Experimentalists believe that the limits are true. On the other hand, no theoretical criterion for the limit is obtained from the steady-state equations of the combustion wave. That is, the equations describe combustion waves without differentiating between mixtures that are known to be flammable and mixtures that are known to be nonflammable. Therefore, for nonflammable mixtures the combustion wave becomes unstable to perturbations and thus disappears (7). Conversely, for flammable mixtures the combustion wave can overcome perturbations—i.e., it returns to the steady state after being perturbed.

This may be understood as follows. Suppose that a steady-state combustion wave is established with a temperature profile as shown by the solid line in Figure 1, *A*. If some small volume of unburned medium, on entering the source zone, would receive a slightly stronger-than-average stimulus so that it would liberate heat at a rate slightly in excess of the statistical kinetic average, the temperature in that volume would increase above the steady-state profile. The flow of heat from the perturbed volume to the cooler wave regions would accelerate and the flow of heat from the hotter wave regions into the perturbed volume would decelerate. Because the temperature gradient is steeper on the cool side of the volume than on the hot side, more heat would flow during the perturbation to the cooler regions than would be retained by the hotter regions. Consequently, the enthalpy in the perturbed volume would decrease but in the adjacent volume elements it would increase, the increase being larger on the cool side than on the hot side. As the wave continues to propagate, the temperature adjacent to the perturbed volume would increase above the steady-state profile, and within the perturbed volume it would drop below, so that a ripple would develop in the profile as shown by the dotted line in Figure 1, *A*. The boundary of the source zone is extended toward the unburned side so that the width of the source zone is increased beyond that of the steady state.

In the higher temperature region of the source zone the rate of heat liberation decreases because here the temperatures drop below the steady-state profile. This is illustrated in Figure 1, *B*, where the solid line represents the distribution of the rate of heat liberation per unit volume, q, in the unperturbed wave, and the dotted line represents the distribution of q as modified by the temperature ripple. The area comprising the qdx-integral gains in width but loses in height, the former representing the advance of the source zone front beyond the steady-state position, and the latter representing the decrease of the rates q in the source zone. Depending upon which effect predominates, the total source strength (represented by the qdx-integral) either increases or decreases. In the former case, the wave momentarily accelerates and then returns to the steady state as the temperature ripple passes over the wave crest into the burned medium. In the latter case, the heat transferred to the sink zone plus the heat retained by the combustion products as they leave the source zone, momentarily exceeds the heat generated in the source zone, so that the temperatures drop still further. This results in further decrease of the source strength, and so on. Consequently, the wave does not return to the steady state but deteriorates.

In another description of the flammability condition, the authors (7) introduced the average rate of heat liberation, q, defined by

$$\bar{q}s = \int_{-\infty}^{+\infty} q\,dx \qquad (1)$$

where s is a measure of the width of the source zone. If the width is increased by an element, ds, due to an advance of the source zone front beyond the steady-state position,

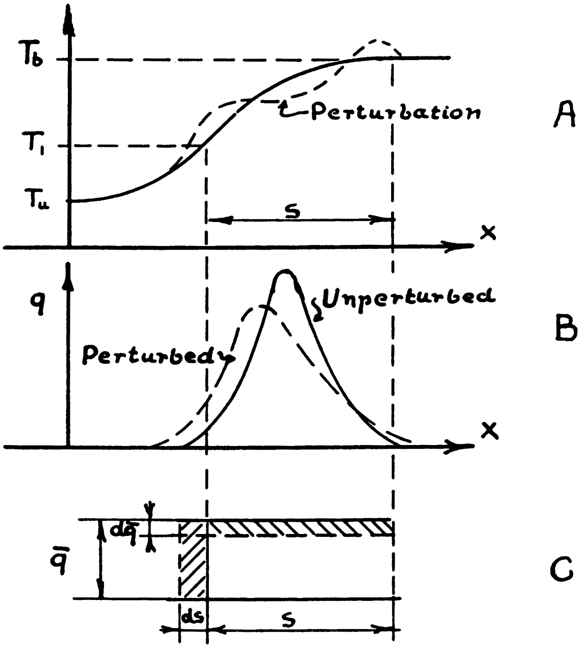

Figure 1. Temperature profile of steady-state combustion wave

A—Temp. profile of combustion wave in steady state. (T_u, T_1, T_b, denote temps. of unburned medium, inflection point, and burned, medium, resp.)—Temp. perturbation.

B—Profile of source strength $\int_{-\infty}^{+\infty} q dx$. Source strength corresponding to temp. perturbation (q denotes rate of heat liberation per unit volume).

C—Same as B, showing source strength in the form

$$\bar{q}s = \int_{-\infty}^{+\infty} q dx,$$

and perturbed source strength as $\bar{q}s + \bar{q}ds - sd\bar{q}$.

the source strength, $\bar{q}s$, is changed by addition of the element, $\bar{q}ds$, and by subtraction of the element, $sd\bar{q}$, as shown in Figure 1, *C*. Depending upon which of the two differentials is larger the total source strength either increases or decreases, so that the flammable region is defined by

$$\bar{q}ds > s \mid d\bar{q} \mid \tag{2}$$

and the nonflammable region by

$$\bar{q}ds < s \mid d\bar{q} \mid \tag{3}$$

the symbol | | indicating that $d\bar{q}$ is a negative quantity. This is in substance the relation given in the authors' treatise (*8*).

Writing Inequality 2 in the form, $ds/s > \mid d\bar{q} \mid /\bar{q}$, the condition for wave stability demands that the percentage increase of source zone width, resulting from a temperature ripple, be larger than the percentage decrease of the average reaction rate. The two sides of the inequality are related by the temperature decrease that results from the distribution of the sensible heat of the source zone over the enlarged zone width. To illustrate the type of relationship that may be expected to govern the stability condition, we shall assume for simplicity that the difference between the flame temperature, T_b, and the average source-zone temperature, T_{av}, increases proportionate to the source zone width,

s, and that $\bar{q}$ follows a simple Arrhenius law—viz., $\bar{q} \sim \exp.(-E/RT_{av})$. Thus, ds/s, becomes $|\, dT_{av} \,| / (T_b - T_{av})$, $|\, dq \,| / \bar{q}$ becomes $(E/RT^2_{av}) \,|\, dT_{av} \,|$, and the stability condition may be written in the form

$$T_{av.} > \left(\frac{T_b}{T_{av.}} - 1\right)\frac{E}{R} \qquad (4)$$

It is reasonable to assume that T_b/T_{av} changes comparatively little with change of T_b as long as the latter is well above T_u. Consequently, as T_b is decreased by adding a diluent to an explosive medium, a critical concentration of the diluent is eventually reached at which inequality 4 is reversed. This depends upon the nature of the diluent and constitutes the limit of flammability.

To obtain the flammability criterion from a more formal development of the combustion wave equations, it is necessary to retain the idea of perturbed heat transfer within the wave independent of the distribution of concentrations of reactants and reaction products. Such treatment has been given by Rosen (*12*), whose result expresses the described physical concept in other form. Layzer (*3*) has investigated a wave model in which no change of total enthalpy (thermal and chemical) is allowed to occur in any wave layer (*4*, *5*). Richardson (*11*) has investigated a wave model in which the reaction rate term is a function of only one parameter—e.g., concentration. Neither of these models yields a flammability criterion in terms of instability to perturbations. Both models possess, in addition to a stable solution of the steady-state equation, unstable solutions whose physical meaning constitutes unlimited extensibility of the reaction zone into the unburned medium, that is, unlimited rate of propagation of the source zone. It would seem, therefore, that a realistic description of the combustion wave, including a limit condition, is obtainable only by retaining excess enthalpy in the model.

Ignition

Concerning the origin of the excess enthalpy in a combustion wave, it is obvious that it derives from either the heat furnished to the explosive medium by an independent source or from the heat of the combustion products behind the wave. In the example of a spherically growing flame, the wave area, and hence the total amount of excess enthalpy continuously increase. Evidently, the ignition source can furnish only an initial amount of this energy, and after the flame has grown to some size the additional demand is met at the expense of the heat content of the burned gas—that is, some of the chemically liberated heat is retained in the wave, so that the temperature T_b behind the wave is somewhat lower than the adiabatic flame temperature $T_b{}^\circ$. As the flame radius increases from r to $r + dr$, the increase of wave surface per unit area is $2dr/r$, and in first-order approximation the increment of excess enthalpy is $dh = h \times 2dr/r$. It is seen that the differential quotient, $dh/dr = 2h/r$, vanishes for large radii but is very large near the origin, so that a critical flame radius should exist below which the excess enthalpy cannot be furnished by the heat liberated in the wave but must be furnished, instead, by the ignition source.

On this basis, it is seen that the source must supply a minimum energy, H, which enables the flame to grow to a critical diameter, d, beyond which the wave can propagate under its own power.

Minimum ignition energy may be written

$$H = \pi d^2 h \qquad (5)$$

where πd^2 is the area of the combustion wave at the surface of the critical flame volume and h being the excess of enthalpy per unit area.

For physical realization of ignition by the minimum amount of energy, it is necessary that the energy, H, be imparted to a volume that is small compared to the volume of diameter, d, and that the energy release occur in a time that is short compared to the time required for the flame to develop to the critical diameter, d. Electric sparks are the most likely means to realize these conditions. Furthermore, it is clear that no heat sink must touch the flame before it has grown to diameter, d; hence, the metallic spark

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Table I. Comparison of Experimental and Calculated Minimum Ignition Energies H Atmospheric Pressure and Room Temperature

Fuel Content, Fraction of Stoichiometric	S_u, Cm./Sec.	$T_b - T_u$, °C.	$\mu \times 10^5$, Cal./Cm.Sec., °C.	d, Cm.	Min. Ign. Energy Cal. × 10^6		Ratio, $H_{calcd.}$ $H_{exp.}$
					$H_{caldc.}$	$H_{exp.}$	
			CH_4-O_2				
0.3	80	1900	6.3	0.072	24	10	2.4
0.45	175	2350	6.4	0.050	6.7	3.1	2
0.75	304	2700	6.5	0.027	1.4	1.4	1
1.2	305	2700	6.7	0.058	4.9	5.0	1
1.5	122	2350	6.9	0.165	109	110	1
1.58	87	2200	6.9	0.38	790	430	2
			C_3H_8-O_2				
0.4	240	2200	6.1	0.038	2.5	1.7	1.5
0.6	335	2550	6.0	0.028	1.1	0.68	1.6
0.8	382	2700	5.9	0.024	0.77	0.50	1.5
0.8	382	2700	5.9	0.024	0.77	0.50	1.5
1.0	375	2750	5.9	0.022	0.65	0.48	1.3
1.2	320	2700	5.8	0.024	0.88	0.63	1.4
1.4	235	2500	5.7	0.028	1.5	1.0	1.5
1.9	30	1300	5.6	0.045	15	6	2.5
			1.1 $CH_4 + O_2$. Nitrogen Added				
N_2/O_2 = 0.5	240	2640	6.3	0.045	4.5	5.3	0.9
1.0	170	2510	6.4	0.053	8.4	9	0.9
1.86	110	2320	6.5	0.079	2.6	20	1.3
air	42	1900	6.5	0.25	590	110	5
			H_2-Air				
0.67	100	1610	7.2	0.071	18	6.2	3
1.01	195	2000	8.0	0.064	10	4.5	2
1.35	265	1940	9.0	0.076	12	6.6	1.8
1.92	190	1550	9.0	0.165	63	49	1.3
			C_3H_8-Air				
0.7	28	1570	6.5	0.42	2000	530	4
0.9	35	1870	6.5	0.24	630	140	4
1.0	40	1940	6.5	0.19	360	92	4
1.28	27	1820	6.5	0.17	400	59	7
1.40	17	1730	6.5	0.20	820	62	13
1.50	12	1530	6.5	0.25	1620	70	23
			CH_4-Air				
0.7	15	1600	6.5	0.29	1800	180	10
0.8	27	1700	6.5	0.22	610	100	6
0.9	35	1850	6.5	0.20	430	72	6
1.0	43	1950	6.5	0.21	410	72	6
1.1	42	1900	6.5	0.25	590	110	5
1.25	25	1800	6.5	0.45	2900	400	7

electrodes must be separated beyond a critical distance—the quenching distance. In the first approximation, the latter may be identified with diameter, d, and its experimental determination is possible by variation of the electrode distance.

The quantity, h, in Equation 5 is not likely to be greatly different from its value in a plane adiabatic combustion wave. Taking x as the coordinate normal to such wave, h becomes the integral of the excess enthalpy per unit volume along the x-axis, so that the differential quotient, dh/dx, represents the excess enthalpy per unit volume in any layer, dx. Assuming the layer to be fixed with respect to a reference point on the x-axis, the mass flow passes through the layer in the direction from the unburned, u, to the burned, b, side at a velocity, S, transporting enthalpy at the rate Sdh/dx. Because the wave is in the steady state, heat flows by conduction at the same rate in the opposite direction, so that

$$\mu dT/dx = Sdh/dx \tag{6}$$

where μ is the coefficient of heat conductivity. For order-of-magnitude calculations consider the ratio μ/S to be constant and equal to its values on the unburned side. This is suggested both by the fact that the increase of μ with temperature is partly compensated by the corresponding increase of S and that the enthalpy excess may be expected to exist predominantly at relatively low temperature levels on the unburned side. The velocity S is taken to be S_u, the burning velocity, and Equation 6 on integration yields the equation originally derived by the authors (*9*)

$$h = \frac{\mu}{S_u}(T_b - T_u) \tag{7}$$

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Values of μ are available for numerous gases and gas mixtures. Burning velocities have been measured on burner flames, and flame temperatures, T_b, can be computed thermodynamically. It is thus possible to put Equation 5 to a test by comparing experimental values of minimum spark-ignition energies with values calculated from data on quenching distances, burning velocities, heat conductivities, and flame temperatures.

Table I (*1*) shows a comparison of experimental and calculated minimum ignition energies for several series of fuel-oxygen and fuel-air mixtures. A discussion of these results will be prefaced by a consideration of the limitations of the thermal model in predicting the magnitude of the excess enthalpy h. In gaseous explosive mixtures, enthalpy is transported not only in the form of sensible heat by heat conduction but also in the form of chemical enthalpy by the diffusion of reactants into the reaction products. The transport of heat occurs in the direction, burned to unburned, whereas the net transport of chemical enthalpy occurs in the direction, unburned to burned. The existence of an excess enthalpy in the form of heat is dependent upon the enthalpy flux by heat conduction being larger than the opposing enthalpy flux by diffusion of reactants. If these opposing fluxes were equal then no mass element of the combustion wave would contain more than the initial total enthalpy of the mixture; there would be no excess enthalpy and therefore no minimum of the spark energy required for ignition. This does not occur in nature.

However, it is clear that the calculation of the excess enthalpy from a model in which diffusion is neglected, as in Equation 7, yields values that are larger than those in an actual wave. The discrepancy between the actual value of h and that calculated from the no-diffusion model depends on whether change of mixture composition throughout the wave width is caused essentially by chemical reaction or whether interdiffusion of reactants and reaction products makes a significant contribution. It may be surmised that in rapidly reacting mixtures diffusional change of mixture composition is negligible but that in slowly reacting mixtures it becomes increasingly important. Accordingly, we would expect the computed value of h to be in substantially better agreement with the experimental value in rapidly reacting mixtures than in slowly reacting mixtures. Moreover, the discrepancy would show the calculated values to be always larger than the experimental values and to become increasingly larger as the mixture is diluted either by an excess of one of the reactants or by addition of inert gas. Inspection of the mixture compositions, and the last column of Table I shows that these considerations are borne out. The agreement between the calculated and experimental values of h is surprisingly good for the very rapidly reacting stoichiometric mixtures undiluted with inert gas.

The foregoing demonstrates that the existence of excess enthalpy is a prerequisite for a conceptual understanding of the real combustion wave. The growing awareness of this situation is illustrated in recent discussions (*2*).

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Application of Chemical Reactor Theory to Combustion Processes

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Many branches of the kinetic theory of combustion processes have reached a stage where the theoretical concepts are fairly clear but where new experimental facts are essential before real progress can be made. Though valuable experimental work is proceeding, in many cases new experimental techniques seem to be required to provide novel information, without which theories cannot decide between conflicting views. This paper gives an analysis and interpretation of the literature, which may serve as a guide to workers in the combustion and allied fields.

Minimizing the combustion chamber volume of high output combustion equipment is invariably a major goal in the design of such equipment. The over-all kinetics of chemical reaction between the fuel and oxidant generally sets an ultimate minimum for this volume.

Combustion rates in low output combustion equipment are usually limited by heat and mass transfer processes. These include the evaporation of fuel drops, mixing of air and fuel, and heating the mixture to ignition temperature. It is usual to assume that the actual burning process (of chemical reaction) takes negligible time in comparison with the time required for the transfer processes. However, as the transfer processes are made faster, or the reaction rate slower, conditions can eventually arise such that the time required for chemical reaction becomes all-important. (There are instances where even though chemical reaction is not the rate-controlling process, it is of primary importance. The reaction time may be orders of magnitude smaller than the residence or mixing time, and still be the critical factor in maintaining smooth combustion in many cases.)

This may occur in low-pressure, high-output equipment where the maximum possible space heating rates are desired. A knowledge of the reaction times required by chemical kinetics limitations, with no mixing limitations, is then of great significance. There are no design improvements in equipment which can possibly reduce the total reaction time to a value lower than that demanded by the over-all reaction kinetics. Knowledge of kinetics limiting time helps point out what theoretical gains in performance are possible in actual equipment.

An intense interest in combustion rates limited by kinetics has been expressed in many recent reports (*2, 11, 13, 41, 42, 47, 51, 56*).

This presentation emphasizes current developments rather than a historical review, and gives an analysis and interpretation of the literature which may serve as a guide to new workers in the combustion field and workers in allied fields. A more elaborate, more complex treatment of chemical kinetics and/or reaction rates has been published

(*23, 30, 31, 49, 54*), as well as a very comprehensive collection of reports dealing with various phases of combustion (*20, 22, 36, 48, 53*).

Chemical Reaction Concepts

The use of chemical reaction rates in combustion processes is necessary to remedy one deficiency in the study of thermodynamics. The first and second law, which in essence form the basis of thermodynamics, permit the prediction of the transformation of energy from one form to another and the utilization of energy for useful work. They fail to predict the rate at which energy can be transformed or utilized. To introduce the time variable into the thermodynamic system being studied, recourse is made to chemical kinetics. Hence, chemical kinetics is the study of the rate at which various radicals or compounds, usually termed species, appear or disappear.

Basic Concepts of Chemical Kinetics. The rate at which any constituent of the initial mixture undergoing chemical reaction disappears is generally expressed as a modified form of the law of natural decay (or growth). This law in its simplest form is usually written as

$$\frac{dG}{dt} = r = -kG \qquad (1)$$

where G is the property being measured, t is the time variable, r is the rate at which G is changing, and k is the growth or decay constant which essentially determines the speed at which growth or decay processes progress (*37*). The application of this type of expression to chemical processes involving more than one species or constituent yields an expression for the rate (r_i) at which any specified species changes as follows,

$$r_i = -k_i(C_1^aC_2^bC_3^c\cdots) = \frac{dC_i}{dt} \qquad (2)$$

where the C's are concentrations (*34*). The order of reaction, now specified as α, is equal to the sum of the exponents. In Equation 2, α would be $(a + b + c \cdots)$. This sum, by definition, is one for a first-order reaction, two for a second-order reaction, and so on. In reactions of simple orders, the exponents are equal to the number of molecules which must combine simultaneously to form the product. It is important to remember that Equation 2 corresponds to the number and kind of molecules which actually do combine, and does not correspond to the molecular proportions used in the stoichiometric equation representing the over-all reaction.

For example, the reaction equation of carbon monoxide with hydrogen is usually written as

$$CO + 2H_2 \rightarrow CH_3OH \qquad (3)$$

which implies that one molecule of carbon monoxide would have to combine with two molecules of hydrogen to produce a molecule of methanol (*32*). Equation 3 implies a ternary simultaneous collision; however, it is probable that the actual reaction proceeds along these suggested lines:

$$CO + H_2 \rightarrow HCHO \qquad (4)$$

$$HCHO + H_2 \rightarrow CH_3OH \qquad (5)$$

Formaldehyde is formed as an intermediate product. This suggested two-step reaction would indicate two second-order reactions occurring in sequence. The over-all apparent order of reaction of Equation 3, if expressed in a form suggested by Equation 2, could be of noninteger order. If one of the reactions suggested by Equations 4 or 5 was extremely fast compared to the other, the reaction would essentially be controlled by the slower one and would appear to be of the second order. Similarly, the standard combustion equation of hydrocarbons with air is usually written as

$$\begin{aligned} C_wH_u + \left(w + \frac{u}{4} + e\right)O_2 + 3.76\left(w + \frac{u}{4} + e\right)N_2 \rightarrow \\ wCO_2 + \frac{u}{2}H_2O + e\,O_2 + 3.76\left(w + \frac{u}{4} + e\right)N_2 \end{aligned} \qquad (6)$$

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where *e* represents the excess oxygen supplied (*39*). This illustrated reaction might seem to imply that one molecule of hydrocarbon collides with $(w + u/4)$ molecules of oxygen. As a result of such a multiple body collision, w molecules of CO_2 and $u/2$ molecules of water vapor are formed. For a hydrocarbon such as propane, C_3H_8, one molecule of propane would have to collide simultaneously with five molecules of oxygen. Such a collision would be extremely improbable. The products of combustion, in addition to carbon dioxide, water vapor, and nitrogen, also contain to a greater or less extent amounts of carbon monoxide, free hydrogen, and aldehydes, and we may surmise that the actual combustion process consists of a large number of intermediate reactions encompassing many intermediate constituents. The inherent complexity of the intermediate reactions has prevented any detailed mechanism of combustion from being postulated. Such a lack of knowledge need not prevent us from collecting the intermediate reactions into one over-all reaction. This method has been used in many treatments, particularly those involving the reactions of paraffin hydrocarbons.

Effective Over-all Chemical Reaction Orders. Values of the effective over-all reaction order α have been obtained by many investigators. The published data are not comprehensive enough to permit any definite correlations to be made between reaction orders, pressure, temperature, and mixture ratios (*26*). One or more of the three basic types of flame measurements are used in determining reaction orders, these being flame thickness, burning velocity, and quenching distance. Reaction order data are available in the more recent literature for the following mixtures, obtained by the indicated method for various pressures, temperatures, and mixture ratios.

Method	Mixture	Reference
Flame thickness	Propane–air	(*24*)
Burning velocity	Propane–air	(*17, 35, 38*)
Burning velocity	Methane–air	(*17, 38*)
Quenching distance	Propane–air	(*4, 28*)
Quenching distance	Propane + $5O_2$ + $2.1N_2$	(*5*)
Homogeneous turbulent reactor	Iso-octane–air Solvent naphtha–air	(*43*)

The values of α, for the mixtures given, range from 1 to 2.5 over a wide selection of the variables already mentioned. It is generally agreed that for theoretical studies of simple flame configurations an over-all reaction order very close to 2 may be used for paraffin hydrocarbons (*1*). Longwell and Weiss recently found a value of $\alpha = 1.8$, assuming homogeneous burning in a spherical turbulent combustion chamber (*43*). We may, therefore, write an approximate expression for the rate of disappearance of the fuel as

$$\frac{dC_f}{dt} = -kC_f^{\omega}C_o^{\beta} \qquad (7)$$

where C_f is the fuel concentration, C_o is the oxygen concentration, and k is the specific reaction constant. The exponents ω and β are constants of unknown magnitude whose sum may be assumed equal to 2 in many instances, but in general, must be determined by experiment.

Specific Reaction Constant. The specific reaction constant k was originally proposed in the form

$$k = A \exp(-E/RT) \qquad (8)$$

by Arrhenius (*33*). According to this investigator, a reaction can take place only when the colliding molecules possess an energy content greater than the mean value by some finite amount. This excess above the mean is termed the activation energy, E. According to a Maxwell Boltzman distribution law, the fraction of the total available molecules possessing an excess of energy at least equal to E is $\exp(-E/RT)$. The steric frequency, collision factor A, represents a measure of collision frequency—i.e., collisions per unit volume per second of the right kind of molecules—of molecules available for collision with a resulting chemical reaction available for the molecules possessing at least the activation energy. It is modified by the requirement that, in some instances, successful collisions occur only when the colliding particles are properly oriented, in addition to having enough energy. In Equation 8, R is the universal gas constant and T is the absolute flame temperature. Recent work has extended the determination of specific reaction rate constants to a much more complex plane to include liquids, but without any significant change from the form of Equation 8 for gases (*29*). As a result, the combination of Equations 7 and 8 yields the following approximation for the specific reaction rate of the disappearance of fuel in a burning mixture of fuel and oxygen:

$$r_f = \frac{dC_f}{dt} = -AC_f^{\omega}C_o^{\beta} \exp{(-E/RT)} \tag{9}$$

Theoretical treatments may include a temperature term in the expression for A in Equation 9, presumably to make the rate constant temperature-independent (*43*).

Theoretically Ideal Flow Reactors

In dealing with chemical reactions involved in constant flow systems, the available reaction time or mixture residence time is essentially the time the reacting mixture spends within the boundaries of the reactor. However, the chemical reaction time required is a function of the degree of completeness of reaction. Under idealized conditions, two types of flow reactors could be visualized. In the first type, an infinitesimal mass could be considered as moving through the reactor in an imaginary compartment progressively altering its composition and temperature. There would be no diffusion associated with this type of hypothesis. The second type could be considered as one in which the turbulence is so great that the charge (fuel and/or air) on entering the boundaries of the reactor is immediately mixed completely with the charge (combustion products) in the reactor. The discharge from the reactor would be of the same composition as the composition throughout the reactor in this hypothesis. Neither case can be obtained absolutely, although long tubes of small diameter tend to approach the first type of reactor, while spherical combustors tend to approximate the second type.

Idealized Reactor with Progressive Mixing. A reactor system of the first type under steady state flow conditions may be described by an expression, as follows, where the number of moles of constituent I converted in an infinitesimal volume, dV, would be given by

$$r_i dV = n_i dy_i \tag{10}$$

where r_i = reaction rate (moles of I per unit volume–unit time)
V = reactor volume
n_i = reactor feed rate of I (moles of I per unit time)
y_i = fraction of I converted

If x_i is the mole fraction of I contained initially in the molar reactor feed rate m (composed of all constituents), then

$$r_i dV = x_i m dy_i \tag{11}$$

For the first type of reactor in which the reactants move progressively through the reactor, an integration of Equation 11 yields

$$\frac{V}{x_i m} = \int_0^{y_i} \frac{dy_i}{r_i} \tag{12}$$

Remembering, however, that by hypothesis r_i is everywhere in the reactor a function of the concentration and the temperature, it is seen that integral Equation 12 can be solved only approximately.

Idealized Reactor with Instantaneous Mixing. For a reactor of the second type, a homogeneous system, where the composition, temperature, and pressure is everywhere the same, Equation 11 is immediately integrable to

$$r_i V = x_i m y_i \tag{13}$$

In a system where the constituent i is fuel burning with air, r_i from Equation 9 may be expressed as

$$r_i\,(\text{fuel}) = r_f = -AC_f^{\omega}C_o^{\beta}\exp(-E/RT) \tag{14}$$

The product $x_i m$ is equal to W_f/M_f where W_f is the weight rate of fuel flow and M_f is the molecular weight. The concentrations may be expressed as the mole fraction times the molar density or

$$C_i = x_i\gamma_T = x_i\gamma_m(T_m/T) \tag{15}$$

where γ_T = mixture density at temperature T (molar)
γ_m = mixture density at temperature T_m (molar)
T_m = ambient inlet temperature

The combination of Equations 13, 14, and 15 yields

$$VA(x_f\gamma_m T_m/T)^{\omega}(x_o\gamma_m T_m/T)^{\beta}\exp(-E/RT) = (W_f/M_f)y_f \tag{16}$$

where the mole fraction, x_i, is expressable as

$$x_i = \frac{(W_i/M_i)(1 - y_i)}{m} \tag{17}$$

the subscript o denoting oxygen. Equation 16 may be rewritten as

$$VA\gamma_m{}^{\alpha}\left[\frac{T_m}{T}\right]^{\alpha}\exp(-E/RT)\left[\frac{W_f}{M_f}(1 - y_f)\right]^{\omega}\left[\frac{W_o}{M_o}(1 - y_o)\right]^{\beta} = \frac{W_f}{M_f}m^{\alpha}y_f \tag{18}$$

In theory this equation is solvable if the kinetic constants A, E, and the reaction order α $(= \omega + \beta)$ are known, and if two additional conditions are satisfied—namely, the relation between y_o and y_f and variance between T and y_f.

Both Longwell's group (*42*) and Avery's group (*2*) originally assumed that the concentrations of fuel and oxygen are equally important in determining the reaction rate and fixed ω and β at unity. [Longwell and Weiss have recently determined α experimentally (*43*).] Longwell further assumed that, if the mixture is lean, all the fuel that burns does so by consuming a stoichiometric amount of oxygen; and, if the mixture is rich, the oxygen and fuel combine in the proportions present in the original mixture. That is, if $y_f W_f/M_f$ moles of a saturated hydrocarbon having a composition of C_wH_{2w+2} are consumed, a stoichiometric number of moles of oxygen (y_oW_o/M_o) which equals $(3w + 1)y_fW_f/2M_f$ must be used. These assumptions along with Equation 6 yield a relation between y_o and y_f as follows:

$$y_o = \frac{3w + 1}{2}\,\frac{W_f}{M_f}\,\frac{M_o}{W_o}\,y_f \tag{19}$$

or, because there are μ moles of air per mole of oxygen in air, where $\mu = 4.76$,

$$y_o = \frac{3w + 1}{2}\,\frac{M_a}{M_f}\,\frac{W_f}{W_a}\,y_f\mu \tag{20}$$

The substitution of y_o in Equation 18 yields, for $\omega = \beta = 1$,

$$\frac{VA\gamma_m{}^2}{\mu y_f}\left[\frac{T_m}{T}\right]^2\exp(-E/RT)\,\frac{(1 - y_f)(1 - \delta y_f)}{1 + W_fM_a/W_aM_f} = m \tag{21}$$

where $\delta = (3w + 1)\mu M_aW_f/2M_fW_a$ when the fuel-air ratio is less than the stoichiometric weight fuel-air ratio and $\delta = 1$ at weight fuel-air ratios richer than stoichiometric.

The relation between the temperature of the reactor, T, and the fraction of fuel burned, y_f, can be expressed from an energy balance of the reactor system. This yields

$$cT - c_mT_m = y_f\Delta H_m - Q \tag{22}$$

where c = molal specific heat
ΔH_m = molal enthalpy of combustion referred to the initial temperature, T_m
Q = heat losses or gains per mole of reactor fluid

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Assuming that Q is zero and the specific heat does not change, y_f as a function of T may be expressed as

$$y_f = (T - T_m)/(T_f - T_m) \tag{23}$$

where T_f is the adiabatic flame temperature.

By combining Equations 21 and 23, y_f or T may be eliminated and a solution may be obtained if the kinetic constants E, A, and T_f are known. The solution would be in the form of the molal flow

$$m = \frac{AV\gamma_m^2}{\mu} T_m^2\psi(T, W_f/W_a) \tag{24}$$

Another method of treatment used by DeZubay and Woodward (*14*) is to revert to Equation 13 for each constituent. If the constituents are considered as fuel, oxygen, and diluent (nitrogen for fuel-air combustion)

$$V \sum_i r_i = m \sum_i x_i y_i \tag{25}$$

The model of the reaction may be hypothesized in the following manner. The total molal flow, m, splits into an infinite number of elemental masses on entering the boundaries of the reactor. A certain fraction, y, of these elemental masses burns to chemical equilibrium composition and attains the adiabatic flame temperature. The remainder $(1 - y)$ remains unburned. It is further assumed that all of the constituents of the burned fraction act only as diluents and can in no way contribute anything further to the reaction.

This would mean that for every mole of fuel consumed per unit time an amount of oxygen equal to the initial molal oxygen-fuel ratio would be consumed. It is expected that this assumption would be good near the stoichiometric ratio and be poor in the very rich and very lean region. As a result of this assumption, y_i must equal y, the nitrogen in the burned elemental masses being credited to the reacted portion. Then Equation 25 reduces to

$$V \sum_i r_i = my \sum_i x_i \tag{26}$$

But, $\sum x_i$ is the sum of all the mole fractions, which by definition is unity; therefore

$$V \sum_i r_i = my \tag{27}$$

The total reaction rate of the mixture undergoing combustion would be the sum of the reaction rates of the individual constituents—namely, the fuel and oxidant. Hence,

$$\begin{aligned} \sum_i r_i &= r_f + r_o \\ &= r_f + \frac{1}{\mu}\frac{W_aM_f}{W_fM_a} r_f \end{aligned} \tag{28}$$

From Equation 14, we express r_f as

$$r_f = A(\exp -E/RT)\gamma_m^2(T_m/T)^2 x_o x_f$$

where the mole fractions of oxygen and fuel are given as

$$\begin{aligned} x_o &= \frac{(1-y)}{\mu} \frac{W_a/M_a}{W_f/M_f + W_a/M_a} \\ x_f &= (1-y)\frac{W_f/M_f}{W_f/M_f + W_a/M_a} \end{aligned} \tag{29}$$

Proceeding as before we have an equation representing the molal flow, m, which corresponds to Equation 21 as follows, for $\omega = \beta = 1$,

$$\frac{AV\gamma_m^2}{\mu y}\left[\frac{T_m}{T}\right]^2 (\exp -E/RT) \frac{(1-y)^2[1 + (1/\mu)W_aM_f/W_fM_a]}{[1 + W_fM_a/W_aM_f][1 + M_fW_a/W_fM_a]} = m \tag{30}$$

An inspection shows that Equation 30 would give smaller values of molal flow m than Equation 21.

For a comparison of these equations, we may assume a fuel-air ratio and inlet ambient temperature and use an accepted activation energy of 30,500 cal. per gram-mole for propane fuel burning with air (Table I). Having an inlet temperature and the fuel-air ratio fixed, the flame temperature may be found from Figure 1, which contains some of the findings of Smith, Edwards, and Brinkley (*50*). On Figure 2, Equations 21 and 30 are shown for an activation energy of 30,500 cal. per gram-mole, an inlet temperature of 537° R., a (Rankine) flame temperature of 3280° R., and a propane-air ratio of 0.0425 pound per pound. The large differences are due to the fundamental assumptions made in formulating each hypothesis and to the use of the same kinetic constants in both equations.

Table I. Kinetic Constants

Reference	Fuel	Oxidant	A/μ, CC./Gram-Mole	E, Kcal./Gram-Mole	α
(*2*)	Hydrocarbon	Air	3.0×10^{14}	33	2
(*11*)	C_3H_8	Air	1.89×10^{14}	31	2
(*11*)	H_2	Air	1.55×10^{12}	14	1.8
(*1*)	C_4H_{10}	O_2	5.4×10^{13}	21	2
(*43*)	Hydrocarbon	Air	...	42	1.8
(*25*)	C_3H_8	O_2–N_2	...	33	2
(*15*)	C_3H_8	Air	...	25 to 38	2
(*19*)	CH_4	Air	...	26	2
(*19*)	C_2H_6	Air	...	26	2
(*19*)	C_3H_8	Air	...	26	2
(*19*)	C_5H_{12}	Air	...	26	2
(*19*)	H_2	Air	...	16	2

Determination of Kinetic Constants

The flame temperature, T_f, can be evaluated by thermodynamic methods. A simplified treatment of a method is given in detail by Lichty (*40*). Excellent extensions of this method are available in a series of machine calculated reports (*50*).

To evaluate the activation energy, E, and the collision frequency factor, A, recourse may be made to Semenov's equation (*18*). To accommodate noninteger orders of

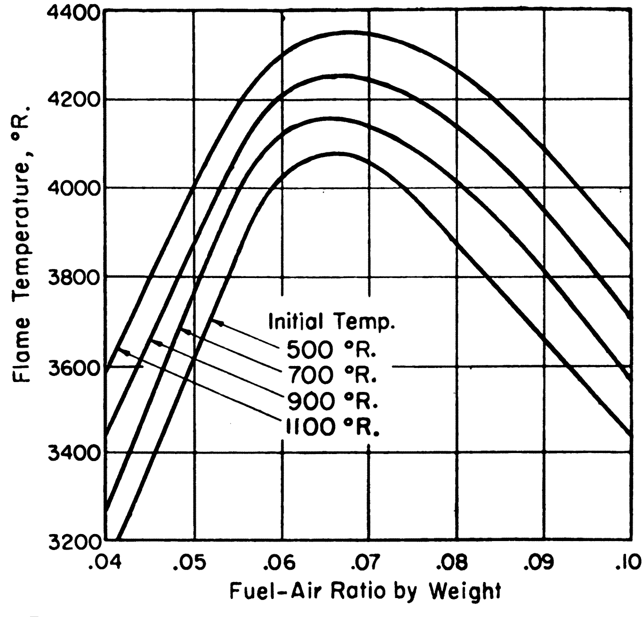

Figure 1. Flame temperatures of propane-air mixtures

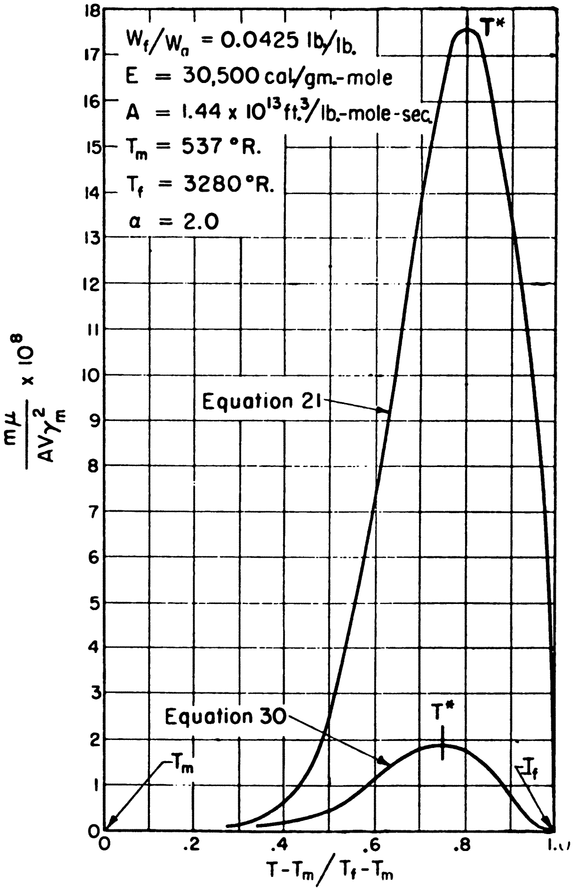

Figure 2. Flow parameter vs. reactor temperature

reaction Semenov's equation is suggested as

$$V_f^2 = \frac{2A\lambda c^\alpha C^{\alpha-1}}{\gamma_a c_a^{\alpha-1}} (T_a/T)^\alpha (\lambda/c\gamma d)^\alpha (N_a/N)^\alpha \frac{(RT/E)^{\alpha+1}}{(T - T_a)^{\alpha-1}} (\exp -E/RT) \tag{31}$$

where λ = thermal conductivity
C = moles of reactants per unit volume (oxygen + fuel)
d = diffusivity
N = number of moles
V_f = flame velocity

Subscript a refers to the ambient state; quantities without subscripts refer to the final state.

Avery (*2*) suggests a further modification of Equation 31 for second-order reactions, $\alpha = 2$, in the form

$$V_f^2 = \frac{2AC\lambda_a}{\gamma_a c_a} (N_a/N)^2 (\lambda_a/c_a\gamma_a d_a)^2 (RT/E)(\exp -E/RT) \frac{T^{1.91} T_a^{1.09}}{(T - T_a)^3} \tag{32}$$

where the variation in the properties λ, c, γ, and d is estimated at the flame state by the temperature exponentials. If experimental data are available for flame velocities (V_f) at various fuel-air ratios, and the flame temperatures are also available from experimental or calculated sources, Equation 32 can be applied at two fuel-air ratios. Such an applica-

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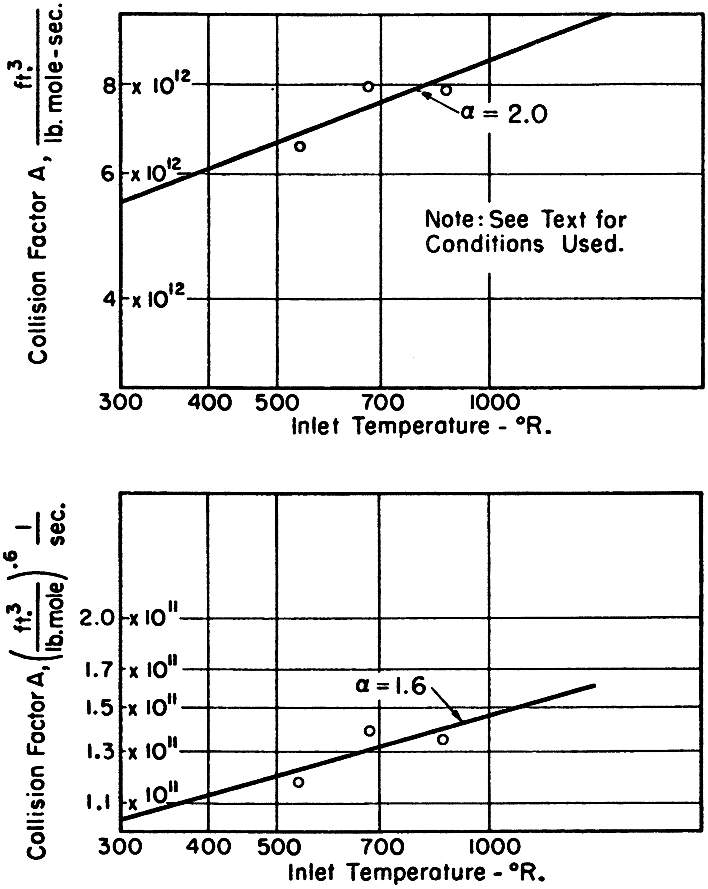

Figure 3. Variation of collision factor with temperature for propane-air mixtures using the Semenov equation

tion results in two equations in two unknowns, A and E. If such a scheme is carried out, the following values are obtained for propane-air mixtures:

$A = 1.44 \times 10^{13}$ cubic feet per pound-mole-second

$E = 30{,}500$ calories per gram-mole

Table I contains kinetic constants for various fuel-oxidant mixtures from various sources. A different procedure of evaluating kinetic constants and reaction orders has been described (*43*).

DeZubay (*12*) has calculated the change in the collision factor with temperature (propane-air mixtures) by use of the Semenov equation based on the following conditions: activation energy of 33 kcal. per gram-mole; flame velocities at an air-fuel ratio of 14.1 of 38.4, 58.2, and 83.3 cm. per second at inlet temperatures of 537°, 672°, and 852° R., respectively; flame temperatures [extrapolated to an air-fuel ratio of 14.1 (*50*)] of 4022°, 4091°, and 4185° R. at inlet temperatures of 537°, 672°, and 852° R., respectively. This variation of A *vs.* inlet temperature is shown in Figure 3.

General Assumptions and Limitations of Equations

Mathematical interpretations of the homogeneous chemical reactor have been presented along with the major assumptions attendant in formulating the models. The general assumptions and limitations of the equations are discussed here.

The previous intent has been to use kinetics simply as a tool to describe qualitatively the particular aspect of combustion under study. Numerical values of the kinetic constants were thus assumed for illustrative purposes or approximated from other types of data by making admittedly questionable major assumptions. Approximations include, for example, the extrapolation of low temperature hydrocarbon oxidation rates to high temperature hydrocarbon combustion rates. Other schemes involve application of semiempirical laminar flame speed theories or of flow patterns in the wake of a bluff body immersed in an air stream (*43*).

An assumption involving heat losses from the reactor is made in most treatments. The effect of heat transfer on the maximum reaction rates of a homogeneous reactor has been treated by DeZubay and Woodward (*14*). It was found that a lowering of the reactor surface temperature appreciably lowered the chemical reaction rates. Longwell and Weiss (*43*) found, for example, a loss equal to 5% of the maximum adiabatic heat liberated reduces the maximum heat release rate by more than 30%, while a 20% heat loss reduces the rate about 85%. One should not assume an adiabatic system without some definite knowledge of the magnitude of the heat losses.

Equation 6 implies that all the carbon reacts with oxygen to form carbon dioxide and all the hydrogen reacts with oxygen to form water. This, however, is not the case, as the temperatures obtained during the combustion process are generally sufficiently high to dissociate an appreciable part of the products of combustion. This dissociation is accompanied by the reconversion of thermal energy to chemical energy. Thus, the dissociated products will have chemical energy associated with them, so that the net chemical energy available for conversion to thermal energy is lowered. The maximum attainable temperatures for hydrocarbon-air mixtures will be lower than those indicated by an energy balance, assuming complete conversion of chemical energy to thermal energy. Any results based on data taken at temperatures above about 3500° R. would be of questionable significance without some adjustment for dissociation effects. Approximations for these effects may be made from the work of Mulready (*45*).

The burning velocity is controlled by the rates of chemical reactions and transport processes in the reaction zone, and chemical reaction rates vary exponentially with temperature and depend on the partial pressures of the reactants (concentrations). These are strongly influenced by diffusion (molecular and/or eddy). Any treatment, therefore, which ignores these effects would not be complete.

A judicious choice of the activation energy is most important in treatments involving chemical kinetics. For example, Friedman (*23*) states that for a propane-air mixture, the data of Dugger and Heimel (*16*) lead to a value of about 37 kcal. per gram-mole for E when a first-order reaction is assumed and about 27 kcal. per gram-mole when a second-order reaction is assumed. If this is considered to be a complex reaction involving both first-order and second-order steps, then little can be concluded from these measurements—i.e., data of Dugger and Heimel (*16*)—concerning the activation energies of the individual steps. In connection with the choice of activation energy, the Rice-Herzfeld treatment of isothermal chain reactions shows that the apparent activation energy of the over-all reaction may be considerably less than the activation energy of the slowest step (*46*).

One must also consider whether it is meaningful to speak of a temperature in the reaction zone. If internal degrees of freedom are ignored, one should ask whether a translational temperature always exists in the reaction zone—i.e., in each layer is the distribution of molecular velocities approximately in accord with the Maxwell-Boltzmann law? Rough calculations show that the thickness of the zone of intense chemical reaction for a deflagration wave is of the order of magnitude of the ratio of the mean free path to the Mach number (*27*). For relatively slow burning flames (cold flow velocity ~40 cm. per second), the reaction zone is ~1000 mean free paths in thickness; hence, there is very little possibility of abnormal molecular velocity distributions. For very fast flames (cold flow velocity ~1000 cm. per second), the reaction may be only 20 or 30 mean free paths in thickness; and, some slight departure from the Maxwell-Boltzmann distribution is conceivable (*23, 30, 31, 49, 54*).

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The collision factor and the activation energy were obtained previously for propane by the simultaneous application of the Semenov equation (Equation 31) at two fuel-air ratios where the values of the flame velocity and flame temperatures were available. The accuracy of this method for determining A and E is expected to be fair, since for accuracy, the Semenov equation must meet the condition that $E/RT \geq 10$. For propane, E/RT is of the order of 8.

Great care should be exercised in formulating any assumptions pertaining to the stoichiometry of the reactions. For example, in the models used herein, the final results are critically dependent upon the relation between the oxygen consumed and the fuel consumed and how the flame temperature is assumed to vary with the fuel consumed. The range—i.e., lean and/or rich fuel-air ratios—over which the needed assumption must be valid should be thoroughly investigated.

Applications of Kinetic Theory

Stability of Combustors. Several applications to actual combustion phenomena are possible with the concept of the homogeneous reactor. For stability or blowout predictions, it is possible to evaluate the maximum values of the flow quantity $(m\mu/AV\gamma_m{}^2)$ as a function of the fuel-air ratio in accordance with Equation 30. This is shown as a curve on Figure 2, which can explain blowout phenomena. If a flame exists in the reactor at low flows, it will be at a temperature near T_f where the concentration of the reactants in the reactor is very small. As the flow is increased, the concentration of the reactants increases; but, the exponential component of the specific reaction rate decreases until a maximum flow is undergoing partial reaction at a temperature corresponding to T^*. If the flow is further increased, the temperature can no longer accommodate the larger flow. The only region to which the temperature can shift is T_m where any flow is possible with no reaction occurring. Hence, the maximum flow that can pass through the reactor and still maintain combustion would be the maximum value at temperature T^*. This would imply that instability or blowout would be determined by the condition that the partial derivative of the flow quantity $(m\mu/AV\gamma_m{}^2)$ with respect to temperature must equal zero for a constant fuel-air ratio (Equation 30). In theory, it is possible to evaluate maximum values of the flow quantity $(m\mu/AV\gamma_m{}^2)$ for any fuel-air ratios, provided that the flame temperature T_f and the kinetic constants A and E are known.

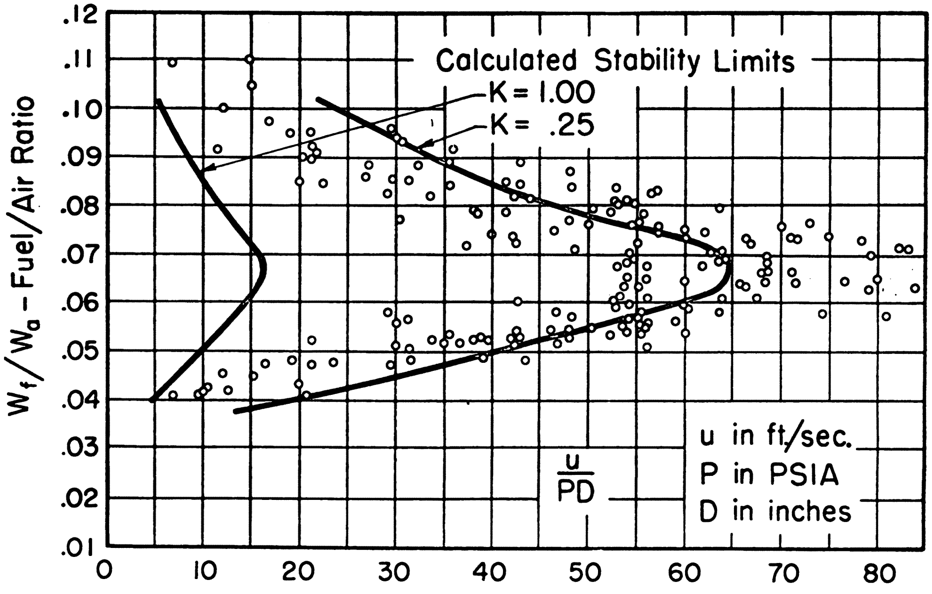

Figure 4. Flame stability of disks in propane-air mixtures

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An experimental verification of this has been presented (*14*), and the correlation is good, considering the nature of the assumptions and the uncertainty connected to the kinetic constants.

An explanation of the blowout characteristics of simple disks can be made with simple reaction rate theory. The works of DeZubay (*9*, *11*), both verified by exhaustive experimental results, serve as an example of the application of reaction rate theory to a homogeneous reactor for the purpose of predicting stability—i.e., the reaction zone in the wake of a bluff body located in a high velocity gas stream was assumed to be a homogeneous reactor. A typical curve of DeZubay's is shown on Figure 4. On this curve K is the ratio of the flow introduced into the reactor to the free flow intercepted by an area the same size as the disk. The maximum value of $(m\mu/AV\gamma_m{}^2)$ can readily be shown to be proportional to (u/PD) where u is the flow velocity past a disk of diameter D and P is the burner pressure. A direct application of simplified reaction kinetics is made by Bragg (*6*, *7*) in his theoretical treatments of high altitude combustion chamber operation and the qualitative prediction of stability limits.

Specific Heat Release Rate. To utilize many combustion systems most effectively, the maximum power output is to be obtained for the smallest possible size and weight. As a result, the physical size of the combustion chamber as well as all other components should be held to a minimum. This requirement specifies that the specific heat release should be as high as possible. This quantity, usually expressed in energy units per unit volume, unit time, and unit pressure squared, is a measure of the ability to heat the gases used in the thermodynamic cycle. Some idea of the orders of magnitude of prevailing heat releases in combustion equipment can be obtained from the values in Table II.

Table II. Specific Heat Releases in Combustion Equipment

Equipment	Heat Release, B.T.U./Cu. Ft.-Hr.-Atm.^{2}
Domestic boiler	$0.01\text{–}0.03 \times 10^6$
Navy boiler	$0.20\text{–}0.25 \times 10^6$
Industrial gas turbine	$0.70\text{–}3.00 \times 10^6$
Aircraft gas turbine	$4.00\text{–}11.0 \times 10^6$

The specific heat release can also be estimated from the flow quantity $(m\mu/VA\gamma_m{}^2)$. The specific heat release, denoting it by S, is defined and evaluated as follows

$$S = mc(T - T_m)/VP^2 \tag{33}$$

$$S = m\mu c(T - T_m)A/V\gamma_m{}^2AR^2T_m{}^2\mu \tag{34}$$

Using the conditions for obtaining Figure 2, one may also obtain Figures 5 and 6. Figure 5 shows the heat release as a function of the combustion efficiency (defined as the enthalpy rise of the mixture divided by the maximum available chemical energy). From this curve, it can be seen that the high heat releases can be realized only if the combustion efficiency is sacrificed. Figure 6 shows the maximum heat release as a function of the equivalence ratio—i.e., Figure 6 is the locus of the maximum values of curves like the one of Figure 5, determined at various fuel-air ratios. A maximum heat release occurs at slightly rich mixtures and has a value of about 170 mega-B.t.u. per cubic foot-hour-atmosphere^2. This value is about one half of the heat release of that obtained in a laminar flame reaction zone, and occurs at all fuel-air ratios at a sacrifice of maximum attainable temperature. That is, the reactor temperature rise is only in the order of eight tenths the adiabatic flame temperature rise. Specific heat release rates are discussed and attempts at predicting them (based on homogeneous reaction rate theory) for a spherical reactor are made by Longwell and Weiss (*43*). The difference between the predicted value of 170 mega B.t.u. per cubic foot-hour-atmosphere^2 of Figure 6 and the maximum value of about 300 mega B.t.u. per cubic foot-hour-atmosphere$^{1.8}$ determined experimentally by Longwell and Weiss may be due to the reactor type, fuel type, and the differences in activation energies employed. A different method for predicting heat release rates through the use of simplified reaction kinetics is presented by Bragg (*6*) along with some experimental verification of the theory.

Scaling of Combustion Systems. Recently, some attempts to predict the scaling

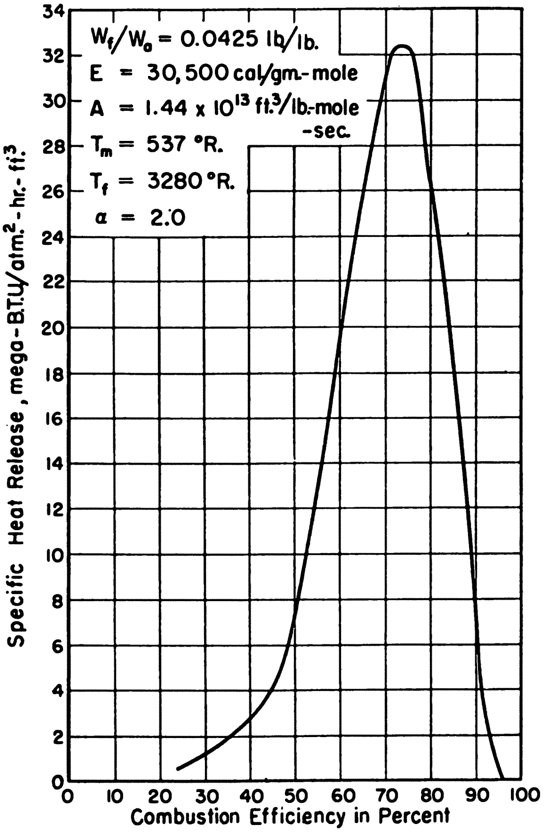

Figure 5. Specific heat release as a function of combustion efficiency

characteristics of combustion systems—i.e., "scaling up" small scale prototype dimensions to full scale models—through the use of reaction rate theory have been made (*3*, *43*, *55*). These predictions have not yet been verified experimentally, although the work of Longwell (*43*) and of the writer offers preliminary justification. A paper on the scaling of gas turbine combustion systems has recently been presented by Stewart (*52*). The component processes occurring in a combustion chamber are examined to determine the operating conditions under which a geometrically similar model chamber should be tested to produce results applicable to a full size unit. A paper by Bragg and Holliday (*8*) deals with the applicability of simple combustion data—laminar flame speed, and ignition delay—to the problem of turbulent combustion, with correlation, in the light of such data, of the performance of combustion chambers under altitude conditions, and finally, with the application of such data and correlations to the design of the best combustion chamber to fulfill the requirements of a given project.

Miscellaneous Applications. The work discussed thus far has dealt mainly with the treatment of the combustion zone as a reactor of the homogeneous type. To extend the treatment of the concept of the homogeneous reactor to can-type burners—i.e., similar to those used in aviation gas turbines—it would be necessary to reduce the burner to a series of volumes, each behaving as a homogeneous reactor. The piloting zone could be considered as the first of such homogeneous reactors. Each subsequent section could then be treated in a similar fashion, if sufficient allowance could be made for the additional air introduced. Such an approach would disregard any mixing phenomena and would probably indicate a performance more favorable than the actual case.

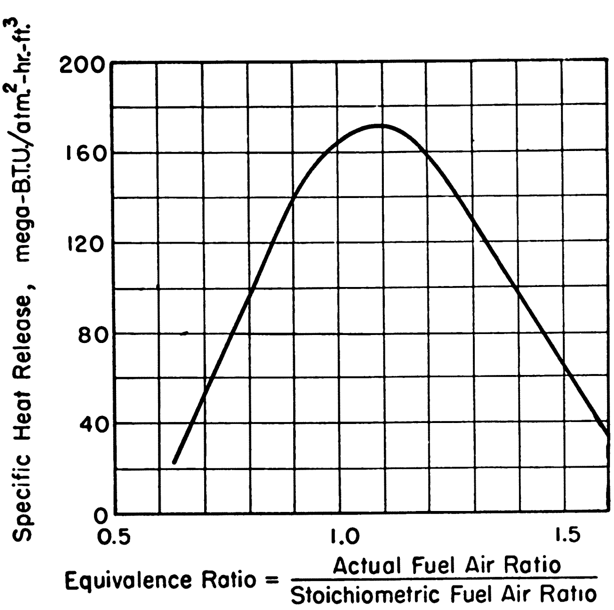

Figure 6. Maximum heat release for a homogeneous reactor

An attempt at such a treatment has been made by DeZubay and Woodward (*10, 13*). Though only a few specialized cases were investigated theoretically, the results were encouraging enough to prompt further work along these lines.

The work of Mayer and Carus (*44*) gives a theoretical analysis of flame propagation in a laminar flame model based on simplified reaction kinetics.

Future Work

The important phases of combustion in which a great deal of work is needed are clearly enumerated in a panel discussion held during the Fifth Symposium on Combustion (*21*). Those phases referring to the application of chemical kinetics are thoroughly discussed.

Many branches of the kinetic theory of combustion processes have reached a stage where the theoretical concepts are fairly clear but where new experimental facts are essential before real progress can be made. Though valuable experimental work is proceeding, in many cases new experimental techniques seem to be required to provide novel information, without which theories cannot decide between conflicting views.

In summary, the important themes of which those interested in future work should be cognizant are: What are the relationships between combustion kinetics at extremely high temperatures, and the reactions studied at low temperatures? Is some kind of extrapolation valid from one temperature range to the other? How important is the transfer of internal energy in combustion kinetics involving chain mechanisms? What factors determine the stability of those free radicals and labile molecules generally important for combustion? These few themes are by no means exhaustive in scope but should serve to give the reader a feeling for the present state of affairs.

The writer echoes the wishes of many workers in the combustion field in hoping that heterogeneous combustion systems will eventually lend themselves to treatments similar to those used with the homogeneous reactor.

Nomenclature

a = subscript denoting air or ambient conditions; exponent
b = exponent

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c = molal specific heat at constant pressure; exponent
d = diffusivity; differential of
e = atoms of excess oxygen supplied
f = subscript denoting flame or fuel
i = subscript denoting the i^{th} species
k = specific reaction (growth or decay) constant
m = molar reactor feed rate of all species combined; subscript denoting mixture
n = molar reactor feed rate of a particular specie
o = subscript denoting oxygen
r = reaction rate
t = time
u = flow velocity; number of hydrogen atoms in a hydrocarbon
w = number of carbon atoms in a hydrocarbon
x = mole fraction of a species contained in reactor feed rate
y = fraction of a species converted to products of combustion
A = steric frequency factor
C = species concentration (molar)
D = disk diameter
E = activation energy
G = any property being measured
H = enthalpy
M = molecular weight
N = number of moles
P = pressure
Q = heat losses or gains per mole of reactor fluid
R = universal gas constant
S = specific heat release
T = flame temperature (absolute)
T_f = adiabatic flame temperature (absolute)
V = reactor volume
V_f = flame velocity
W_a = weight rate of air flow
W_f = weight rate of fuel flow
W_o = weight rate of oxygen flow
α = reaction order (effective over-all)
β = exponent
γ = molar density
δ = $(3w + 1)(M_a W_f)\mu/2(M_f W_a)$ in lean fuel-air ratio range; equals unity at fuel-air ratios equal to or greater than stoichiometric
λ = thermal conductivity
μ = moles of air per mole of oxygen in air (=4.76)
ψ = function of
ω = exponent

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Kinetics of the Oxidation of Graphite

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This review is restricted primarily to forms of carbon obtained by pyrolysis of hydrocarbon and having to a rather large extent, by virtue of prolonged heat treatment, the graphitic lattice structure. Rate studies include the activated chemical processes between graphite and oxygen, water vapor, and carbon dioxide. Various experimental methods used in rate studies are described. The results are explained on the basis of mechanisms believed to be important in the oxidation of graphite. Future investigation should be directed toward obtaining more information about structural changes in graphite during chemical reaction. Physical methods for characterizing graphite include low temperature adsorption isotherms for determining surface areas and surface heterogeneities, and x-ray diffraction patterns for determining the degree of graphitization.

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It is difficult to give a comprehensive review of the oxidation of carbon in all its common forms, in all ranges of pressure and temperature, and in all oxidizing media. Certain restrictions must be placed on the extent of the survey, in order to emphasize essential features. In all heterogeneous reactions, transport is an important process in the succession of events leading from reactants to products, but it has been largely ignored here. This may be justified on the basis that few reliable data are available which adequately describe the diffusion processes in carbon oxidation and that the more specifically chemical effects must be clarified before diffusion effects can be understood. There is a temperature of reaction, a pressure of reactants, and a porosity of sample at which a diffusion process becomes rate-controlling, but these are discussed only in so far as they represent limits to the regions of chemical processes. These latter processes are usually classed as chemisorption of reactants, reaction on the surface, and desorption of products.

The oxidizing media discussed are exclusively gases, which is consistent with the de-emphasis of diffusion phenomena. These gases are oxygen, carbon dioxide, and water vapor, although the oxygen reaction is treated much more thoroughly than the others.

Considerable emphasis is given to the structural features of carbon (both surface and internal) as revealed by recent physical measurements. There is a strong feeling among investigators that many of the contradictory results from carbon oxidation are caused by differences in structural parameters. Certain features about which there is general agreement are usually explained on the basis of unmeasured changes in structure.

In the first place, the carbon should be as free as possible of chemical impurities, especially metals, which catalyze the reaction. This eliminates the natural graphites from consideration, because they leave at least 1% ash on ignition; the principal metals in the ash are silicon, aluminum, alkali and alkaline earth metals, titanium, iron, and manganese (*48*), many of which are known to catalyze carbon oxidation.

On the other hand, artificial graphite prepared by pyrolysis of hydrocarbons is objectionable because its crystal structure resembles that of thermodynamically stable graphite to only a limited extent. As Ruff (*63*) has pointed out, the so called β-graphite is probably α-graphite with certain crystal faults which can be removed in a continuous manner by heat treatment. A considerable body of physical measurements have been made in recent years, relating the change of crystal and surface parameters to conditions of heat treatment and preparation of pyrolytic graphite. These effects have not been given nearly enough attention by investigators of graphite oxidation. Thus, this review includes numerous references to the type of information obtained by such physical measurements on pyrolytic graphite as x-ray diffraction patterns, electron micrographs and diffraction patterns, low temperature adsorption isotherms, and magnetic susceptibility.

Chemical Kinetics

The kinetics of graphite oxidation seems to be divided into at least two distinct ranges of temperature between 500° and 2000° C. from the standpoint of both experimental methods and reaction mechanisms. The dividing temperature is in the neighborhood of 1000° C. It is important that both of these ranges of temperature be studied by the same methods, in order to eliminate differences due to parameters inherent to the apparatus, but a number of practical difficulties are involved.

High Temperature Region (1000° to 2000° C.). The high temperature kinetics must be studied at very low pressures in order to avoid a diffusion-controlled process (*71*). Gulbransen and Andrew (*32*) report that transport at normal pressures becomes rate-determining above 700° C. Thus investigators have usually resorted to the use of cold-wall reaction vessels, only the graphite being heated. This is accomplished by passing an electric current through a graphite filament and in nearly all cases no attempt is made to preheat the reactant gases. Langmuir (*42*) introduced this technique in an investigation of the extent of adsorption of oxygen and carbon dioxide, and the composition of the desorbed products. His results are only qualitative. Most of the kinetic studies using heated filaments have been patterned after those of Meyer (*53*) and Martin and Meyer (*49*). In a subsequent article (*52*), Meyer gives a brief but comprehensive review of the results of his work, with a description of the apparatus and method. According to Meyer, in order to avoid secondary reactions in the $C + O_2$, carbon dioxide, and water vapor reactions, the following conditions must hold: low pressure ($<5 \times 10^{-2}$ mm. of mercury), rapid and continuous removal of reaction products, and a smooth graphite surface. This surface is prepared by passing methane over a carbon filament at temperatures ranging from 2500° to 3000° C. Some of the data obtained for the $C + O_2$ reaction are outlined below. The order of reaction with respect to oxygen pressure was unity in all cases.

Table I. Carbon-Oxygen Reaction

Investigator	Temp. Range, ° C.	$E^{\pm}$, Kcal./Mole
Eucken (*20*)	800–1200	21
Meyer (*52*)	900–1250	20–30
Strickland-Constable (*70*)	800–1100	26
Sihvonen (*69*)	800–1400	28

The work of Sihvonen is complicated not only by its tremendous volume but also by its rather limited accessibility. He has given a review of his work with a fairly complete bibliography (*68*); another review contains a considerable number of experimental curves (*66*). At very high temperatures (> 1400° C.) both Meyer and Sihvonen independently observed effects that have not been observed by any other workers. The $C + H_2O$ reaction becomes zero-order with respect to water vapor pressure and the activation energy has a value of about 90 kcal. per mole (*52, 65, 66*). Meyer reports identical Arrhenius plots for $C + CO_2$ and $C + H_2O$ in this region. The $C + O_2$ reaction

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is also zero-order in this region, but with a somewhat smaller energy of activation (70 kcal. per mole).

These energy values are much too small to represent the activation energy for graphite sublimation. Honig (*35*) and Chupka and Inghram (*13*) have recently measured sublimation rates of graphite filaments with the mass spectrometer. Fragments up to C_8 were observed by Honig, but C_3 was probably the principal molecule sublimed. The activation energy for sublimation of the C_1 fragment is 177 ± 10 kcal. and is about the same or greater for other fragments.

These observations lead one to believe that all graphite oxidation reactions at temperatures above 1400° C. are controlled by an identical process—desorption of surface oxides. This should apply at least for $C + CO_2$ and $C + H_2O$.

However, there are good reasons for doubting the reliability of this conclusion. Strickland-Constable (*71, 72*) has for a long time contended that this high temperature zero-order reaction is a result of glow discharge from the graphite filaments. Meyer (*51*) has recently answered this criticism and given a critical comparison of his own studies of $C + H_2O$ and $C + CO_2$ reactions with those of Strickland-Constable. However, Duval (*19*) has shown that a small amount of mercury vapor, which could be introduced into the reaction vessel from a diffusion pump or manometer, causes discharge and that the activation energy for this thermal emission of electrons is 90 kcal. per mole. Furthermore, Duval reports that for the $C + O_2$ reaction in the presence of the glow discharge a considerable amount of carbon dioxide is formed (30 to 50% of the total $CO + CO_2$), although when mercury vapor is excluded from the reaction vessel and the glow discharge is not present, very little carbon dioxide is formed. This indicates that carbon monoxide is the primary product of the reaction between carbon and oxygen. Meyer, on the other hand, reports that carbon dioxide constitutes approximately one third of the reaction products of $C + O_2$ above 1600° C. Duval finds a first-order reaction in the absence of glow discharge, but does not report the order in the presence of discharge. Additional evidence that the primary product of the $C + O_2$ reaction is carbon monoxide is given below.

There is an intermediate region of temperature (1200° to 1500° C.) for the $C + O_2$ reaction, in which the rate *vs.* temperature curve displays a maximum. There is general agreement on this point among Duval (*19*), Eucken (*20*), Meyer (*53*), Strickland-Constable (*71*), and Sihvonen (*69*). Above the temperature of maximum rate the rate decreases very rapidly. Strong hysteresis effects are observed, which indicate that the immediate history of the graphite sample is an important factor in the reaction kinetics. The usual interpretation placed on these observations is that in this range of temperatures there is interaction between crystal growth in the graphite and oxidation of the graphite, since the rates of these two processes are then of comparable magnitude. Thus Sihvonen (*69*), who finds the maximum to be at 1450° C., says that the surface area undergoes a change between 1400° and 1500° C. Strickland-Constable (*70*) states that the change in the graphite surface occurs at 1200° C. Duval (*19*) shows that the fraction of effective collisions between oxygen and graphite has a maximum value at 1100° C. and explains it on the basis of mobile carbon atoms and recrystallization. Audubert and Busso (*3*) find the maximum to be at 1550° C. The rate of oxidation depends on the number of active centers or carbon atoms with high free valence. Busso (*9*) explains that these carbon atoms are on the edges in the prismatic planes and that only above 2000° C. would one expect basal plane carbon atoms to be attacked by oxygen.

Dienes (*16*) has calculated the energy of activation required for self-diffusion in graphite. For vacancy diffusion, $E^{\pm} = 160$ kcal. per mole. The treatment is not applicable to diffusion along grain boundaries or pores.

Criticism of Carbon Filament Method. The carbon filament technique has several obvious shortcomings. Principal among these is the lack of preheating of the reactant gases. Recent investigations by Binford and Eyring (*7*) indicate that a change in the order of reaction may result from preheating the steam in the $C + H_2O$ reaction. Strickland-Constable (*72*) finds the order to be 0.6 with respect to water vapor at 1000° C. and to increase towards unity as the temperature of the filament is raised. This indicates

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that adsorption of reactants is the slowest step in the reaction. Binford and Eyring find the reaction to be zero-order in the same temperature range, indicating that preheating speeds up the adsorption process to such an extent that reaction on the surface or desorption of products becomes rate-controlling. Sihvonen discusses the problem of preheating (*67*) and reports considerable increases in rate for C + H_2O (*65*) and C + CO_2 (*69*) upon preheating the reactants.

The methods of temperature measurement of graphite filaments are also subject to criticism. Temperature must be measured by an optical pyrometer. Duval (*19*) admits a possible error of 50° C. due to uncertainty in the calculated emissive power of a dull graphite surface (*60*). Furthermore, the temperature range of investigation cannot be extended far below 1000° C. without making arbitrary extrapolations of temperature *vs.* voltage curves.

Low Temperature Region (500° to 1000° C.). Relatively few investigations have been conducted in this temperature range with adequate elimination of catalytic and diffusion effects. The advantages of low temperature study are that temperatures can be accurately measured by thermocouples and that both gaseous and solid reactants can be heated to the same temperature prior to reaction. Gulbransen (*29, 30*) has developed a gravimetric method for studying heterogeneous reactions at high temperatures, using a microbalance constructed within a vacuum system. Recently Gulbransen and Andrew (*31*) have extended the temperature range by using ceramic furnace tubes which fuse directly to Pyrex 7740. Thus in a double-walled furnace tube they are able to maintain a pressure of 10^{-6} mm. of mercury at 1200° C. for a considerable length of time.

For the C + O_2 reaction Gulbransen and Andrew (*31*) report a value for $E^{\pm}$ of 36.7 kcal., which is considerably above that determined in the high temperature filament experiments. Wicke (*78*) in an interesting paper designed to relate the high temperature work to the low temperature work proposes that the true value for $E^{\pm}$ in the absence of diffusion is 58 kcal. per mole for the C + O_2 reaction. As $k \propto k_0^{1/2}$, where k = apparent rate constant (first-order, diffusion-controlled) and k_0 = true rate constant, according to Wicke, the high temperature experiments, for which different values for $E^{\pm}$ varying from 20 to 30 kcal. per mole have been found, are actually diffusion-controlled. Intermediate values of $E^{\pm}$ represent reactions in which the rate is only partially controlled by diffusion. Wicke's proposal must be regarded as speculative until additional information can be obtained regarding gaseous diffusion phenomena within graphite.

From absolute rate theory, having determined the activation energy experimentally, one may calculate rate constants for a variety of rate-controlling steps in heterogeneous reactions (*26*). Gulbransen (*28*) has made such calculations for immobile adsorption with and without dissociation, mobile adsorption with activation energy and without activation energy (Hertz-Knudsen mechanism), desorption, and first- and second-order chemical reactions on the surface. The calculations for mobile adsorption agree most closely with the experimental value and thus it is proposed to be the rate-controlling step. However, the calculated value for immobile adsorption with dissociation is near enough to the experimental value to be considered as a possibility.

For the C + CO_2 reaction from 500° to 900° C., Gulbransen and Andrew (*34*) obtain rate data which indicate that steady-state conditions were not attained, at least at the higher temperatures. However, using a carbon-14 tracer technique, they show that between 700° and 800° C. there is a rapid reaction to give carbon monoxide and surface oxide, followed by a slow decomposition.

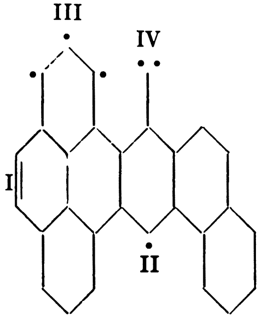
Several other low temperature investigations, two in air (*41, 55*) and two in steam (*37, 44*), are interesting from the standpoint of showing the complications that arise when diffusion, catalysis, and product inhibition of the surface become important. Long and Sykes (*46, 47*) have studied catalytic effects for C + H_2O and C + CO_2 reactions and propose slightly different mechanisms for catalysis by transition metals and by alkali metals.

Primary Products of C + O_2 Reaction. In early graphite filament experiments (*26, 49, 52, 53*), carbon dioxide was thought to be one of the primary products of the C + O_2 reaction. In recent years, this has been largely discredited and it is now believed that above 1000° C. the primary product of reaction is exclusively carbon monoxide. Thus Duval (*19*) finds that if mercury vapor is rigorously excluded from the reaction chamber, practically no carbon dioxide is found in the reaction products. Lewis and von Elbe (*43*) point out that hydrogen-containing chain carriers are strong catalysts for the CO + O_2 reaction. Thus traces of water vapor would be expected to increase the rate of formation of carbon dioxide. The use of inhibitors such as phosphoryl chloride, which are known to react strongly with the chain carriers, has been useful in clarifying the nature of the primary products of the C + O_2 reaction. Arthur (*1*) has shown that the ratio $CO/CO_2 = 10^{3.4} \exp(-12{,}400/RT)$. Thus at the highest temperature, there is less than 10% carbon dioxide in the reaction products, and the ratio of carbon monoxide to carbon dioxide is increasing rapidly. Unfortunately, the addition of such inhibitors as phosphoryl chloride also causes a decrease in the over-all C + O_2 reaction rate and thus there may be a corresponding change in reaction mechanism.

Wicke (*79*) has presented rather convincing evidence that carbon monoxide is the primary product in the 900° to 1500° C. range. Using a graphite tube in a furnace and a quartz jet to introduce air into the tube, he is able to vary the linear flow rate over a range of 1 to 50 meters per second and thus study the effect of extremely high flow rates on product composition. He finds that the ratio of carbon monoxide to total CO + CO_2 approaches unity when the average length of time the reactants spend in the graphite tube becomes very small (about 10^{-4} second).

Several investigators have attributed certain frequencies of light emission in the combustion region around graphite to the formation of carbon dioxide. Arthur and Bleach (*2*) found that the addition of phosphoryl chloride to the air stream quenched a previously visible blue glow surrounding the graphite. Thus he associates the emission with the $CO + \frac{1}{2} O_2 \rightarrow CO_2$ reaction. On the other hand, Busso (*11*) has analyzed the ultraviolet emission spectra (1900 to 2800 A.) from a graphite filament in 1 to 10 cm. (of mercury) of air at 1500° C. Assignments are made for transitions from electronically excited states of both carbon monoxide and carbon dioxide to their ground states. For pressures of air above 5 cm. of mercury, carbon dioxide emission is observed, but below 5 cm. of mercury there is only carbon monoxide emission (*10*). Emission bands between 2600 and 2680 A. are found which indicate the presence of OH radicals (*8*). Their presence might be responsible for the carbon dioxide formation, which is observed above 5 cm. of mercury.

Quantum Mechanical Treatment of Graphite. Various quantum mechanical models have been proposed to account for difference in reactivity for different carbon atoms in graphite. Busso, Daudel, and coworkers (*12*) calculate free valence for various types of edge carbon atoms. Busso (*9*) summarized these as shown below.



I. Banana bonds, free valence = 0.75, reactive
II. π-Orbital electron unpaired, free valence = 1.70, radical, very reactive
III. Resonance, stabilized, less reactive than II
IV. Extremely reactive

Long and Sykes (*46*, *47*) use a molecular orbital method of calculating bond order.

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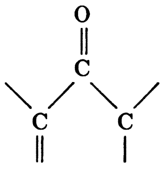
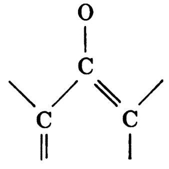
In their electronic theory of catalysis, configuration 1 is preferred to configuration 2 by interaction of the catalyst with the π-electrons of the graphite lattice.



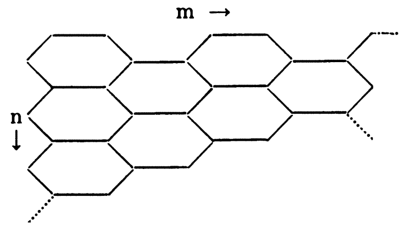
1



2

There is a smaller energy barrier for carbon monoxide leaving the surface in 1 than in 2.

Coulson and Baldock (*14*) have applied Bloch wave functions to an examination of surface states in graphite. They find that one edge of the basal plane has surface states and the other does not—that is, along *n* and along *m*, respectively, as shown below.



This they admit is a "formal" model and cannot be applied to "real" problems.

Reviews of Articles on Oxidation of Graphite. The most recent review of graphite oxidation kinetics is that of Mayers (*50*) in 1934. However, a number of symposia on reactions of carbon have been organized in recent years and many of the papers reviewed here are taken from these collections. Specifically the symposia are to be found in Volume 47 of *Journal de Chimie Physique* and in Volumes 44 and 45 of *Industrial and Engineering Chemistry.* Many of the papers in the former journal are written in English.

Physical Measurements on Graphite

The results of chemical kinetic studies indicate that future investigations should be directed toward a closer examination of changes occurring in the graphite during oxidation.

X-Ray Diffraction. A considerable amount of information about the temperature dependence of graphite lattice parameters has been collected within the past few years.

Franklin (*24*) classifies carbons as either graphitizing or nongraphitizing on the basis of their crystal growth in the 1000° to 3000° C. region. In general, graphitizing carbons contain much hydrogen. In this category are pitch coke, coal cokes, and poly (vinyl chloride) char. During the early stages of development the crystallites remain mobile. Growth is thought to occur by movement of layers and not by individual atoms. Nongraphitic carbons contain little hydrogen or much oxygen, and cross linking occurs. Examples of this type are low rank coals (oxygen-rich), sugar charcoal, and poly (vinylidene chloride) char.

According to Franklin (*22*), graphite carbons are composed of crystallites containing from 30 to 150 layers (basal planes) whose diameters vary from 80 to 600 A. Crystallites tend to be parallel to one another and layers within crystallites are parallel to one another. The basal planes within the crystallites may be within a group of graphitic layers (carbon atoms along the *C*-axis are directly above and below one another in alternating planes, *C*-axis spacing = 3.354 A.) or turbostratic layers (random rotation and translation of one plane with respect to the other, *C*-axis spacing = 3.44 A.).

Franklin (*23*) proposes that the transition between a graphitic group and a turbo-

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stratic group occurs abruptly and that the *C*-axis spacing represents an average of the two types. Thus there is a simple correlation between the observed *C*-axis spacing and the degree of graphitization, or, more specifically, the fraction of displaced layers, *p*.

Bacon (*5*) has confirmed the validity of Franklin's interpretation by studying temperature variation of x-ray diffraction patterns and by neutron diffraction. Bacon (*4*) finds a slight difference in Franklin's *p vs.* interlayer spacing curve for $p < 0.2$.

Iley and Riley (*36*) have prepared graphite by cracking hydrocarbons in the presence of a fused silica support at 800° to 1300° C. Both moist and dry preparations at 1000° to 1200° C. contain from 0.5 to 1% hydrogen. They propose that these hydrogen atoms are on peripheral carbon atoms and probably inhibit crystal growth.

Pinnick (*57*), from a study of crystallographic changes in carbon blacks between 1000° and 3000° C., suggests that for basal planes having diameters below 150 A. there is little tendency for the turbostratic structure to be lost. Above 150 A. interplanar forces, which increase as the square of the diameter, become great enough to cause orientation of the basal planes. Pinnick also finds that the diameter of the carbon black particle serves as an upper limit to the diameter of the crystallite which can be made from it.

White and Germer (*77*) deposit carbon from a hydrocarbon on quartz at 1000° C. X-ray reflection patterns indicate that the basal planes of the graphite lie parallel to one another and to the quartz surface.

Riley (*25, 62*) proposes an open form of graphite, which may be visualized as composed of *o*-tetraphenylene residues folded back on themselves.

Hardly any effort has been made to relate the x-ray diffraction data to high temperature gaseous oxidation rate data. Walker, McKinstry, and Wright (*75*) have proved that in the $C + O_2$ reaction at 1100° C. there is no interplanar penetration by oxygen. The graphite used is composed of petroleum coke and coal tar pitch graphitized at 2500° C. The fraction of displaced layers in the crystallites as determined by average interlayer spacing is 0.2. Walker, McKinstry, and Pustinger (*74*) studied the $C + CO_2$ reaction at 1100° C. Using the interlayer spacing as a criterion, they report that the less graphitic carbon is the more reactive.

Electron Diffraction and Electron Microscopy. A limited amount of information regarding graphite structure has been obtained by the use of electron beams. Grisdale (*27*) has measured the "degree of orientation" using electron diffraction methods on films of pyrolytic carbon deposited on a silica surface under a variety of conditions. Oxidation of the graphite causes an increase in the degree of orientation.

Schaeffer, Smith, and Polley (*64*) observe from electron micrographs that carbon black particles heated to 3000° C. change from spherical to polyhedral in shape. Kmetko (*40*) makes similar observations and has shown that the polyhedral structure extends throughout the body of the particle in some cases.

Equilibrium Adsorption of Gases at Low Temperatures, Surface Area. Low temperature adsorption isotherms could furnish much useful information about the change in chemical nature and the change in size of the graphite surface during oxidation. Few investigators have made use of this valuable tool as a supplement to kinetic data on graphite oxidation. There is strong evidence that differential heat of adsorption *vs.* fractional coverage curves as determined from adsorption isotherms give a measure of the crystallographic heterogeneity in graphite. Beebe and Young (*6*) show that the differential heat of adsorption initially decreases with surface coverage, passes through a minimum value, and then increases to a maximum in the neighborhood of the first monolayer. The decrease is caused by surface heterogeneity, as the more reactive fraction of the surface is the first to combine with the adsorbate (argon). The subsequent increase in differential heat is caused by lateral interaction of the adsorbed atoms. This region of decreasing differential heat gradually disappears as carbon black graphitized at successively higher temperatures is used For a graphitization temperature of 2700° C. there is practically no downward trend in the differential heat curve for $V/Vm < 1$, and increasing surface coverage.

Jura and Criddle (*38*) observe inflection points in the adsorption isotherms for argon on graphite at surface coverage of less than a monolayer. These are interpreted as

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polymorphic transitions in the adsorbate as opposed to crystallographic heterogeneity, although "energetically inhomogeneous" adsorption is considered a possibility.

Crowell and Young (*15*) compare their differential heats of adsorption with those of Jura and Criddle (*38*) and conclude that there were errors in the low surface coverage region of the latter investigation due to the effect of thermal transpiration on pressure measurement.

Polley, Schaeffer, and Smith (*59*) observe stepwise isotherms for argon, nitrogen and oxygen on graphite at $-195°$ C. The steps become more pronounced as the graphitization temperature of the carbon black adsorbate is increased. The steps appear at multiples of 0.85 V_m and are to be expected for homogeneous surfaces.

Pierce and Smith (*56*) have observed a Type III isotherm for water vapor on a highly graphitized carbon black (graphon, 80 square meters per gram) at 28.9° C. They suggest that water vapor adsorption occurs only on the most active sites and that the entire surface is probably never covered.

Loeser and Harkins (*45*) have made a critical comparison of the Brunauer-Emmett-Teller and Harkins-Jura methods of calculating the surface area of graphite by adsorption of *n*-heptane at 25° C. The lower limit of surface area which can be measured by the Harkins-Jura method using *n*-heptane is given as 2500 sq. cm.

Gulbransen and Andrew (*33*) show that the $C + O_2$ reaction at 500° C. causes an increase in surface area as determined by krypton adsorption isotherms.

Walker, Foresti, and Wright (*73*) have studied surface area as a function of the amount of carbon consumed by the $C + CO_2$ reaction at 900° to 1000° C. They find that an increase in internal surface area increases the rate of reaction until the graphite sample is about 10% consumed. Thus in one case the area changes by a factor of 14. Both rate and area become constant after 10% consumption of the sample.

However, Walker and Wright (*76*) claim that the area of graphite measured at very low temperatures might not be the area that is important to high temperature oxidation kinetics. This, they point out, would depend on porosity and other structural features of the solid.

Other Physical Methods. Several other physical methods might add new information when accompanied by kinetic studies.

DENSITY. Dresel and Roberts (*18*) have observed a significant increase in the density of artificial graphite for only 0.5% consumption by oxygen at 500° C.

MAGNETIC SUSCEPTIBILITY. Pinnick (*58*) has correlated the magnetic susceptibility of synthetic graphite with the *a*-dimension of the lattice plane. There is a sharp increase in susceptibility as *a* grows from 50 to 150 A., and the susceptibility remains constant thereafter to 1000 A. Juza (*39*) has shown that the adsorption of oxygen on charcoal at room temperature is molecular, as magnetic susceptibility does not change.

EVAPORATED CARBON FILMS. Evaporated metal films have been extremely valuable in the study of chemisorption. It would be desirable to study chemisorption on a similarly prepared carbon surface. Olsen, Smith, and Crittendon (*54*) made an unsuccessful attempt to evaporate graphite pellets from a tungsten basket. Doehard, Goldfinger, and Waelbroeck (*17*) used a metal evaporator to evaporate carbon onto glass slides. Rideal and Trapnell (*61*) have studied hydrogen adsorption on evaporated carbon films. Farber and Darnell (*21*) report rates of evaporation of electrically heated graphite filaments 1/16 inch in diameter in the temperature range 2100° to 2600° C.

Conclusions

The kinetics for the $C + O_2$ reaction fall rather naturally into the following temperature ranges.

500° to 1000° C. Carbon monoxide and carbon dioxide formed simultaneously. $E^{\pm}$ for carbon monoxide greater than $E^{\pm}$ for carbon dioxide by 12.4 kcal. per mole. Only 10% carbon dioxide formed by 900° C. Order of the reaction uncertain, because of presence of diffusion effects in most investigations.

1000° to 1200° C. Carbon monoxide only primary product. $E^{\pm}$ between 20 and

30 kcal. per mole. First-order rate with respect to oxygen; thus adsorption the rate-controlling step.

1200° to 1500° C. First-order with respect to oxygen. Recrystallization of graphite gives rise to hysteresis effects and rate maximum in the rate *vs.* temperature curve.

1500° to 2000° C. Possibly zero-order (L. Meyer) but probably first order (X. Duval, R. F. Strickland-Constable) with respect to oxygen. Observations complicated by diffusion effects, thermionic electron emission, and recrystallization.

Thus, there is considerable evidence that the nature of graphite oxidation is strongly dependent on the nature of surface heterogeneities. Attack by oxygen probably occurs on prismatic rather than basal planes.

The following specific recommendations are made for future investigations:

Development of one method to study the entire temperature range, with preheating of reactant gases and accurate temperature measurement.

Introduction of structural parameters of graphite into the empirical rate equations.

Only then may one confidently apply absolute rate theory and establish the nature of the detailed rate-controlling mechanism.

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Acetylene as an Intermediate in Combustion of Petroleum Hydrocarbons

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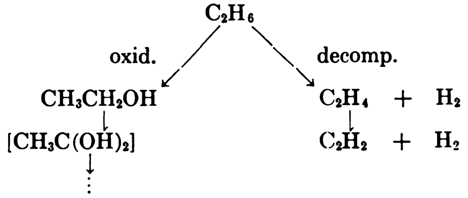
Laboratory and industrial-scale processes show that acetylene is one intermediate in carbon formation in the combustion of petroleum hydrocarbons. This is not only a result of thermal decomposition but a part of the complex of reactions occurring in the oxidation system. Steps resulting in the immediate production of acetylene seem to be molecular decomposition of molecules, or free radicals, or dehydrogenation, followed by combination or addition of oxygen. Peroxide formation may occur also. These reactions may be a general source of the hydrocarbon flame bands.

In 1892, Lewes (*13*, *14*, *66*) first proposed that acetylene is an important intermediate in combustion processes. He suggested a theory of luminosity of flames based upon its formation and subsequent "incandescent decomposition." This did not prove successful as a general explanation of luminosity, but in recent years a modified version of this concept has been advocated by Porter (*58*, *59*) and others. They suggest that acetylene is the starting point for the major reactions of carbon formation in flames and combustion.

Production of acetylene from natural gas and other petroleum hydrocarbons has grown sharply and it is predicted to exceed that from carbide within about 10 years (*26*). One of two important processes, the Sachsse process (*3*, *6*, *8*, *10*, *36*, *63*) involves the formation of acetylene in flames in the partial combustion or oxidation of methane.

Because there are important practical processes involving the formation of acetylene in combustion of hydrocarbons, and its reaction, it seems timely to review the background and present evidence on formation and reaction of this particular intermediate.

In earlier work, acetylene was not considered as an intermediate in the combustion proper, but, rather, as a product of thermal decomposition occurring as a side reaction due to the heat released by oxidation of part of the hydrocarbon. Egloff, Schoad, and Lowry (*21*) suggested, for example, the following scheme of reactions for ethane:



This viewpoint was consistent with the known increase in stability of acetylene relative to other hydrocarbons at temperatures in the range (*9*, *71*) of 1100° K. and above,

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and with experimental results on thermal decomposition of hydrocarbons (*22*). It has been the basis for industrial processes (*11, 12, 23, 37, 63*), particularly the Wulff process, which is the second of the two chief processes for producing acetylene from hydrocarbon gases. This involves rapidly alternating but separate cycles to produce heat by combustion and using the heat to decompose hydrocarbons.

The nature of the chain reactions which must occur both in oxidation and decomposition reactions, however, makes it clear that these cannot actually occur as parallel or independent processes in the same gaseous systems. Instead, consider a single system with numerous reaction steps occurring, some of which may lead to oxidation and others to decomposition products. Pease, in studies of the oxidation of propane and butane (*55*), noted as early as 1929 that oxidation must be accompanied by decomposition. He suggested that oxygen acts to "burn off" hydrogen from the hydrocarbon. A number of workers (*1, 70, 73*) noted the effect of oxygen in initiating and catalyzing pyrolysis reactions. Ethylene oxide (*48, 50*) and peroxides (*57*) have similar effects. Arthur and Napier (*2*), in studies of the carbon formed in diffusion flames, found strong evidence for the presence of hydroxyl and carbonyl groups and thus that the reactions producing the carbon must involve oxygen or oxygenated molecules and not just pyrolysis.

Acetylene is not easy to detect in such reaction systems because of its high reactivity, but there is strong evidence for its occurrence when the experimental conditions and techniques are such as to permit observations of unstable or transitory intermediates.

Knox, Norrish, and Porter (*38, 56*), using their technique of "flash photolysis," whereby a substance is suddenly raised to high temperature by a very intense light flash and the resulting pyrolytic reactions observed spectroscopically, clearly observed acetylene as an intermediate in the formation of carbon by flash photolysis and pyrolysis of ketene. MacCormac and Townend (*47*) found acetylene in cool flames of ether and oxygen, with 50 mole % ether and temperatures in the range of 320° to 395° C.

Foner and Hudson (*25*), using an extension of the mass-spectroscopic method of analyzing gases at various stages of methane-oxygen flames originally developed by Eltenton, found acetylene increasing to a maximum, then decreasing sharply in concentration as reaction proceeds. Kydd (*39*) used a probe to take gas samples from rich methane-oxygen flames. He found a similar maximum in acetylene concentration as the probe was raised more and more above the burner port. Relatively large amounts of acetylene were found, even in the cooled products and at compositions—e.g., 57% methane—for which equilibrium calculations show the amount of acetylene formed should be vanishingly small.

Prescott, Hudson, Foner, and Avery (*60*) extended the mass-spectrographic technique to the study of composition profiles across a low-pressure, propane-air flame under somewhat lean conditions. The appearance and disappearance of hydrogen, carbon monoxide, ethylene, and acetylene in the flame were demonstrated clearly. The proportion of acetylene was not high. Nonetheless, it is evident that the formation of acetylene is not just a result of pyrolysis of excess hydrocarbon by heat released in combustion of part of the gas. It is a result of reactions which must occur to some extent in all hydrocarbon combustion, but which would not be observable except by special techniques, or under conditions—such as rich flames or cool flames—where the later reactions of acetylene can be minimized.

Formation of Acetylene in Combustion Reactions

In considering the reactions for formation of acetylene in a combustion system, it is worth-while to note, first, the evidence as to the nature of the oxidation and pyrolysis reactions as separate processes. (No attempt is made to review all the voluminous literature in these fields but rather to consider results of significance to the immediate problem.)

Although there are many questions about individual steps in oxidation processes, investigators agree generally (*15, 16, 46, 47, 72*) that reaction is initiated by some source

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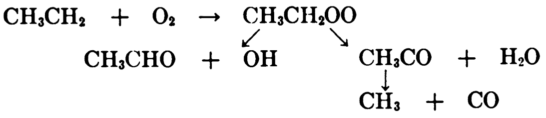
of free radicals, followed by peroxide formation. There are questions as to the extent of reaction at various positions, but general agreement is that secondary and tertiary hydrogens will be attacked preferentially. Thus

$$RCH_2CH_2R' + O_2 \rightarrow RCHCH_2R' + HO_2$$
$$RCHCH_2R' + O_2 \rightarrow RCH(OO)CH_2R'$$

Various reactions may then follow. Lewis and von Elbe (*46*) suggested



$$CH_3CH_2 + O_2 \rightarrow CH_3CH_2OO \rightarrow CH_3CHO + OH \quad \text{or} \quad CH_3CO + H_2O;\ CH_3CO \rightarrow CH_3 + CO$$

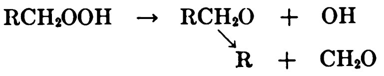
or, for branched chains,

$$RCHOOCH_2R' \rightarrow RCHO + R'CH_2O$$
$$R'CH_2O \rightarrow R' + CH_2O$$

Walsh, Boord, and others (*15*, *16*, *72*) used the sequence

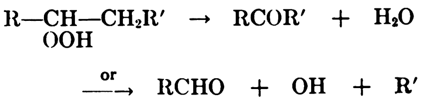
$$ROO + RH \rightarrow ROOH + R$$
$$RCH_2OOH \rightarrow RCHO + H_2O$$

or



$$RCH_2OOH \rightarrow RCH_2O + OH;\quad RCH_2O \rightarrow R + CH_2O$$

or

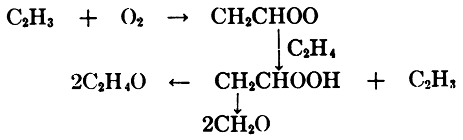


$$\underset{OOH}{R{-}CH{-}CH_2R'} \rightarrow RCOR' + H_2O$$
$$\xrightarrow{\text{or}} RCHO + OH + R'$$

Boord (*16*) also noted the possibility, suggested by Cullis, Hinshelwood, and others, that

$$ROO + RH \rightarrow ROOR$$
$$ROOR \rightarrow 2RO$$

For olefins (*7*, *46*) the corresponding type of process would be



$$C_2H_3 + O_2 \rightarrow CH_2CHOO \xrightarrow{C_2H_4} CH_2CHOOH + C_2H_3;\quad CH_2CHOOH \rightarrow 2C_2H_4O;\quad CH_2CHOOH \rightarrow 2CH_2O$$

It may be seen that the peroxidation mechanism leads primarily to degradation of the carbon chain, but that numerous dehydrogenation reactions are occurring also.

Storch (*65*) reviewed the probability of acetylene formation in thermal reaction, as shown in experiments such as the early ones of Bone and Coward (*13*). Voge and Good (*69*) and Laidler (*40*) reviewed more recent results. In general, reaction seems to follow a chain mechanism of the type originally suggested by Rice and Herzfeld:

$$C_2H_6 \rightarrow 2CH_3 \qquad E = 84\ \text{kcal.}$$
$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \qquad 8\ \text{kcal.}$$
$$C_2H_5 \rightarrow C_2H_4 + H \qquad 40\ \text{kcal.}$$
$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \qquad 7\ \text{kcal.}$$
$$H + C_2H_5 \rightarrow C_2H_6 \qquad 0\ \text{kcal.}$$

With higher hydrocarbons, there are additional possibilities, particularly for isomerization and splitting of radicals (*69*).

The experiments of Hinshelwood and his collaborators (*32*, *35*) gave strong evidence for the occurrence of unimolecular decomposition, such as

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad (1)$$

Under ordinary conditions, this may not be a major reaction, but for the problem of acetylene formation it is notable that Cvetanovic and Callear (*19*), and Mitchell and Le Roy (*49*), in studies of the photosensitized decomposition of ethylene, found a unimolecular mechanism. Ingold and Stubbs (*33*) also found that the decomposition of propylene starts with a molecular rearrangement and decomposition:

$$C_3H_6 \rightarrow CH_4 + C_2H_2 \qquad (2)$$

Under ordinary conditions of combustion, where high temperatures result from heat released in the oxidation processes, both thermal and oxidation types of chain reactions can be expected and the actual sequences of reaction must be intermingled. For the production of acetylene from higher hydrocarbons, the net processes must have a twofold effect—first, to reduce the carbon chain to two-carbon units, and second, to remove hydrogen. The peroxidation steps can cause degradation of large molecules to smaller fragments such as ethyl and propyl radicals, which may in turn give unsaturated compounds such as ethylene and propylene. Further oxidation, however, should result in effectively complete fragmentation of the carbon chains. This is shown in work on the combustion of ethylene (*7*, *46*), on the ethylene oxide decomposition flame (*27*), and on the reaction of oxygen plus ethylene (*18*). Reactions of the type

$$C_2H_4O \rightarrow CO + CH_4$$

are common. Under conditions where excess oxygen is present for reaction with free radicals or olefins the amount of acetylene formed is likely to be small. Formation of acetylene is favored in rich mixtures, but can occur even in lean ones.

For the second phase of reaction, the dehydrogenation, the presence of oxygen or oxygenated fragments can have a major effect. Reactions such as

$$\underbrace{C_2H_4 + O_2 \rightarrow C_2H_3 + H}_{\text{(or ROO, RO, OH, R, H)}} \qquad (3)$$

become possible under conditions much milder than those necessary for ordinary thermal decomposition. This step may be followed by further reaction to give acetylene (*5*, *61*, *68*, *70*):

$$C_2H_3 + X \rightarrow C_2H_2 + HX \qquad (4)$$

or

$$C_2H_3 \rightarrow C_2H_2 + H \qquad (5)$$

Szwarc (*67*) also suggested reactions of the type

$$C_3H_6 + H \rightarrow C_2H_4 + CH_3$$

These are the hydrogen-removal reactions which Pease (*55*), von Elbe (*70*), Walsh (*72*), Bailey and Norrish (*4*), Baldwin, Corney, and Simmons (*5*), Satterfield and Reid (*61*) and others noted. The effect is in accord with various experimental results. Appleby and coworkers (*1*) studied the accelerating effect of oxygen on butane decomposition, and Malinovsky and Stoyanovskaya (*48*) studied the accelerating effect of ethylene oxide on cracking of substituted benzenes. Plank and Nace (*57*) observed the effect of cumene hydroperoxide in the cracking of cumene. Dugger, Weast, and Heimel (*20*) found that preheating propane-air mixtures to 867° K. had appreciable effect on flame velocities, and that unsaturated products (propylene and ethylene) plus carbon were formed.

In addition to the chain mechanisms, appreciable acetylene may form by uni-

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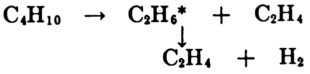
molecular decomposition reactions such as those noted above in thermal decomposition. The work of Newitt, Schmidt, and Thornes (*51, 52, 53*), and Ingold and Stubbs (*33*) on propylene, in particular, suggests that this decomposition may be an appreciable source of acetylene [though Szwarc (*67*) suggests a chain mechanism]. The work on ethylene (*18, 19, 49*) indicates that here also direct molecular decomposition may be an alternate to the type of chain shown above.

Spall and coworkers (*64*) found evidence for the effect of production of an activated molecule in reaction, specifically for the case:

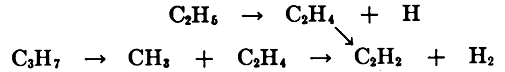


$$\begin{tikzcd} C_4H_{10} \arrow[r] & C_2H_6^* \arrow[d] & + \; C_2H_4 \\ & C_2H_4 & + \; H_2 \end{tikzcd}$$

Added ethane does not give the same effect.

The decomposition of free radicals is another type of unimolecular process of importance to this system. This may include reactions such as

and



$$\begin{tikzcd} & C_2H_5 \arrow[r] & C_2H_4 \arrow[dr] & + \; H \\ C_3H_7 \arrow[r] & CH_3 \; + \; C_2H_4 \arrow[rr] & & C_2H_2 \; + \; H_2 \end{tikzcd}$$

(6)

(7)

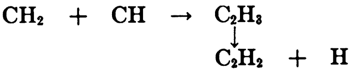
which were discussed by Leigh and Szwarc (*43, 44*), Bailey and Norrish (*4*), and Satterfield (*61*). Baldwin, Corney, and Simmons suggested alternative reactions where oxygen is present (*5*). Other radicals may also be involved. The decomposition of peroxidic or other oxygenated fragments (*4, 70*) is likely to play a major role in degradation of the carbon chain. Gray (*30*) recently summarized data on the stability of alkoxy radicals noting that in general C—C splitting predominates over C—H. Levedahl (*45*) found two- and four-carbon acetylenes in autoignition reactions of benezene with oxygen. These probably result from ring opening followed by decomposition of the resulting fragment.

A final possibility for a type of reaction resulting in acetylene formation which must be considered is that of combination of radicals. This is not likely to be significant in most systems, but in the case of methane reactions it becomes of particular interest. The production of ethylene, and acetylene in the thermal decomposition of methane requires some sort of combination reaction (*40, 65*). Kassel suggested a mechanism involving methylene radicals:

$$CH_4 \rightarrow CH_2 + H_2 \tag{8}$$

$$2CH_2 \rightarrow C_2H_4 \rightarrow C_2H_2 + H_2 \tag{9}$$

Rice and Dooley suggested one involving CH_3. Mirror tests gave no conclusive results on the gas-phase reaction. Wiever and Burton (*74*) reported "apologetically," that their results on the electric discharge indicate steps such as

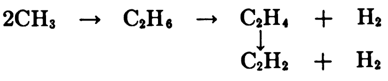


$$\begin{tikzcd} CH_2 \; + \; CH \arrow[r] & C_2H_3 \arrow[d] \\ & C_2H_2 \; + \; H \end{tikzcd}$$

(10)

Foner and Hudson (*25*), however, detected only CH_3 in the mass spectra of methane-oxygen flames.

The recombination most likely to be of importance seems to be:



$$\begin{tikzcd} 2CH_3 \arrow[r] & C_2H_6 \arrow[r] & C_2H_4 \arrow[d] \; + \; H_2 \\ & & C_2H_2 \; + \; H_2 \end{tikzcd}$$

(11)

Reactions of Acetylene in Combustion

The two chief possibilities to be considered for reactions of acetylene in flames and combustion must also be those of oxidation as contrasted to decomposition, recognizing again that these must be intermingled in actual reaction systems.

Oxyacetylene and acetylene-air flames have been widely used and studied and the results show that acetylene must disappear very rapidly in any oxygenated system at high temperatures. The acetylene reaction is one of the most rapid of combustion reactions, acetylene reacting with oxygen even faster than hydrogen (*17*).

On the basis of work by Bone and Andrew, Spence and Lenher with Kistiakowsky, and Steacie and MacDonald—which includes some evidence of formation of glyoxal—Lewis and von Elbe (*46*) suggested the mechanism

$$C_2H_2 + CHOCO \rightarrow CHOCHO + C_2H \qquad (12)$$

$$C_2H + O_2 \rightarrow CHOCO \qquad (13)$$

$$CHOCO + O_2 + CHOCHO \rightarrow HCO(OOH) + 2CO + CHO$$

$$CHOCHO + O_2 \rightarrow CHOCO(OOH)$$

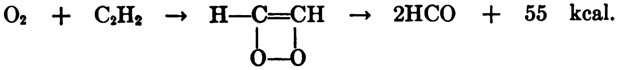
$$\swarrow \qquad \searrow$$

$$CHOCOO + OH \text{ or } CHOCO + HO_2$$

$$CHOCO \xrightarrow{\text{wall}} \text{destruction}$$

This leaves various questions unanswered—especially, whether the third step may not actually involve a sequence of simpler reactions.

In recent work particular emphasis has been given to studies of flame spectra and the evidence as to the formation and reaction of excited species such as C_2, CH, OH, and HCO from acetylene and oxygen (*17, 29, 31, 41, 42, 54*). The occurrence of excited hydrocarbon flame bands attributable to HCO radicals led Herman, Hornbeck, and Laidler (*31*) to suggest the reaction



$$O_2 + C_2H_2 \rightarrow \begin{array}{c} H-C{=}CH \\ |\quad\ | \\ O-O \end{array} \rightarrow 2HCO + 55\ \text{kcal.} \qquad (14)$$

as the source of these radicals. It has also been suggested that, for other hydrocarbon systems, acetylene is an intermediate which is the source of the HCO radicals (*42*).

At lower temperatures, Young, Vogt, and Nieuwland obtained peroxides from acetylenes and oxygen (*75*), but at higher temperatures oxygen initiates decomposition of acetylene (*50, 73*). Furthermore, Gaydon, with Broida (*17*) and Wolfhard (*29*) reported that excited HCO does not come directly from the acetylene molecules. This was based upon the relative occurrence of HCO and DCO in flames of mixtures of hydrogen and C_2D_2. As possible sources which might be considered, they suggested the reactions

$$C_2 + HO_2 \rightarrow HCO + CO \qquad (15)$$

$$H_2O + CH \rightarrow HCO + H_2$$

$$CO_2 + CH \rightarrow HCO + CO$$

Because these observations deal only with excited HCO, care must be used in any generalizations from them. Nonetheless the experiments suggest that other reactions than the addition-decomposition step shown above must be important.

An alternative pathway was suggested by Herman, Hornbeck, and Laidler to explain the appearance of C_2 and CH bands:

$$C_2H_2 + O_2 \rightarrow C_2H + HO_2 \qquad -60\ \text{kcal.} \qquad (16)$$

$$C_2H + O_2 \rightarrow HCC(OO) \qquad +50\ \text{kcal.} \qquad (17)$$

$$HCC(OO) + C_2H_2 \rightarrow HCC(OOH) + C_2H \qquad -10\ \text{kcal.} \qquad (18)$$

$$HCC(OOH) \rightarrow HCCO + OH \qquad -30\ \text{kcal.} \qquad (19)$$

$$HCCO \rightarrow CH + CO \qquad -75\ \text{kcal.} \qquad (20)$$

$$HCC + O_2 \rightarrow HO_2 + C_2 \qquad -120\ \text{kcal.} \qquad (21)$$

$$2CH \rightarrow C_2 + H_2 \qquad +30\ \text{kcal.} \qquad (22)$$

The deuterium tracer experiments of Broida and Gaydon indicated that CH does not come from acetylene itself, a peroxide, or a polymer, so they suggested

$$C_2 + OH \rightarrow CH + CO \qquad (23)$$

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This would not, however, necessarily replace Step 20, because this would give excited CH.

Experiments by Ferguson, using carbon-13 as tracer (*24*), showed that C_2 is not formed directly from acetylene or a simple polymer, but comes from single-carbon fragments. This would indicate that Reaction 22 is the probable source of C_2, rather than 21. Gaydon and Wolfhard (*29*) postulated that some type of polymerization occurs and that C_2 radicals result from fragmentation of such polymers. This was based partly on the fact that C_2 bands show up in a later zone of diffusion flames than does solid carbon. Ferguson's results on distribution of isotopic carbon were also in disagreement with this, if the mechanism is one of simple polymerization and resplitting of C_2 groups. Another difficulty is that if Reaction 15 is the source of HCO and the C_2 in turn comes from polymer, it is not easy to explain the occurrence of HCO bands in flames with excess oxygen, where polymerization would not seem to be likely.

At present it seems that no proposed mechanism can successfully explain all observations on flames, flame spectra, and the tracer experiments.

In the decomposition reactions of acetylene major interest must be in the problem of carbon formation. This problem has been the subject of a number of recent reviews (*2*, *56*, *58*, *59*, *62*, *66*). Porter (*58*, *59*) advocated the viewpoint that acetylene is the precursor of carbon in any hydrocarbon system. This is a somewhat controversial point which is not specific to the present discussion. There is no question that when acetylene is formed, decomposition to carbon is one reaction by which it will disappear.

Carbon formation from acetylene starts with a reaction such as 3:

$$C_2H_2 + O_2 \rightarrow C_2H + HO_2$$

The simplest possibility for later steps

$$C_2H \rightarrow C_2 + H \tag{24}$$

or

$$C_2H + O_2 \rightarrow C_2 + HO_2 \tag{25}$$

$$C_2 \rightarrow C(s)$$

can be eliminated on the basis of the energy needed, and the spectroscopic evidence and carbon-tracer experiments discussed above. Kistiakowsky and Zinman (*76*) concluded that solid carbon is formed by condensation in detonation of very rich oxyacetylene mixtures, but this is quite a different system from ordinary flames.

The second stage of reaction must involve certain combination steps, and these may be accompanied by dehydrogenation. (This is similar to the suggestion of Gaydon and Wolfhard for oxyacetylene flames.) It is not established whether these may be of the type

$$C_2H + C_2H_2 \rightarrow C_4H_3 \rightarrow C_4H + H_2 \tag{26}$$

or a chain such as

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{27}$$

$$H + C_2H_2 \rightarrow H_2 + C_2H\text{, etc.} \tag{28}$$

The behavior of decomposition flames of acetylene (*50*, *73*) indicates a chain mechanism, and there is evidence, from data on paramagnetism, for the presence of free radicals in the solid carbon itself (*34*). However, these effects could result with either type of mechanism, and do not furnish any clear indication with regard to dehydrogenation alone.

Reactions such as

$$C_4H_3 + R \rightarrow C_4H_2 + RH, \tag{29}$$

where R may be oxygen or hydroxyl, must also be considered as possibilities in combustion systems. Oxygen or oxygenated fragments probably play a role in the hydrogen-stripping reactions for acetylene just as for other hydrocarbons. The data of Arthur and Napier (*2*) on hydroxyl and carbonyl in carbon from diffusion flames and of Gaydon and Fairbairn (*28*) on oxygen in carbon formed in the afterglow of a discharge appear to confirm this.

The necessity for postulating combination steps raises questions regarding the nature of the intermediates which may be formed from acetylene and then reacted to form carbon. Various types have been suggested, such as aromatics, fulvene-type cyclic compounds, and highly unsaturated aliphatics. There is evidence for formation of all such types in thermal reactions of acetylene, but not enough is known of their chemistry to determine which might be of most significance as an intermediate under combustion conditions. It is probable that no one type actually controls the reaction. Parallel with the chemical question here, there is an important physical question of whether the nucleus for the ultimate carbon particle is a droplet of liquid polymer or a small bit of solid.

It is this tendency toward combination rather than decomposition—a tendency which is almost unique to acetylene among the ordinary hydrocarbons—which is the basis for the theory of Porter and others, that formation of acetylene is the precursor of carbon formation in all hydrocarbon-combustion systems. At high temperatures, other hydrocarbons react by fragmentation—splitting C—C and C—H bonds—to give smaller and smaller carbon chains. Acetylene may, on the other hand, react by combination and thus perhaps build toward larger structures such as a carbon particle.

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Role of Formaldehyde in Combustion

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Recent research which has extended and strengthened previous interpretations of the role of formaldehyde in combustion processes is cited and discussed. Formaldehyde participates in two regimes in the oxidation of hydrocarbons in the low and high temperature regions. In the former, there appears to be considerable variation among individual hydrocarbons, but, in general, formaldehyde decreases the induction period while inhibiting cool-flame formation. In the high temperature region, above about 400° C., formaldehyde must be ascribed the role of degenerate chain-branching agent.

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One of the striking aspects of the combustion of hydrocarbons and hydrocarbon derivatives is the universal occurrence of formaldehyde in the reaction products. In view of the remarkable property of appearing as a common denominator of combustion processes, it is natural to inquire whether formaldehyde plays a significant role in determining the course of reaction. The evidence that has accumulated regarding the contribution of reactions of formaldehyde to the mechanism of combustion is cited and discussed.

Nature of Hydrocarbon Oxidation

It is generally acknowledged that the oxidation of hydrocarbons takes place by two different mechanisms depending on the temperature. Both modes of oxidation are thought to involve degenerate chain branching (*54*) in which a moderate amount of a relatively stable intermediate functions as a branching agent. At temperatures below about 400° C. (the precise temperature range depends on the particular hydrocarbon as well as the pressure and composition) a period of little or no pressure change is followed by acceleration of the reaction to a maximum rate. Low temperature oxidation processes are characterized by the formation of oxygenated species such as alcohols, aldehydes, acids, and peroxides. However, the identity of the essential intermediate is not known with certainty. The available evidence appears to favor either a higher aldehyde or peroxide (*2, 4, 39, 43, 64*). Single and multiple cool flames (*4, 40, 41*) have been observed under favorable conditions of pressure, temperature, and composition. Above the temperature limit of cool flames, a transition region is found in which the reaction rate exhibits a negative temperature coefficient (*31, 47, 61*). With further increase of temperature, a new mechanism of oxidation becomes operative (*44, 45, 57*), involving a second induction period followed by a steady-state reaction which may lead to thermal explosion. It is generally believed, although it has been established conclusively in only a limited number of cases, that in the high temperature region, the key intermediate is formaldehyde.

Experimental work in the field of hydrocarbon oxidation has resulted in a number of proposed reaction mechanisms (*11*, *37*, *42*, *49*, *64*). Although there is general agreement concerning the over-all nature of the processes involved, there are considerable variations in the formulation of the specific chemical reactions and in the identification of the chain carriers, particularly in the low temperature regime. The two modes of hydrocarbon oxidation have been critically discussed in several recent review articles (*32*, *33*, *38*, *43*, *63*).

Reactions of Formaldehyde

The role of formaldehyde in combustion can be evaluated with more certainty when the thermal- and photodecomposition and the oxidation are established. The thermal decomposition occurs at a reasonable rate above about 450° C. with an apparent activation energy of 45.3 kcal. (*17*). The major products of the reaction are carbon monoxide and hydrogen. Fletcher (*17*) interpreted the pyrolysis as a homogeneous, bimolecular reaction, at least in the range of 30 to 400 mm. and 510° to 607° C. Longfield and Walters (*34*) showed that the decomposition is radical-sensitized and occurs at a faster rate with addition of 1% of ethylene oxide. That the mechanism of thermal decomposition of pure formaldehyde is a chain process was shown by experiments with mixtures of normal and deuterated formaldehydes in which HD is formed in the absence of isotope mixing of the formaldehydes (*28*). The propagating steps appear to be $HCO \rightarrow H + CO$ and $H + CH_2O \rightarrow H_2 + HCO$.

Photolysis yields information on the stability of the HCO radical, an important consideration in the mechanistic interpretation of hydrocarbon-combustion processes. Gorin (*22*) determined the heat of dissociation of the HCO radical to hydrogen and carbon monoxide as equal to or greater than 26 kcal. (27 kcal. in the light of more recent thermodynamic data), because 3650 A. radiation appeared to be effective in initiating chains. Iodine was used as a detector of hydrogen atoms by hydrogen iodide formation. Radiation of 3650 A., corresponding to 78 kcal., causes the initial carbon-hydrogen bond rupture, while 105 kcal. are required for the reaction $CH_2O \rightarrow 2H + CO$. The difference between these quantities is the dissociation energy of HCO to H + CO.

Calvert and Steacie (*10*) assign a lower limit of 14 kcal. for the activation energy of this reaction on the basis of a measured over-all activation energy and a kinetic mechanism for the photolysis at 3130 A. This imposes a corresponding upper limit on the dissociation energy of HCO. Schoen (*53*), using deuterium as a detector of hydrogen atoms through HD formation, established a threshold for the energy required to break the first carbon-hydrogen bond in formaldehyde. Gorin's value was confirmed. Because of the competing reactions $H + CH_2O \rightarrow H_2 + HCO$ and $H + H_2 \rightarrow H_2 + H$ the amount of HD formed was low. The first reaction was favored, and the method lacked sensitivity. This objection was overcome by photolyzing mixtures of formaldehyde and deuterated formaldehyde (*29*), HD formation in the absence of exchange between formaldehydes indicating hydrogen atom formation. The value of 27 kcal. or greater for the dissociation energy of HCO was firmly established.

Because this value has been found independently of a choice of detailed kinetic processes, the mechanism postulated by Calvert and Steacie for the photolysis of formaldehyde requires modification. If, for example, a reaction such as $HCO + CH_2O \rightarrow H_2 + CO + HCO$ is operative (*58*) then the activation energy measured for the rate of hydrogen production can no longer be simply associated with the activation energy of the reaction $HCO \rightarrow H + CO$ less that of the wall reaction $HCO \xrightarrow{\text{wall}}$ products.

The oxidation of formaldehyde has received the attention of several investigators (*1*, *7*, *18*, *24*, *32*, *52*, *55*, *56*, *62*), and some aspects of the mechanism are now fairly well understood. The activation energy in the range from 300° to 375° C. is about 25 kcal. per mole. Harding and Norrish (*24*) give a value of 35 to 45 kcal. for the range 400° to 475° C. Initiating steps proposed are $CH_2O + O_2 \rightarrow HCOOH + O$, $CH_2O + O_2 \rightarrow CHOO + OH$, or $CH_2O + O_2 \rightarrow CHO + HO_2$. Lewis and von Elbe (*32*) specify termination by $HCO_3H + CHO \rightarrow CH_2O + CHO_3$, CHO_3 being considered inert in the 300 to 375° C. region. Scheer (*52*) suggests destruction of CHO_3 in a collisional process to give carbon monoxide and inactive HO_2. For chain continuation there has been proposed $CHO + O_2 + CH_2O \rightarrow HCO_3H + CHO$ and $HCO_3H + CH_2O \rightarrow CHOO + H_2O + HCO$ with HCO acting as a chain carrier. The disposition of CHOO is not specified. In a slightly different mechanism both HCO and HCO_3 continue the chain with $HCO + O_2 \rightarrow HCO_3$ and $HCO_3 + CH_2O \rightarrow HCO_3H + HCO$. Inclusion of a third body in the former reaction may be preferred because it is highly exothermic.

It was first noted by Spence (*56*), that mercury had an accelerating effect on the formaldehyde oxidation. Lewis and von Elbe (*32*) suggest that the absence of an induction period in the experiments of Axford and Norrish (*1*), compared to those of Snowdon and Style (*55*), was to be attributed to the destruction of peroxides by mercury vapor from heated mercury cutoffs in the Axford-Norrish experiments. This was confirmed in Scheer's work, where mercury vapor eliminated the induction period. A freshly cleaned surface had an effect similar to mercury vapor. It was found that although the induction period represents only a slow pressure rise, extensive reaction occurs, the Δp during this time being unrelated to the formaldehyde consumption.

Rates for the oxidation are consistent with the equation

$$-\left[\frac{d(\mathrm{CH_2O})}{dt}\right]_0 = \mathrm{K}(\mathrm{CH_2O})_0^2.$$

Because the rate is independent of vessel size in the presence of mercury vapor, and inert diluents decrease the rate (*1*), it is concluded that initiation and termination are gas phase, and peroxides are destroyed at the wall in mercury free systems. A more detailed understanding of the mechanism of formaldehyde oxidation requires quantitative consideration of peroxides such as performic acid, and unequivocal evidence for the identification of chain carriers.

Role of Formaldehyde in Low Temperature Region of Hydrocarbon Oxidation

The role of formaldehyde in hydrocarbon combustion varies with the hydrocarbon and the experimental conditions, principally the temperature. There are two distinguishable regions characterized by fairly distinct oxidation mechanisms. The lower region is considered first.

Methane reacts only slowly with oxygen below 400° C. Ethane oxidation was observed by Bone and Hill (*8*) at 290° to 323° C. Formaldehyde, a reaction product, was found to increase, reach a maximum, and then decrease. Addition in amounts of 1% to a 3 to 1 ethane-oxygen mixture at 316° C. and 720 mm. eliminated the induction period, but other additives such as nitrogen dioxide, acetaldehyde, ethyl alcohol, or water, were also more or less effective.

Propane oxidation has been studied extensively below 400° C. (*16, 25, 30, 41, 46-8, 60*). Newitt and Thornes (*41*) charted the cool flame region and made several significant observations on the occurrence of formaldehyde. They found that formaldehyde increases as the reaction proceeds but the higher aldehydes go through a maximum and then decrease in initially equimolar mixtures of propane and oxygen at 460 mm. and 274° C. (below the cool-flame zone) after a 15-minute induction period. The maximum for peroxides occurs at an appreciable time interval after the higher aldehydes but simultaneously with the maximum for formaldehyde. Slow combustion at 360 mm. and 400° C. (beyond the cool-flame zone) shows different behavior. Peroxides and aldehydes form a much larger proportion of the liquid products. Formaldehyde, present in smaller quantities and appearing later than the higher aldehydes, diminishes as the reaction proceeds. At 400 mm. and 294° C. (in the cool-flame zone) higher aldehydes rise to a maximum just before the cool flame and then decrease after its passage. Formaldehyde increases up to the time of the first cool flame, showing only small variations thereafter. These observations were made on a per cent propane burnt basis. Repa and Shtern (*50*) studied the cool-flame oxidation of propane at 280° C. and 420 mm. They found that aldehydes increased in concentration until the third cool flame and then remained constant. Preliminary addition of acetaldehyde did not alter the final concentration of formaldehyde, suggesting that formaldehyde is not a product of acetaldehyde degradation.

Harris and Egerton (*25*) reported that formaldehyde added to a 1 to 1 mixture of oxygen and propane at 300° to 340° C. increased the induction period. Satterfield and Wilson (*51*) ascribe formaldehyde formation in propane oxidation above 370° C. to $CH_3 + O_2 \rightarrow CH_2O + OH$.

As pointed out by Mulcahy (*37*), the general behavior of butane is similar to that of pentane and hexane. Bardwell (*3*) investigated the cool-flame phenomenon in butane oxidation, and found that formaldehyde was the principal aldehyde formed, its ratio to acetaldehyde being about 4 to 1 immediately prior to or following the first cool flame. Formaldehyde, added to the reaction mixture, lengthened the induction period defined as the time between introduction of the reactants to the vessel and the first cool flame. However, 10 mm. of added formaldehyde lowered the pressure limit for two-stage ignition from 280 mm. to 240 mm. Batten, Gardner, and Ridge (*5*) observed that formaldehyde appeared before the higher aldehydes in the low-temperature oxidation of isobutane. The higher aldehydes become important only at the end of the induction period. This is in contrast to the behavior of propane, and is doubtless due to structural differences of the hydrocarbons.

Moderate amounts of formaldehyde exerted an inhibiting effect by increasing the induction period in pentane and hexane oxidation (*13*). The higher aldehydes and formaldehyde appear in approximately equivalent amounts. Decomposition of alkoxy radicals, $RCH_2O \rightarrow R + CH_2O$, is considered the source of formaldehyde. The effect of added formaldehyde is shown in Table I.

Table I. Influence of Formaldehyde on Induction Period of "Spectroscopically Pure" Hexane (*13*)

Hexane, 50 Mm. Temp., 225° C. Oxygen, 200 Mm.

CH_2O, Mm.	Induction Period, Min.
0	18, 20, 12
0.25	17
0.4	15
1.5	40, 60
3.0	120
5.0	>180
6.0	>180

Cullis and Hinshelwood (*13*) noted that their "spectroscopically pure" hexane contained an impurity. With pure *n*-hexane the concentration of formaldehyde remained constant during the induction period, but the inhibiting effect of formaldehyde was still observed.

Garner, Long, and Temple (*19*), using a flow system so that large amounts of reaction products could be collected, observed a ratio of acetaldehyde to formaldehyde of about 4.5 to 1 in the oxidation of hexane at 310° C. in a stoichiometric mixture. Bailey and Norrish (*2*) studied the oxidation of hexane in the cool-flame region. The considerable quantities of formaldehyde in the products were presumed to arise from alkoxy-radical decomposition and a methyl radical-oxygen reaction.

Table II. Effect of Formaldehyde and Acetaldehyde on Induction Period of Propylene Oxidation (*6*)

Temp., 340° C. I = Induction period ρ = Maximum rate ΔP_∞ = Total pressure change

CH_2O, Mm.	C_3H_6 Mm.	O_2 Mm.	I Min.	ρ Cm./Min.	ΔP_∞ Cm.
0.0	51.0	70.5	15.0	1.1	1.76
2.0	49.0	70.0	6.6	1.0	1.76
4.5	51.0	69.0	4.0	1.0	1.75
8.0	51.5	71.0	3.0	1.0	1.76
20.0	50.0	70.0	—	0.6	2.4
CH_3CHO, Mm.					
1.5	49.0	71.0	3.3	1.2	1.80
3.0	48.5	70.0	0.0	1.3	1.82
4.0	51.5	71.0	—	1.6	1.85

Bawn and Skirrow (*6*) found that formaldehyde reduced the induction period in the gas phase oxidation of the simpler olefins such as propylene, 2-butene, and 1-hexene. Data for propylene are given in Table II. An analysis of the products from the reaction of 50 mm. of propylene and 140 mm. of oxygen at 340° C. gave the ratio of formaldehyde to total aldehyde to peroxide as 3 to 25 to 5 after a 7-minute induction period. 2-Butene, oxidized at 290° C. and a total pressure of 82.5 mm., gave formaldehyde, acetaldehyde, and acrolein as the aldehydic products, with formaldehyde, as in the case of propylene, appearing in relatively small amounts.

Mulcahy and Ridge (*39*) considered the kinetics of the oxidation of propylene in some detail. Both formaldehyde and acetaldehyde shorten the induction period, defined as the time between introduction of the reactants and appreciable pressure change. Table III shows the effect of both added formaldehyde and acetaldehyde. There is essential agreement between the results of Bawn and Skirrow, and Mulcahy and Ridge, on the effect of the aldehydes, with acetaldehyde being much the greater. Mulcahy and Ridge state that the addition of formaldehyde or acetaldehyde in amounts approximately equivalent to their concentrations at the end of the normal induction period, about 7 mm. and ~1.5 mm. respectively, produce about equal effects. This conclusion appears to be only tentative, however, as the effect of acetaldehyde increases very markedly in the vicinity of 2 mm. Formaldehyde inhibits cool-flame formation but leaves the maximum rate unchanged. That formaldehyde added initially has an accelerating effect is cited as evidence for the autocatalytic nature of its rise in concentration during the induction period, and does not result merely from the breakdown of another substance building up autocatalytically. In view of the rather moderate effects of the addition of even large quantities of formaldehyde, the argument is not compelling.

Table III. Effects of Addition of Formaldehyde and Acetaldehyde on 70 Mm. of Propylene Plus 350 Mm. of Oxygen at 291° C. (Mulcahy and Ridge)

CH_2O	Mm. Added	*I*, Minute	
	0	26–29	weak cool flame
	7.5	15	ρmax. = 18.5 mm. per minute
	18	~11	ρmax. = 18.5
	26	~10	ρmax. = 18.5
CH_3CHO	0	25^a, 28^b. 27.5^a	[a] cool flame and ignition [b] weak cool flame.
	2	16	ignition
	4	4	—
	5	3	ignition
	6.5	0.5	ignition
	8.5	<0.5	ignition

Chamberlain and Walsh (*12*) studied the oxidation of diethyl and diisopropyl ether to gain an insight into hydrocarbon oxidation. Such phenomena as cool-flame formation, low and high temperature regions of oxidation, and ignition to hot flames, occur. Formaldehyde inhibits cool flames in ethers, and both formaldehyde and acetaldehyde inhibit the low temperature slow oxidation, the effect of the former being much the greater. The effect of acetaldehyde is opposite that observed with hydrocarbons, so that the analogy between ether and hydrocarbon oxidation must be accepted with reservations. Chamberlain and Walsh suggest that the inhibiting effect of formaldehyde may be ascribed to a condensation reaction of formaldehyde with hydroperoxides.

Among other substances studied for their resemblance to hydrocarbons in their oxidation behavior are the aliphatic amines (*14*) and methyl ethyl ketone (*4*). In the former, formaldehyde shortens the induction period, while in the latter, it has little effect.

Cool flames, characteristic of the low temperature region of oxidation of hydrocarbons, show a luminescence due to transition of electronically excited formaldehyde molecules to the ground state. Topps and Townend (*59*) give a ratio of 10^6 for the number of hydrocarbon molecules reacting to the number of quanta emitted. Gaydon (*20*) pointed out that in view of the possibility of collisional deactivation before a radiative transition, production of excited formaldehyde molecules need not be so rare an event as the factor 10^6 might indicate. Because at least 77 kcal. are required for the excitation, Walsh (*64*) has suggested that only a radical-radical reaction could be sufficiently exothermic to produce excitation. Lewis and von Elbe (*32*) proposed the reactions

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$$CH_3 + HO_2 \rightarrow CH_2O^* + H_2O \quad \text{or}$$

$$CH_3 + CHO_3 \rightarrow CH_2O^* + H_2O + CO$$

both of which are exothermic by over 100 kcal. However, methane oxidation does not show chemiluminescence, although CH_3, CHO_3, and HO_2 are presumed present during the reaction. Gaydon, Moore, and Simonson (*21*) favor the reaction suggested by Damköhler and Eggersglüss (*15*), $RCH_2O + R' = RR' + CH_2O^*$ and propose that R and R′ might be H and OH, respectively.

The data for assessing the role of formaldehyde in the oxidation of hydrocarbons below 400° C. are summarized in Table IV. It is evident that generalizations at this time are premature, and it is difficult to determine whether the difference reported for the various hydrocarbons are indeed characteristic of the individual species, or that such extraneous effects as variation in surface conditions, sampling techniques, precision of analytical methods, or reactions between end products such as peroxides and aldehydes are significant.

Table IV. Effect of Formaldehyde on Oxidation of Hydrocarbons and Allied Substances below 400° C.

Reactant	Conditions	Formaldehyde Added	Effect
Methane	No reaction		
Ethane (*8*)	3:1 Ethane-oxygen, 316° C., 720 mm. pressure	1%	Eliminated induction period
Propane (*25*)			Increased induction period
Butane (*3*)	1:1 Butane-oxygen, 280 mm. pressure		Lengthened time to appearance of cool flame
Pentane (*13*)			Increased induction period
Hexane (*13*)	1:4 Hexane-oxygen, 225° C., 250 mm. pressure		Increased induction period
Propylene (*6, 39*)	5:7 Propylene-oxygen, 340°C., 120 mm. pressure	2.0 to 20.0 mm.	Decreased induction period
	1:5 Propylene-oxygen, 291° C., 420 mm. pressure	7.5 to 26.0 mm.	Decreased induction period
2-Butene (*6*)			Decreased induction period
Diisopropyl ether (*12*)	3:7 Ether-oxygen, 210° C., 100 mm. Quarty vessel	3 mm.	Increased induction period
Ethylamine (*14*)	285° C.		Decreased induction period
Propylamine (*14*)			
Methyl ethyl ketone (*4*)	328° C.		Little effect

Formaldehyde, in sufficient quantities, can suppress cool-flame formation. Jost (*27*) presents evidence indicating that cool flames are a form of branched-chain explosions. It has been suggested that the cool-flame reaction is quenched by its own reaction product, formaldehyde, and arrested short of complete release of chemical enthalpy. This seems unlikely, however, because in systems exhibiting multiple cool flames the concentration of formaldehyde after the first cool flame does not drop; in some cases it increases, and yet does not suppress subsequent cool flames. Bardwell (*3*), and Bardwell and Hinshelwood (*4*) explain cool flame phenomena by a modified theory of Salnikov. This thermal theory is further supported by the results of Knox and Norrish (*30*) in the ethane-oxygen system. The key intermediate is presumed to be a peroxide by Bardwell and Hinshelwood (*4*). Formaldehyde is considered an inert, stable product with little effect on the reaction.

Kinetic studies indicate that the oxidation of formaldehyde below about 300° C. and at small concentrations should be very slow. The expression for the rate is proportional to the square of the formaldehyde concentration. Formaldehyde might be expected to be inactive in inducing hydrocarbon oxidation in this region.

This is in marked contrast to the higher aldehydes which oxidize much more readily, at temperatures as low as 100° C.—e.g., acetaldehyde (*35*). The mechanism by which formaldehyde reduces the induction period in hydrocarbon oxidation below 300° C. is not evident. An inhibiting effect is explicable on the basis of removal of free radicals, as Lewis and von Elbe (*32*) have pointed out. This could occur by $CH_2O + R \rightarrow RH + HCO$. HCO is then oxidized to the relatively inert CHO_3 which diffuses to the wall and is destroyed. Above 300° C. formaldehyde is oxidized more rapidly, giving rise to free radicals, and it is not surprising to find that the induction period in some hydrocarbon oxidations is shortened.

The low-temperature oxidation represents a complex system and can be better interpreted when the elementary reactions are firmly established. We are inclined to assign formaldehyde only a minor role in the low-temperature regime. Further experimental work is required to clarify the interactions between formaldehyde and peroxides, the radical-induced formaldehyde oxidation, and the effect of formaldehyde addition in the low-temperature hydrocarbon-oxygen systems. It has been established that mercury vapor is effective for the destruction of peroxides. Mercury vapor addition to systems in the cool-flame zone would perhaps be of value in assessing not only the role of peroxides, but also that of formaldehyde in this interesting region.

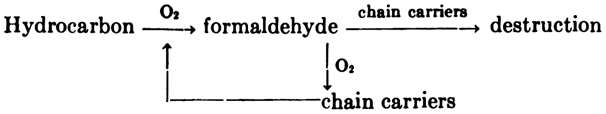
Role of Formaldehyde in High-Temperature Region

An important feature of the high-temperature oxidation of hydrocarbons is the progressive accumulation of formaldehyde during the induction period and the influence that it may exert on the subsequent course of reaction. Detailed studies of the role of formaldehyde in the combustion of hydrocarbons at temperatures above 400° C. have been reported for methane, ethylene, and cyclopropane.

According to a recent review (*63*), the important features of the slow combustion of methane are:

> Minute traces of formaldehyde are formed spontaneously from methane and oxygen. Chain carriers are formed by reaction of formaldehyde and oxygen. Formaldehyde is formed by reaction between chain carriers and methane. Formaldehyde is destroyed by reaction with chain carriers.

The reaction sequence may be visualized diagrammatically in the following manner:



It is clear that the concept of formaldehyde as the relatively stable intermediate responsible for degenerate branching is a fundamental one in elaborating the kinetics of methane oxidation. Indeed the statement has been made (*64*) that the combustion of methane may be regarded as the formation and oxidation of formaldehyde.

The evidence on which the above considerations are based has accumulated from extensive experimental investigation of the methane-oxygen system (*7, 11, 32, 42–45*). Analytical determinations of the course of reaction during the induction period have established that the increase in formaldehyde concentration is accompanied by a corresponding increase in the rate of methane consumption. The build-up of formaldehyde was found to follow an approximately exponential law, the maximum rate of the reaction being reached at the time the formaldehyde concentration achieved its steady-state value. These observations demand that the induction period be autocatalytic with respect to formaldehyde and predict that the length of the induction period should be shortened by prior addition of formaldehyde. It was found experimentally that small amounts of formaldehyde shortened the induction period while addition of the quantity normally present at the end of the induction period eliminated it altogether. Addition of larger quantities of formaldehyde resulted in a temporary increase of the maximum rate until the steady-state concentration was re-established. The preceeding observations have been taken into account in the various reaction mechanisms proposed for the oxidation of methane. The scheme of Lewis and von Elbe (*32*) will serve as an illustration.

$$CH_2O + O_2 = \text{free radicals} \rightarrow OH \qquad (1)$$

$$OH + CH_4 = H_2O + CH_3 \qquad (2)$$

$$CH_3 + O_2 = CH_2O + OH \qquad (3)$$

$$OH + CH_2O = H_2O + HCO \qquad (4)$$

$$CHO + O_2 = CO + HO_2 \quad (5)$$

$$CHO + O_2 + M = CHO_3 + M \quad (6)$$

$$CHO_3 + CH_2O = 2CO + H_2O + OH \quad (7)$$

$$OH \xrightarrow{\text{wall}} \text{destruction} \quad (8)$$

$$HO_2 \xrightarrow{\text{wall}} \text{destruction} \quad (9)$$

$$CH_2O + O_2 \xrightarrow{\text{wall}} \text{destruction of } CH_2O \quad (10)$$

The degenerate-branching reaction of formaldehyde leading to chain carrier formation is represented by Equation 1. Further increase of the chain carrier concentration with concomitant increase of formaldehyde concentration takes place through Equations 2 and 3. The formaldehyde concentration reaches a steady state owing to the operation of the destructive reaction in Equation 4, whose rate becomes equal to that of the formaldehyde producing reaction sequence, Equations 2 and 3, when a sufficient amount has accumulated. In the steady state, the spontaneous or triggering reaction between methane and oxygen to form traces of formaldehyde may be neglected as it is insignificant compared to Equations 1, 2 and 3. Reactions 5 and 6 which represent a competition between chain-breaking and chain-continuing processes have been included as a means of securing agreement between the theoretical and observed rate law. Reaction 7 is paired with 6 to allow CHO_3 to function as a chain carrier, whereas Equation 9 dictates the heterogeneous destruction of the HO_2 radical formed in Equation 5. Reaction 8 has been introduced to accommodate the diameter and pressure dependence of the rate, and Equation 10 satisfies the observed dependence of the reaction on the nature of the surface. The mechanism presented is not unique, but the authors believe that it represents the least implausible of a very limited number of possibilities.

It has been shown recently (*43*), that the length of the induction period in methane oxidation may be shortened by irradiation of the reacting mixture with ultraviolet light. Utilizing the wave length region 2400 to 3800 A. in which neither the primary reactants nor any possible peroxide intermediates absorb, Norrish was able to accelerate the reaction and induce ignition in cases near the thermal ignition limit. The effect was explained on the basis of a photochemically induced delayed branching of formaldehyde

$$CH_2O + h\nu = H + HCO \quad (11)$$

$$HCO = H + CO \quad (12)$$

leading to an increase in the net branching factor. Recent work on the photodecomposition of formaldehyde (*29*) has established the dissociation energy of the carbon-hydrogen bond in HCO to be close to 30 kcal. Consequently the radical is capable of independent existence at these temperatures and need not necessarily undergo a dissociation as the sole reaction path. The validity of the photo-induced delayed branching argument remains unimpaired and lends additional strong support to the interpretation of formaldehyde as the essential intermediate of methane oxidation.

The oxidation of ethylene in the high temperature region has recently been studied by Harding and Norrish (*24*). The object of this work was to test the hypothesis that formaldehyde plays an important part in the oxidation of ethylene just as it does in that of methane. The experimental results may be summarized as follows:

The reaction starts at a low rate as shown by the rate of pressure change and accelerates in the manner commonly associated with degenerate branching.

The pressure of formaldehyde in the system is built up to a maximum which coincides approximately with the attainment of maximum reaction velocity.

At 400° C. addition of formaldehyde in amounts up to 18 mm. reduced the induction period or eliminated it without affecting the maximum rate of reaction. At 461° C. only 5 to 6 mm. of formaldehyde were needed to accomplish this. When quantities in excess of these values were added, the reaction started at a rate faster than normal, and subsequently settled down to its normal value.

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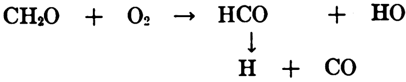
From a study of the maximum rates at different temperatures, the reaction was characterized by an activation energy varying from 26 kcal. at 400° C. to 53 kcal. at 500° C. The pressure-time curves were of the same type throughout the range of temperatures investigated and of the form indicating the presence of a degenerate-branching process. In view of the change in activation energy, it was concluded that more than one such process, depending on the temperature, was taking part. Estimates of the activation energy for formaldehyde oxidation vary between 21 and 30 kcal. (*52*) in the temperature range 300° to 375° C. Determination of the variation between 400° and 500° C. by Harding and Norrish (*23*), the method of ignition limits being employed at the higher temperatures, gave values of 35 to close to 50 kcal.

If it is accepted that the activation energy of a chain reaction is largely that of the process generating chains, then the parallelism in the behavior of the energies of activation for the ethylene and formaldehyde oxidations may be interpreted on the basis of the degenerate-branching reaction; the former is identical with the initiation reaction for the latter. Two possible reactions were suggested

$$CH_2O + O_2 \rightarrow HCOOH + O \tag{13}$$



$$\begin{array}{l} CH_2O + O_2 \rightarrow \underset{\displaystyle H + CO}{\overset{HCO}{\downarrow}} + HO_2 \end{array} \tag{14}$$

the first being approximately thermoneutral and the second approximately 50 kcal. endothermic (*23*). The variable over-all activation energies of the oxidation of ethylene and formaldehyde are thus ascribed to the changing relative importance of the two reactions as the temperature is increased.

In view of the evidence cited, it is clear that reactions of formaldehyde make a substantial contribution to the kinetics of the high-temperature oxidation of ethylene. However, attention should be drawn to one further observation of Harding and Norrish (*24*). The maximum pressure of formaldehyde developed at 400° C. approximates 6 mm., whereas the amount just necessary to eliminate the induction period at this temperature is close to 18 mm. This result suggests that another intermediate may play a part without affecting the kinetics of the reaction. In this connection it was observed that ethylene oxide was formed and built up to a small steady-state concentration during the induction period. The relative ineffectiveness of prior addition of ethylene oxide in reducing the induction period is consistent with the conclusion that formaldehyde plays the dominant role.

The slow combustion of cyclopropane between 380° and 430° C. has been investigated by McEwan and Tipper (*36*). A period of inappreciable pressure rise was followed by acceleration to a maximum rate, after which the rate fell until the pressure became constant. During the period of acceleration there was an exponential relationship between the pressure rise and the time. These observations imply that a degenerate chain-branching mechanism is involved. The similarity between the variation of the maximum rate and the net-branching factor with temperature and pressure of reactants, and also the dependence of the maximum rate on the initial pressures of oxygen and cyclopropane rather than the instantaneous pressures at the time of attainment of this rate, support the view that some intermediate was being formed giving rise to delayed branching.

The only organic intermediate found to be present during the reaction was formaldehyde. Its concentration rose to a maximum at about the time of the maximum rate and then fell off. The pressure was approximately proportional to the rate during a large part of the reaction. The maximum pressure was proportional to the oxygen pressure (at low oxygen and constant cyclopropane pressures) and to the pressure of cyclopropane (at constant oxygen pressure). Initial addition of 1 mm. of formaldehyde to a 2 to 1 cyclopropane-oxygen mixture at 300 mm. and 428° C. had a marked effect on the induction period (defined as the time to a small pressure increase—e.g., 1 mm.). Addition of 8 mm. of formaldehyde eliminated the induction period, the maximum rate remaining constant at 11.9 mm. per minute. With amounts of formaldehyde up to

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32.5 mm., the maximum rate increased only slightly up to a value of 14.0 mm. per minute. The last observation is not completely in accord with the experiments of Harding and Norrish on the oxidation of ethylene. They point out that the maximum rate in the ethylene oxidation was reached after a relatively small pressure change, whereas the maximum rate of slow combustion of cyclopropane occurred after about 50% reaction. They conclude that the two reactions are not really comparable.

The mode of formation of formaldehyde is of interest in the case of cyclopropane oxidation. The mechanism advanced involved a complex rearrangement of the cyclopropylperoxy radical to formaldehyde and CH_3CO. The degenerate-branching reaction of formaldehyde was formulated on the following considerations. Lead oxide which markedly inhibits the oxidation of methane (*26*), presumably by efficient heterogeneous destruction of HO_2 radicals, is known to exert a similar effect on cyclopropane combustion (*9*). Thus it seemed probable that branching occurred through the production of HO_2 radicals,

$$H_2CO + O_2 = HO_2 + HCO \tag{15}$$

a large part of the formaldehyde then being oxidized by chain carriers such as OH and HO_2. The proposed scheme is formally analogous to those described for methane and ethylene oxidation.

Formaldehyde may be assigned the role of degenerate-branching agent in the high-temperature oxidation of methane, ethylene, and cyclopropane with a high degree of certainty. In view of the characteristic similarities of methane, ethane, and propane oxidation (*32*, *43*), it is reasonable to assume that formaldehyde exhibits a similar behavior in the oxidation of the higher hydrocarbons and their simple derivatives.

Formaldehyde is a product of the combustion of all hydrocarbons. Studies of the reactions of formaldehyde are important in leading to a better understanding of the mechanism of hydrocarbon oxidation. Its role in the low temperature region is variable but minor, and depends on the individual hydrocarbon and conditions. In sufficient quantities it appears able to suppress cool flames. In hydrocarbon oxidation above 400° C. formaldehyde is an important intermediate responsible for degenerate-chain branching.

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Detonative and Deflagrative Combustion

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The combustion of flammable gaseous hydrocarbon mixtures may be divided into two processes: deflagration, or subsonic combustion, and detonation, or supersonic combustion. Some of the experimental and theoretical aspects of propagation, stabilization, unsteady phenomena, and chemical phenomena of deflagration and detonation are reviewed. The significance of flow parameters in dealing with hydrocarbon combustion is discussed. A brief review of pertinent, important work recently performed in these fields is presented.

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The study of combustion in a flow field presents many complex problems. At the present time, a complete description of the various mechanisms involved seems too complicated to obtain even in the case of the simplest first-order reactions in one-dimensional flow. Simplifying assumptions are necessary in order to obtain either an exact solution to the approximate problem or an approximate solution to the exact problem. This paper discusses some of these assumptions and categorizes the various combustion phenomena which exist in subsonic and supersonic flow.

Combustion models which consider the thickness of the reaction zone usually accentuate either heat conduction mechanisms (thermal theory) or the diffusion mechanisms (diffusion theory) and the models are of necessity of limited value. Simpler models in which the reaction zone or flame front is considered to be an infinitesimally thin discontinuity in the flow, while not simulating exactly the observed conditions, allow the model to be of more general utility and many combustion phenomena become easier to understand because of this simplification. It is the latter approach which is discussed first in this paper—i.e., the combustion process is regarded as a wave phenomenon.

One-Dimensional Waves

Figure 1 illustrates the case wherein a planar wave is pictured to be stationary with respect to the observer and the flow, assumed to be one-dimensional, is passing left to right through the wave. If subscript 1 is used to denote conditions upstream of the

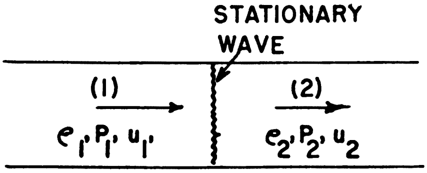

Figure 1. One-dimensional planar wave

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wave (unburned gas in the case of combustion processes) and subscript 2 is used to denote conditions downstream of the wave (burned gas), the following conservation equations may be written to describe the wave:

Conservation of mass

$$\rho_1 u_1 = \rho_2 u_2 \tag{1}$$

conservation of momentum

$$P_1 + \rho_1 u_1^2 = P_2 + \rho_2 u_2^2 \tag{2}$$

conservation of energy

$$h_1 + (u_1^2/2) + Q = h_2 + (u_2^2/2) \tag{3}$$

where P is pressure; ρ is density; u is velocity; h is enthalpy per unit mass; and Q is heat added at the wave per unit mass.

The above equations describe both adiabatic and nonadiabatic waves; in the former case, $Q = 0$.

Equation 2 may be rearranged to give

$$\rho_1 u_1^2 - \rho_2 u_2^2 = P_2 - P_1$$

which upon factoring $(\rho_1 u_1)^2$ and noting from Equation 1 that

$$(\rho_1 u_1)^2 = (\rho_2 u_2)^2$$

becomes

$$(\rho_1 u_1)^2(1/\rho_1 - 1/\rho_2) = P_2 - P_1$$

or

$$\rho_1 u_1^2 = (P_2 - P_1)(V_1 - V_2) = (\rho_2 u_2)^2 \tag{4}$$

where

$$V = \text{specific volume}$$

Inasmuch as $(\rho_1 u_1)^2$ must always be positive, it is noted that the numerator and denominator of the right side of Equation 4 must always possess the same sign.

Table I. Types of Waves

	$(P_2 - P_1)$	$(V_1 - V_2)$	$(U_1 - U_2)$	Process when $Q = 0$	Process when $Q \neq 0$
1	+	+	+	Shock	Detonation
2	−	−	−	Expansion (impossible)	Deflagration

There are indicated in Table I two types of possible waves: one, which produces a pressure increase, density increase, and velocity decrease, and the other, which produces a pressure decrease, density decrease, and a velocity increase. For nonadiabatic waves the former are classified as detonations or explosion waves, and the latter are classed as deflagrations.

Hugoniot Relations. The above classical distinction between detonative and deflagrative combustion has been known to investigators (*2*, *8*, *24*) since the latter part of the nineteenth century. Furthermore, it was usual for these investigators to introduce an equation for the conservation of energy in conjunction with those for mass and momentum conservation and eliminate the velocity terms from this system of equations—i.e., from Equations 1, 2, and 3. The resulting equations, called Hugoniot relations, and the graphs corresponding to these equations are a convenient and standard representation describing combustion phenomena.

The Hugoniot relations, shown in Equations 5 and 6, are identical and may be converted one to the other by noting that $h = e + Pv$,

$$h_1 - h_2 + Q = \tfrac{1}{2}(P_1 - P_2)(v_2 + v_1) \tag{5}$$

or

$$e_1 - e_2 + Q = -\tfrac{1}{2}(P_1 + P_2)(v_1 - v_2) \tag{6}$$

where e is the internal energy per unit mass. For each value of Q selected and for each set value of the initial conditions, (P_1, v_1), a curve may be drawn for P_2, v_2. These curves are called Hugoniot curves and points on the Hugoniot curve are the locus of all possible solutions (P_2, v_2). Figure 2 illustrates such a curve. Points along the curve in region A to B represent end states wherein $P_2 > P_1$ and $v_2 < v_1$, hence a region of detonation. Region C to D is a region where $P_2 < P_1$ and $v_2 > v_1$, or a region of deflagration. Solutions are prohibited in region B to C. The dashed line is representative of a Hugoniot curve for a higher value of Q.

From Equation 4, it may be seen that a straight line from point 0 to some other point M on the Hugoniot curve defines the wave velocity. In general, this line intersects the Hugoniot curve at another point, N. This duality of solutions leads to a further classification of combustion waves, the one whose end state is at M being called a strong detonation wave, and the one within its end state at N being called a weak detonation. The intersection of the tangent to the curve from point 0—i.e., point T—defines a Chapman-Jouguet detonation wave. It has been shown by many investigators that this latter wave possesses the particular property that the velocity of the gas in the wake of the wave is moving at the velocity of sound relative to the front—i.e., at a Mach number of one. Identical considerations may be applied to the deflagrative branch of the Hugoniot curve.

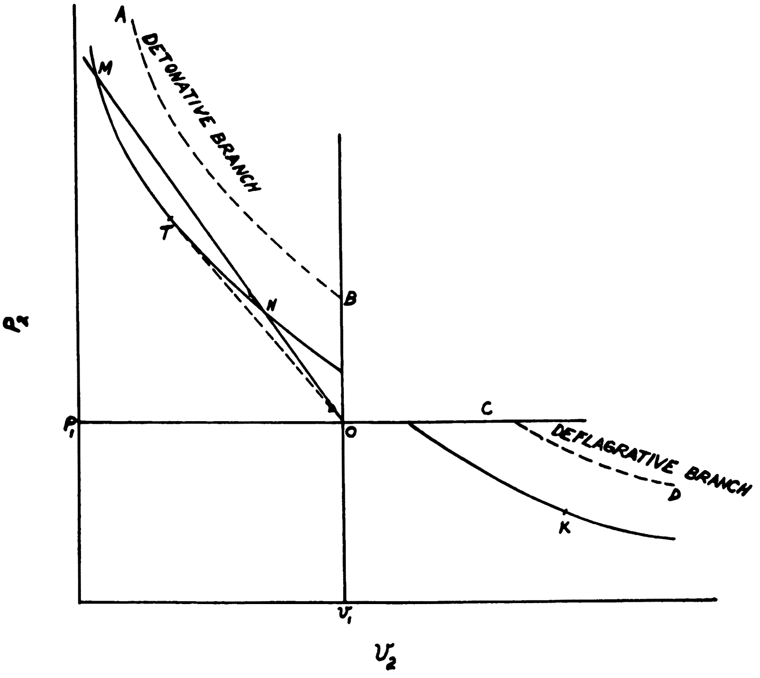

Figure 2. Hugoniot curves

$\phi(M)$ Relations. Application of a similar analysis to the deflagrative branch of the Hugoniot curve leads one to the consideration of further fluid dynamic properties of combustion waves. Attention has been focused on the thermodynamic changes across the waves, this having been accomplished by elimination of the kinetic terms in the conservation equations. If the kinetic terms are retained and the thermodynamic state terms eliminated, many of the obscure points concerning the Hugoniot relations become apparent. Such may be accomplished with extreme ease if, in Equations 1, 2, 3, and 4, the gas is regarded as a perfect gas. For this case the latter system of equations can be solved to

$$\frac{M_1^2\left(1 + \frac{\gamma - 1}{2} M_1^2 + \frac{Q}{C_pT}\right)}{(1 + \gamma M_1^2)^2} = \frac{M_2^2\left(1 + \frac{\gamma - 1}{2} M_2^2\right)}{(1 + \gamma M_2^2)^2} \tag{7}$$

where M, Mach number, is velocity of gas/(speed of sound in the gas); C_p is specific heat at constant pressure; C_v is specific heat at constant volume; and γ is ratio of specific heats.

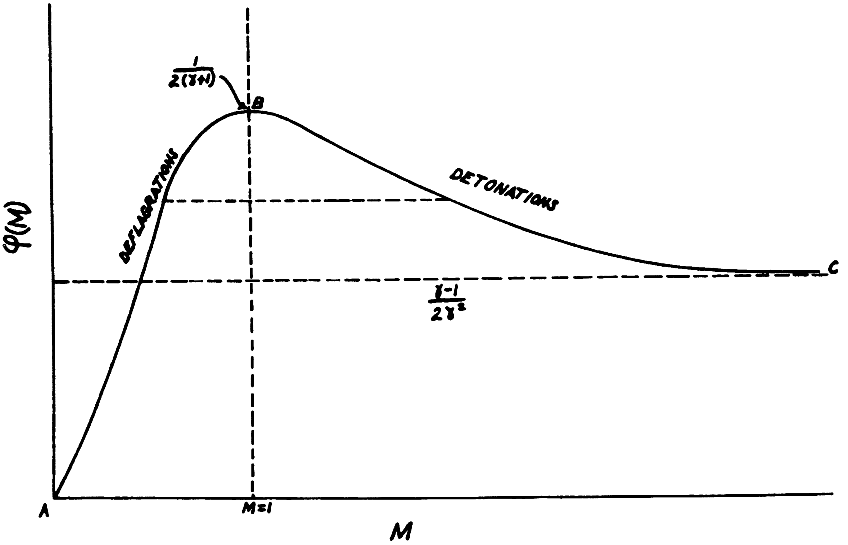

Figure 3. φ (M) vs. Mach number

The function on the right side of Equation 7 is often defined as $\phi(M)$—i.e.,

$$\phi(M) = \frac{M^2\left(1 + \frac{\gamma - 1}{2} M^2\right)}{(1 + \gamma M^2)^2}$$

Figure 3 shows a plot of $\phi(M)$ *vs.* Mach number. It is noted from Equation 8 that when:

$$M = 0 \qquad \phi(M) = 0$$

$$M = 1 \qquad \phi(M) = \frac{1}{2(\gamma + 1)}$$

$$M = \infty \qquad \phi(M) = \frac{\gamma - 1}{2\gamma^2}$$

The plot of $\phi(M)$ represents the locus of all possible solutions for a one-dimensional wave whether the process is adiabatic or nonadiabatic. To clarify some of the properties of this function consider a stationary combustion front possessing an incoming initial Mach number and a value for Q/C_pT. Then from Equation 7, it follows that there will be a solution for the final Mach number, M_2, as long as the value of the left side of the equation lies between 0 and $1/(2(\gamma + 1))$. In the range of values from $(\gamma - 1)/(2\gamma^2)$ to $1/(2(\gamma + 1))$ there will be two solutions for M_2 (Figure 3). A positive value of Q/C_pT increases $\phi(M)$ from its initial value. For the branch of the $\phi(M)$ curve $0 < M < 1$ this corresponds to an increase in M and for $M > 1$ to a decrease in M. Writing Equation 2 in a more suitable form for this discussion, we obtain Equation 9

$$\frac{P_2}{P_1} = \frac{1 + \gamma M_1^2}{1 + \gamma M_2^2} \tag{9}$$

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It follows from Equation 9 that when

$$M_1 < M_2 \qquad P_1 > P_2$$

and when

$$M_1 > M_2 \qquad P_1 < P_2$$

From the previous classification of combustion waves, the region $0 < M < 1$ corresponds to deflagrations and the region $M > 1$ to that of detonations. Point B at which $M = 1$ is the Chapman-Jouguet point. It is seen from the above that detonative combustion is a supersonic phenomenon ($M > 1$) and deflagrative combustion a subsonic phenomenon ($M < 1$).

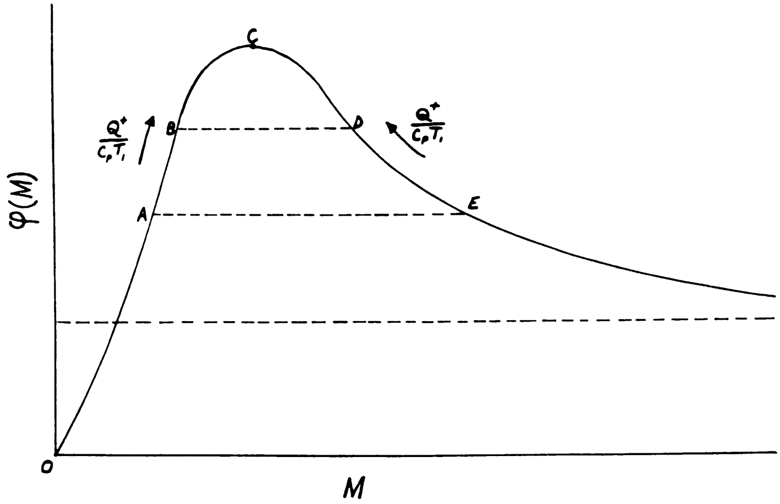

Figure 4. Processes of combustion waves

Equation 7 may be simplified to

$$1 + \frac{Q}{C_pT_{01}} = \frac{\phi(M_2)}{\phi(M_1)} \tag{10}$$

where T_{01}, the stagnation temperature at state 1 (Figure 1), has replaced the static temperature, T_1. It would seem that $\phi(M_2)$ could be made arbitrarily large by making Q/C_pT_{01} sufficiently large. Such is not the case, however, for the solution for M_2 becomes imaginary when the value of $\phi(M_1)[1 + (Q/(C_pT_{01}))]$ exceeds $1/(2(\gamma + 1))$. If $\phi(M_2)$ is replaced in Equation 10 by this maximum value of $1/(2(\phi + 1))$ and solved for Q/C_pT_{01}, then

$$\frac{Q}{C_pT_{01}} = \frac{(M_1^2 - 1)^2}{2(\gamma + 1)(M_1^2)\left(1 + \frac{\gamma - 1}{2} M_1^2\right)} \tag{11}$$

or in terms of Q/C_pT_1

$$\left(\frac{Q}{C_pT_1}\right)_{\text{limiting}} = \frac{(M_1^2 - 1)^2}{2(\gamma + 1)(M_1^2)} \tag{12}$$

If values of Q/C_pT_1 or Q/C_pT_{01} greater than the limiting value are insisted upon, then initial conditions must change to be consistent with the conservation equations. In combustion work, the latter is referred to as "thermal choking."

The same processes traced on the Hugoniot curve may also be traced on a $\phi(M)$ curve. In this way the fluid dynamic aspects of each process are made more perspicuous. The various possible processes are shown in Figure 4 and in Table II.

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Table II. Processes of Combustion Waves

Initial State	Final State	Classification
A	*B*	Weak deflagration
A	*C*	Chapman-Jouguet deflagration
A	*D*	Strong deflagration
E	*D*	Weak detonation
E	*C*	Chapman-Jouguet detonation
E	*B*	Strong detonation

Not all the processes indicated in Table II or Figure 4 are feasible.

A process from E to A is an adiabatic process from supersonic conditions to subsonic conditions and is recognized as a shock wave. The entropy for this process increases from E to A, hence the reverse process from A directly to E entails an entropy decrease and is impossible. A strong deflagration, A to D, is therefore impossible except via C, a path involving an exothermic process from C to D, followed by an endothermic process D to E. It seems unlikely that such a combustion process would be found in nature, although it is not impossible.

The process from A to B is a weak deflagration, the type of combustion wave usually encountered. This combustion occurs at a rate which is governed to a large extent by the multiple diffusion processes within the neighborhood of the flame front. Such processes are leisurely and the propagation rates or "flame speeds" associated with such combustion are on the order of a few feet per second.

The process from A to C is a Chapman-Jouguet deflagration and while possible, it is not usually encountered as a deflagration wave. Flame speeds corresponding to point A are usually much higher than those actually observed. In combustors employing flame stabilization devices, it is possible to reach point C (thermal choking), but this should not be confused with the case of a Chapman-Jouguet deflagration wave.

The process from E to B via A is a process made up of a shock from E to A and a deflagration from A to B. In this case, the high temperatures necessary for initiating the combustion are supplied by the shock rather than by the diffusion processes previously mentioned. This explanation for detonation phenomena was advanced independently by Chapman, and by Jouguet, around 1900. If Q/C_pT_1 is sufficiently large to carry the process to point C, this is a Chapman-Jouguet detonation. As a consequence of the physical means by which detonations are produced, this is the type of detonation usually encountered.

The process from E to D, that of a weak detonation, is open to much discussion. If Chapman and Jouguet's explanation (*8, 24*) of a detonation as a shock plus a deflagration is used, the process is composed of a shock from E to A and a strong deflagration from A via B to D. The strong deflagration, as mentioned earlier, is usually regarded as impossible, hence barring the existence of a weak detonation. A process from E directly to D, however, is permissible. Work on condensation shocks wherein heat is liberated by the condensation to a supersonic stream are at present used as examples of a weak detonation. It is possible to imagine other sets of circumstances under which this process could be induced. For example, a supersonic stream of photosensitive material might be triggered into releasing energy upon passing a light beam. Whether the latter examples are weak detonations depends upon the definition one wishes to choose to describe the phenomenon.

A Chapman-Jouguet detonation wave may be described as an exothermic supersonic wave that propagates itself at the minimum possible velocity consistent with the conservation laws, whereas a Chapman-Jouguet deflagration is an exothermic subsonic wave that propagates itself at the maximum possible velocity consistent with the conservation laws.

Finite Reaction Zone Theories

Detonation. Past investigators have usually considered that a Chapman-Jouguet detonation wave is the only stable detonation wave that normally exists and have expended most of their analytic efforts in describing the change in thermodynamic properties that occurs across this wave. This is accomplished by use of the equations for conservation of mass and momentum together with a suitable representation for conservation of energy. The extremely high temperatures in the wake of these waves complicated the analysis due to the lack of sufficiently exact data for high temperature gases. In later years, with more complete information in this field, calculations have been made with good accuracy which predict detonation velocities in very close agreement to experimental measurements. Such calculations are usually lengthy and tedious.

Recently, efforts have been made to describe the structure of the detonation front where the front is no longer regarded as a discontinuity but as a region through which thermodynamic and hydrodynamic properties change continuously. In most of these analyses the shock is assumed to occur without producing appreciable chemical reaction; then a deflagration is assumed to occur. Sometimes, the assumption has been made that the pressure remains constant throughout the zone of chemical reaction, but it is apparent that the pressure must decrease during this combustion process by a factor of nearly two. Other investigators have attempted to trace the process on Hugoniot curves together with Rayleigh lines. While such a model would describe processes for extremely thick fronts of slowly reacting mixtures, experimental evidence indicates that the reactions are quite rapid with severe temperature gradients. Rayleigh, Fanno, and Hugoniot curves can be used only to give the locus of end points of possible detonation or deflagration waves. They cannot be used to study the structure of any process where thermal, or velocity, or concentration gradients are all important.

The Chapman-Jouguet wave is usually considered as the only stable detonation wave that exists, but actually the type of wave encountered depends only on the boundary conditions imposed. In flame tubes where detonations are generated from accelerating flame fronts, Chapman-Jouguet detonations will ultimately develop when the tube is of sufficient length. If, however, a detonation is forced by a piston in the tube behind the wave or if one is stabilized in a highly supersonic stream in a manner similar to a shock in a supersonic wind tunnel, then, strong detonations can be realized. The latter case of a standing detonation wave has been investigated analytically by Rutkowski and Nicholls (*35*) and found to be feasible for strong detonations as well as for Chapman-Jouguet detonations.

Strong detonations can be discussed qualitatively on Hugoniot or $\phi(M)$ curves but an additional classification is necessary if one is to analyze these waves quantitatively. A convenient means is provided by the introduction into the conservation equations of the function (*1*),

$$f\left(M_1, \frac{Q}{C_pT_1}\right) = \frac{2(\gamma + 1)(M_1^2)\,\dfrac{Q}{C_pT_1}}{(M_1^2 - 1)^2} \tag{13}$$

where M_1, initial Mach number, is u_1/a_1 (Figure 1). For this analysis, assuming a perfect gas, expressions for the thermodynamic state changes may be written in terms of the initial Mach number and Q/C_pT_1 with the following results:

$$\frac{P_2 - P_1}{P_1} = \frac{\gamma F}{\gamma + 1}(M_1^2 - 1) \tag{14}$$

$$\frac{\rho_2}{\rho_1} = \frac{1}{1 - \dfrac{F}{\gamma + 1}\left(\dfrac{M_1^2 - 1}{M_1^2}\right)} \tag{15}$$

$$\frac{T_2}{T_1} = \left[1 + \frac{\gamma F}{\gamma + 1}(M_1^2 - 1)\right]\left[1 - \frac{F}{\gamma + 1}\left(\frac{M_1^2 - 1}{M_1^2}\right)\right] \tag{16}$$

where

$$F = 1 + \sqrt{1 - f}$$

In the case of an adiabatic process (shock), $Q = 0$, $f = 0$, and $F = 2$. For the case where $f = 1$, Equation 13 becomes the equation describing the limiting value of Q/C_pT_1 and hence a Chapman-Jouguet detonation. All the cases of a strong detonation are then described by $1 < F < 2$.

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Deflagration. Deflagration studies have dealt with two main investigations: calculation of the rate of propagation of the combustion wave as a function of the initial conditions, and the mechanism of stabilization of flames on bluff bodies. The first problem consists of only the actual physical processes occurring in a combustion zone, while the second considers these phenomena plus the effect of an extraneous surface. While the latter problem has been attacked more from a phenomenological viewpoint, in that basic processes are understood physically, if not analytically, and experimental data can be correlated well, the first mentioned problem has been studied intensively both theoretically and experimentally. As all of the existing theories of flame propagation are limited by the accuracy of the chemical data, much effort is being expended at the present time on gathering accurate compilations of the physical properties of gases (*20*) and liquids, as well as on doing research on the kinetics of chemical reactions (*24*).

Basically the existing theories of deflagration consist of the purely thermal theories (*6*, *30*, *39*), the purely diffusion theories (*38*), and those theories which take account of the transport of both heat and mass (*21*, *40*). Within these general classifications, there are of course many types of analysis, varying in complexity. As an example, the thermal theories range from approximating the actual temperature profile through a flame by a straight line (*30*), to taking the reaction rate into account by means of an Arrhenius rate law which approximates the over-all reaction (*39*). These thermal models have one point in common, however, in that they all depend upon the definition of a so-called ignition temperature—that temperature at which the reaction is self-supporting. It was shown by von Kármán and Millan (*39*) that so long as this ignition temperature is within a given range, depending on the physical properties of the combustible, the choice of ignition temperature does not influence the value of flame speed. The use of an actual rate law with the thermal model, where the controlling mechanism is the transfer of heat from the hot to the cool gases, results generally in overestimating the rate of propagation.

The so-called diffusion theories of flame propagation, as exemplified by the work of Tanford and Pease (*38*), emphasize the transport of mass, in that concentration of an active radical is assumed to be the rate-controlling property. Its use seems to be fairly limited in that only a few specific reactions have been successfully studied with this theory. What is more interesting, however, is that this theory forms the counterpart to the thermal theory. These two extreme views bracket the actual case, and their study allows a consideration of each of two of the basic flame mechanisms, unencumbered by the other. Actual deflagration depends on both the transport of heat and the transport of mass, and a successful theory should contain both phenomena.

The study of the complete problem of one-dimensional deflagration has been carried out under two schools of thought. Hirschfelder and coworkers (*21*) at the University of Wisconsin have carried out extensive numerical computations of the exact equations, while von Kármán and Penner (*40*) have found approximate analytical solutions to these same equations. Hirschfelder's solutions, containing the exact variation of temperature and concentration of combustible through several first-order reactions, have been indispensable as a guide to the intelligent use of approximations in obtaining analytical solutions and as a test as to the validity of assumptions which have been made in previous works. The approximate analytical solutions developed by von Kármán and Penner are of the utmost value in that they provide a functional dependence of the flame speed on the important parameters. They can be used to calculate the flame speed for a given reaction much more quickly than by the use of numerical methods in the exact solution.

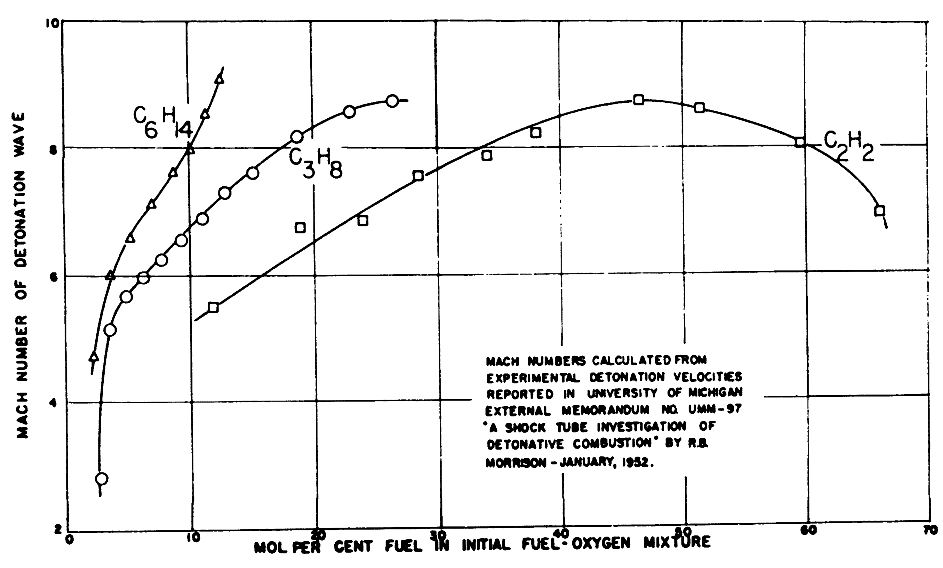
The development of the approximate analytical solution really depends on the work of Boys and Corner (*6*). They first recognized the fact that as the reaction rates are exponential in temperature, in any integral containing this rate, other functions in the integrand can be replaced by approximations accurate only near the hot boundary. This substitution, of course, depends on the fact that the exponential is so large at the hot boundary, compared to its value at the cold boundary, that the greatest additions to the value of the integral are made in the range of variables near the hot boundary. This approximation results in a great simplification of the necessary integrals. While the method of von Kármán and Penner is developed somewhat differently, the final approximations and results are exactly those of Boys and Corner. However, von Kármán and Penner extended the method and, most important, they introduced the extended steady-state hypothesis, which consists of assuming that the concentrations of chain carriers are invariant throughout the reaction. This assumption reduces the number of reactions which it is necessary to consider, and thus allows a rather complex over-all reaction to be very accurately approximated by one or two rate-controlling reactions. The results given by this approximate analytical technique compare very well with the results of the numerical computations carried out by Hirschfelder and his group.

The accuracy of any of the above-mentioned methods of analytically determining the rate of propagation of a deflagration wave depends finally on the validity of the rate laws used, and on the values of the physical constants of the gases under consideration. In particular, the activation energy, and steric factor for any combustible are very important parameters. Much work is being done on the kinetics of chemical reactions, so that more accurate data on reaction rates will be available. It is hoped that this work will lead to better agreement between theoretical and experimental results.

Pressure, Density, and Velocity Changes

Table I indicated that detonations were characterized by pressure increases, density increases, and velocity decreases while deflagrations were characterized by pressure decreases, density decreases, and velocity increases. The magnitude of these changes are required to be determined experimentally at the present time, even though their limits may be obtained analytically. The experimental results of all investigators cannot be discussed here; hence, only selected data showing the trends of pressure, density, and velocity changes (and their interrelationship) are presented.

Detonations. The magnitude of the decrease in velocity which occurs across a detonation wave may be more easily visualized in terms of the Mach number of the detonation wave, since the Mach number behind the wave is one, for the Chapman-Jouguet case, usually encountered in practice. For a given initial pressure and temperature, the velocity with which a supersonic detonation wave propagates itself through an unburned mixture is a function of the initial mixture composition. Figure 5 presents some experimental (*32*) Mach numbers of detonation waves as a function of initial mixture composition. Breton (*7*), Laffitte and Breton (*25*), Bone and Fraser (*4*), Bone, Fraser



MACH NUMBERS CALCULATED FROM EXPERIMENTAL DETONATION VELOCITIES REPORTED IN UNIVERSITY OF MICHIGAN EXTERNAL MEMORANDUM NO. UMM-97 "A SHOCK TUBE INVESTIGATION OF DETONATIVE COMBUSTION" BY R.B. MORRISON - JANUARY, 1952.

Figure 5. Experimental Mach numbers of detonation waves as a function of initial mixture composition

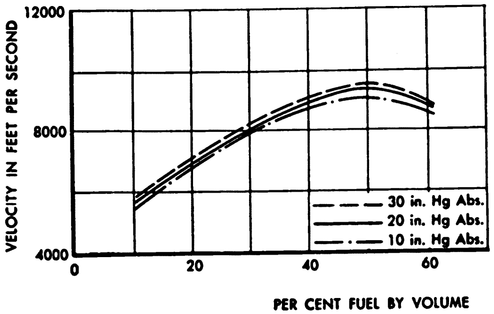


Figure 6. Relation of detonation velocity of acetylene-oxygen mixtures at reduced pressures to mixture ratio

and Wheeler (*5*), Dixon (*13*), Manson and Ferrie (*31*), Morrison (*32*), Berets, Greene, and Kistiakowski (*3*), Fay (*15*), Sheppard (*37*), and others (*26*), have measured the velocity of detonation waves in different mixtures.

The pressure rise across a detonation wave may be computed from the experimental Mach numbers of detonation by using only the conservation of mass and momentum and a state equation, the use of the conservation of energy not being required. For the Chapman-Jouguet case, this pressure rise is

$$\frac{P_2}{P_1} = \frac{1 + \gamma_1 M_D^2}{1 + \gamma_2} \tag{17}$$

In a similar fashion, the density increase across a detonation wave may be computed from experimentally determined Mach numbers of detonation—i.e.,

$$\frac{\rho_2}{\rho_1} = \frac{(1 + \gamma_2)(\gamma_1 M_D^2)}{\gamma_2(\gamma_1 M_D^2 - 1)} \tag{18}$$

The reciprocal of Equation 18 may be used to convert the Mach numbers of detonation shown in Figure 4 to the velocity ratio across a detonation wave.

The magnitude of the initial pressure of the unburned mixture also slightly affects the velocity of the detonation wave, as indicated in Figure 6 (*32*).

Deflagrations. The interrelationship among velocity, density, and pressure which exists when combustion occurs in a duct may be seen in Figure 7, where the experi-

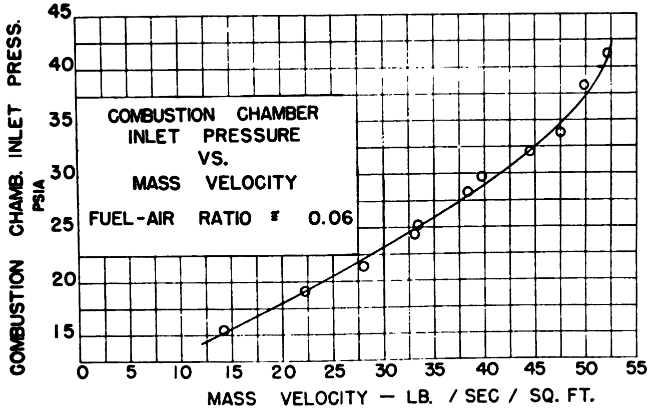


Figure 7. Interrelationship among velocity, density, and pressure when combustion occurs in a duct

mentally measured pressures at the burner inlet are plotted *vs.* the mass velocity (or the product of velocity and density). In this particular system (*41*), the burner discharged directly into the atmosphere and there was a negligible pressure drop due to friction, hence, this graph illustrates the magnitude of pressure decrease attributable to deflagrations occurring in a flowing system.

The magnitude of the velocity increase accompanying deflagration in a duct can be determined from measurements made during the determination of the experimental data presented in Figure 7. Thermal choking, or sonic velocity at the exit of the burner, occurred at all mass velocities greater than approximately 32 pounds per second per square foot. This was equivalent to a linear velocity of about 3000 feet per second for the conditions of the experiment, while inlet velocities of about 250 feet per second were obtained at choking conditions. Thus, a velocity increase of over 10 to 1 is experimentally obtainable in deflagrations occurring in a constant area duct.

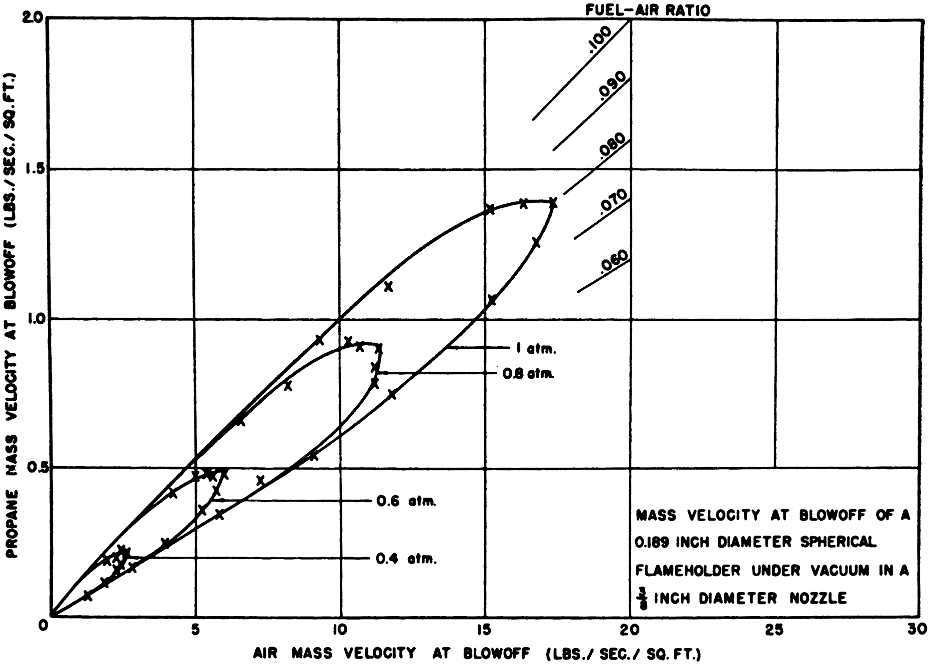


Figure 8. Air mass velocity vs. fuel mass velocity at blowoff

Considering the case when the flame is unconfined, in contrast to deflagration in a duct, the pressure decrease due to burning is much less than the experimental values presented in Figure 7. Jet velocities comparable to the duct inlet velocities are obtainable by inserting a bluff body or flame holder in the flow to stabilize the flame, these velocities being as high as 250 times the laminar flame propagation velocity. The maximum or blowoff velocity of the system is decreased as the ambient pressure level surrounding the flame is decreased. Figure 8 indicates the severe decrease in operating conditions caused by lowering the ambient pressure. In this graph, the air mass velocity is plotted versus the fuel mass velocity at blowoff, the area inside the envelope indicating conditions for which it is possible for a flame to be stabilized on the given spherical flame holder. A large number of investigators (*11*, *22*, *29*, *36*, *44*) have measured blowoff velocities, most of the correlations taking the form of plots of $V_b/(D^a)(P^b)$ versus fuel air ratio, where V_b is the blowoff velocity, D, a characteristic flameholder dimension (values of the exponent a from 0.1 to 1.3 have been obtained) and P, the ambient pressure surrounding the flame. The disagreement between various investigators may be due to different fuel properties (*12*), but different experimental systems undoubtedly are a major cause for the disagreement. Longwell (*28*) stated in his survey paper prepared for the Fourth Symposium on Combustion "that an accurate study of both cone and gutter-type flame holders in one apparatus along with more knowledge of the hydrodynamics as a function of velocity, diameter, heat release, and shape is needed." Recent work by Zukowski and Marble (*47*) on the recirculation zone behind a flame holder is a step in this direction.

It is difficult to divorce the effect of extraneous surfaces from the phenomena which occur in the flame itself. This may be seen in Figure 9 (*10*), which is a plot of the normal

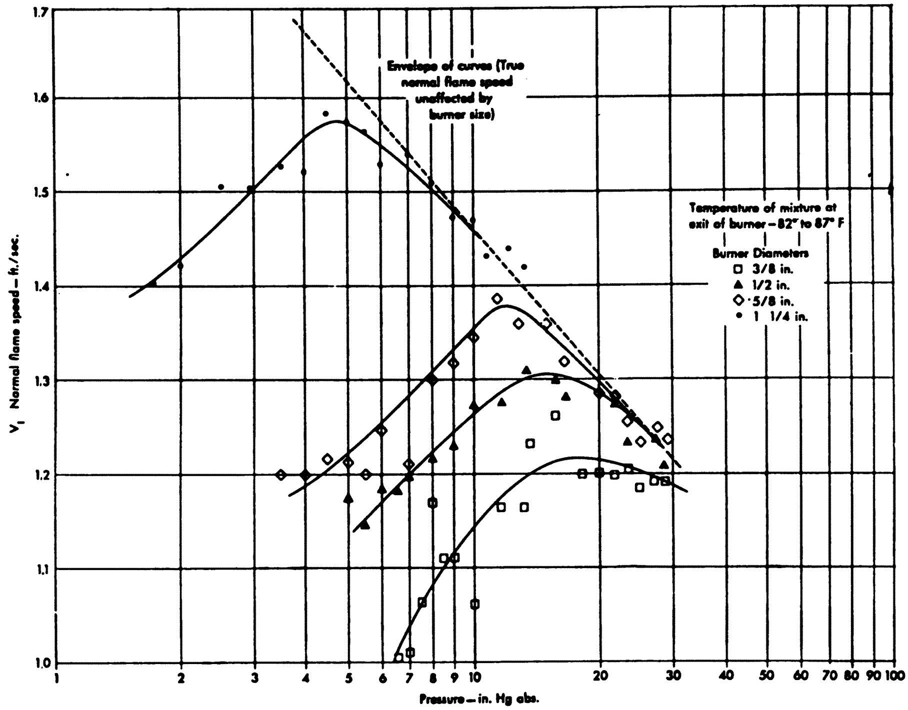


Figure 9. Variation of normal flame speed with logarithm of pressure for propane-air Bunsen flames with four burner sizes

flame speed versus the ambient pressure for four different burner sizes. A reduction in pressure results in increasing flame speed until a point is reached where further reductions in pressure result in a decrease in flame speed. Cullen (*9, 10*) was able to explain this effect by showing that the Bunsen burners themselves acted as a heat sink, and introducing a heat sink into the Mallard-LeChatelier (*30*) analysis, predicted that the ratio of normal flame speed in the presence of a heat sink to its value in the absence of a heat sink was an exponential function of the Peclet number. Wolfhard, who essentially initiated (*46*) the study of low pressure flames, recently (*45*) indicated that Cullen's data could just as easily be correlated on the basis of Reynolds number rather than the Peclet number. This would result in viscosity being added, and thermal conductivity being deleted as a parameter.

Much earlier, Friedman (*18*) proposed that thermal conductivity was an important parameter in the correlation of quenching distance data. Weir and Morrison (*43*) spectroscopically traversed flat flames physically separated from a porous disk and found that the relative intensities of C_2, CH, and OH were decreased as the amount of heat lost from the flame was increased. A large number of investigators have been concerned with experimental verification of flame propagation theories (*17, 19, 23, 27*), but conclusive experiments designed to indicate the relative contributions of heat and mass transfer to flame propagation have not as yet been performed.

Relatively few experiments have been designed to measure directly the density decrease across a deflagration. Dixon-Lewis and Wilson (*14*) used quantitative schlieren techniques to determine density ratios, while Olsen (*34*) used a Mach-Zehnder interferometer. Morrison and Dunlap (*33*) photographed titanium tetrachloride streamlines flowing through an inverted V-flame. By using the conservation of mass and momentum, and measuring the intersection angle of the streamline with the flame front (both in the unburned and burned gases), the ratio of the density of the burned gas to the density of the unburned gas was obtained. Their experimental ρ_b/ρ_u data are compared to theoretical ρ_b/ρ_u data for a propane-air flame in Figure 10.

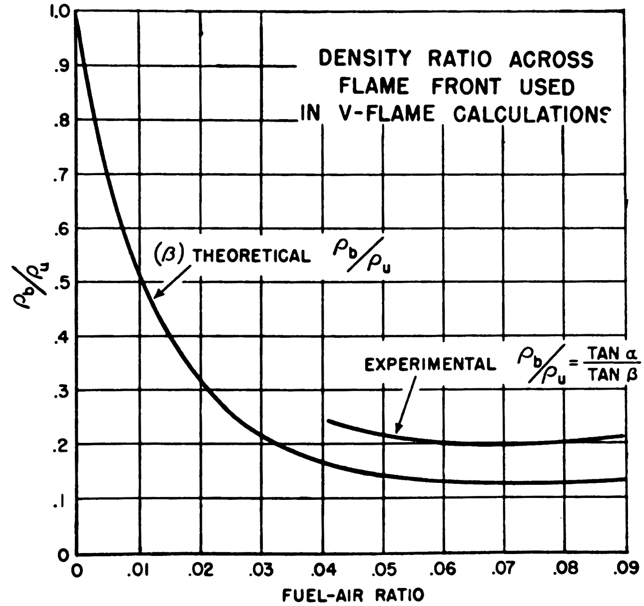


Figure 10. Density ration across flame front used in V-flame calculations

Temperature Changes

Unlike pressure, density, or velocity, the temperature change is in the same direction for both deflagrations and detonations—i.e., the temperature always increases. Many different experimental techniques have been used to estimate flame temperatures. These include thermocouples (shielded, aspirated, and decreasing diameter), wire resistance, optical pyrometers, sonic orifice probes, sodium line reversal techniques, and calculation of rotational temperatures from spectroscopic measurements. Other techniques such as measuring the range of α-particles or x-rays in the gas, ionization measurements, and sonic velocity measurements using a quartz oscillator with shadow photography have been described by Gaydon and Wolfhard (*19*). It is also possible to estimate temperatures from thrust measurements of propulsive devices, or from the density ratio measurements described above.

In deflagration, the limiting temperature is the adiabatic flame temperature. Figure 11 (*41*) presents some temperature measurements made with an optical pyrometer on the exit wall of the same ceramic combustion chamber for which pressure loss data were presented in Figure 5. Temperatures within 500° F. of the adiabatic flame temperature were obtained.

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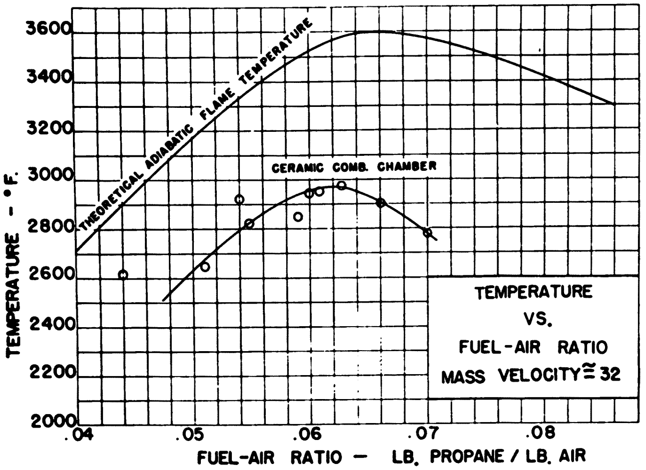

Figure 11. Temperature measurements made with an optical pyrometer on exit wall of same ceramic combustion chamber

In detonation, the temperature behind the wave is not limited to the adiabatic flame temperature, since there is an initial temperature increase across the shock besides the increase due to combustion. Figure 12 (*42*) presents some temperatures computed from the experimental data presented in Figure 5, assuming chemical equilibrium was attained behind the Chapman-Jouguet wave. Temperatures as high as 1200° K. greater than the adiabatic flame temperatures are thus attainable with detonation waves.

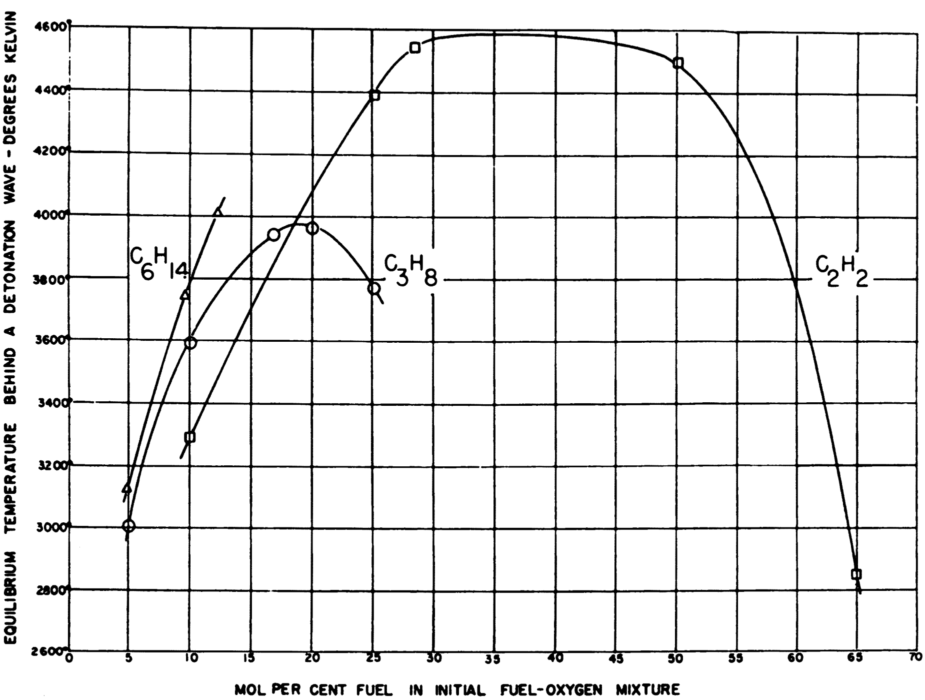

Figure 12. Temperatures computed from experimental data presented in Figure 5, assuming chemical equilibrium was attained behind Chapman-Jouget wave

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Explosion Limit Phenomena and Their Use in Elucidation of Reaction Mechanisms

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The experimental observation of pressure limits for gaseous explosions and methods for determining explosion limits are discussed and critically evaluated. This includes the classical thermal theory of explosion-limit phenomena first mentioned by van't Hoff, as well as the modern branching chain hypothesis of Semenoff. The effect upon the explosion-limit pressures of temperature, composition, vessel diameter, and vessel surface is considered for both thermal and branching-chain explosions. A treatment of the time factor (induction period) for the development of an explosion in quiescent gases in a closed system is also given. Several specific explosion reactions which have appeared in the literature within the past two or three decades are given in some detail. Emphasis is placed upon the use of explosion limit observations as a method for yielding information about the reaction mechanism.

The occurrence of a spontaneous explosion in a chemically reacting system is a complicated process. However, the events that lead to explosion can be characterized as being either of a branching chain or of a thermal nature. Branching-chain explosions occur in systems that react by a chain mechanism, the details of which allow the chain carrier concentration, and hence, the over-all reaction rate to increase without limit, even under isothermal conditions. Such a condition is possible only if one or more of the steps in the reaction chain results in a multiplication of chain carriers—i.e., $X + A \rightarrow Y + Z + B$, where X, Y, and Z are chain carriers.

Thermal explosions may be expected to develop whenever the rate of heat liberation in an exothermic reaction exceeds the rate of heat dissipation by conduction and convection. (An endothermic reaction can never cause a thermal explosion.) Because of the exponential dependence of the reaction rate on temperature, the rate increases rapidly as the temperature rises, until an explosion results. There is little difference, therefore, in the temporal behavior prior to explosion, between explosions that develop as a result of a thermal acceleration of the reaction rate, or those that occur by virtue of a catastrophic build-up of reactive reaction intermediates.

Theory of Thermal Explosions

Historically, an understanding of the underlying causes of a thermal explosion was first demonstrated by van't Hoff (*69*) in 1884. A quantitative mathematical treatment

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is of more recent date, and is chiefly due to the efforts of Semenoff (*53*), Todes (*4, 60*), Frank-Kamenetsky (*16, 17*), Rice (*48*), Chambre (*11*), and their coworkers.

Pressure-Temperature Explosion Limit for Mixtures of Constant Composition. Consider a gaseous, homogeneous, simple ordered, exothermic reaction occurring in a closed vessel. The vessel is assumed to be immersed in a furnace so that the vessel walls always remain at the furnace temperature T_o. For the reaction $mA + nB \rightarrow$ products, with an over-all reaction order $N = m + n$, the reaction rate, r, is given by $r = kC_A{}^mC_B{}^n$, where C_A and C_B, are concentrations of the reactants, A and B. The specific rate constant, k, is assumed to obey the simple Arrhenius relation, $k = Ce^{-E/RT}$, where C, the pre-exponential factor, is independent of the absolute temperature, T; R is the molar gas constant; and E is the energy of activation. The initial reactant concentrations, $(C_A)_o$ and $(C_B)_o$, are given in terms of P, the initial total pressure; X_o, the initial mole fraction of A, and T_o, the initial temperature of the reactant mixture, as follows:

$$(C_A)_o = \frac{(n_A)_o}{V} = \frac{(P_A)_o}{RT_o} = X_o\,\frac{P}{RT_o}$$

and

$$(C_B)_o = (1 - X_o)\,\frac{P}{RT_o}$$

V is the reaction vessel volume, and n_{A_o} and P_{A_o} are the initial number of moles and initial pressure of A, respectively. Therefore, the initial rate of reaction, r_i, can be written as

$$r_i = C\left(\frac{P}{RT_o}\right)^N X_o{}^m(1 - X_o)^n e^{-E/RT} \tag{1}$$

If Q is the exothermic heat of reaction per mole of transformation, the rate of heat release, dq_1/dt, for the small amounts of transformation prior to explosion is given by:

$$\frac{dq_1}{dt} = QVr_i \tag{2}$$

If S is the reaction vessel surface area, and h is the over-all heat transfer coefficient for the reactant mixture, the rate of heat loss, dq_2/dt, to the vessel walls at temperature T_o is given by

$$\frac{dq_2}{dt} = Sh(T - T_o) \tag{3}$$

where T is the mean temperature of the reactants.

Figure 1 (curves 1, 2, and 3) schematically represents the dependence of dq_1/dt upon the temperature, T, at different pressures. The straight line, with T-axis intercept at T_o represents dq_2/dt for a given vessel configuration and mixture composition (Equation 3). The heat transfer coefficient, h, at moderate pressures, is independent of the pressure, so that this same linear relation holds for the three different pressures considered.

At low pressures (curve 1) the gas will initially heat up, because at T_o, the heat generated is greater than the heat dissipated. Therefore, the reaction velocity will increase until temperature T_1 is reached. At this point no further increase in the reaction velocity can occur, as the rate at which heat is generated is equal to its rate of removal. At high pressures (curve 3), the rate of heat generation is always greater than the rate of heat removal, so that the temperature of the gas, and consequently the reaction velocity, will rapidly increase until an explosion occurs.

Curve 2 gives the limiting case between slow reaction and explosion. It is tangent to the straight line representing the rate of heat removal. A slight change in pressure will result in either an explosion or a slow reaction, depending upon the direction of the pressure change. The pressure, P_{cr}, corresponding to this limiting condition is then the lowest explosion pressure for the given vessel configuration and mixture composition at

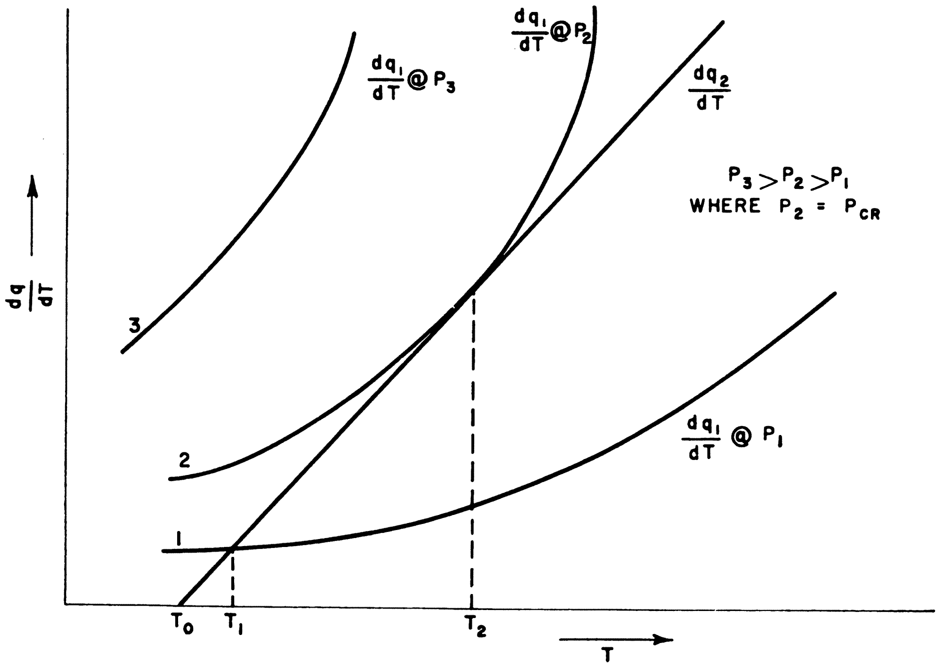

Figure 1. Heat produced, dq_1/dt, and heat conducted away, dq_2/dt, for an exothermic reaction in a vessel of volume, V, at different reactant pressures

the furnace temperature, T_o. For this condition (at the point of tangency), the following two requirements must be fulfilled:

$$\left|\frac{dq_1}{dt}\right|_{T=T_2} = \left|\frac{dq_2}{dt}\right|_{T=T_2} \tag{4}$$

and

$$\left|\frac{d\left(\frac{dq_1}{dt}\right)}{dT}\right|_{T=T_2} = \left|\frac{d\left(\frac{dq_2}{dt}\right)}{dT}\right|_{T=T_2} \tag{5}$$

Applying the first condition and using Equations 1, 2, and 3, the following result is obtained

$$QC\left(\frac{P_{cr}}{RT_o}\right)^N X_o^m(1 - X_o)^n e^{-E/RT_2} = fh(T_2 - T_o) \tag{6}$$

where f is the surface to volume ratio of the reaction vessel. Similarly, from the second condition and Equations 1, 2, and 3, we have

$$QC\left(\frac{P_{cr}}{RT_o}\right)^N X_o^m(1 - X_o)^n e^{-E/RT_2}\left(\frac{E}{RT_2^2}\right) = fh \tag{7}$$

Solving Equations 6 and 7 for T_2 then gives

$$\frac{RT_2^2}{E} = T_2 - T_o \quad \text{or} \quad T_2 = \frac{1 \pm \left(1 - \frac{4RT_o}{E}\right)^{1/2}}{2R/E} \tag{8}$$

As the plus sign in Equation 8 would give a ridiculously high T_2, the negative sign is used. For most reactions $E \gg RT_o$, so that expanding $(1 - 4RT_o/E)^{1/2}$ and neglecting powers in RT_o/E higher than the second, the expression for T_2 becomes

$$T_2 = \frac{1 - \left(1 - \frac{2RT_o}{E} - \frac{2R^2T_o^2}{E^2} - \cdots\right)}{2R/E} = T_o + \frac{RT_o^2}{E} + \cdots \tag{9}$$

Substituting this value of T_2 back into either Equation 6 or 7, remembering that $E \gg RT_o$, the following equation results:

$$P_{cr} = \left(\frac{fh}{QCE}\right)^{1/N} \frac{R^{1+1/N}}{X_o^{m/N}(1 - X_o)^{n/N}} T_o^{1+2/N} e^{E/NRT_o} \tag{10}$$

and taking logarithms yields

$$\ln\left(\frac{P_{cr}}{T_o^{1+2/N}}\right) = \frac{E}{NRT_o} + \frac{1}{N} \ln \frac{fhR^{N+1}}{QCEX_o^m(1 - X_o)^n} \tag{11}$$

Figure 2 schematically represents Equation 10. This is a typical pressure-temperature explosion limit curve for the thermal explosion of a mixture of given composition in a given vessel configuration. In some reactions, however—the hydrogen-oxygen reaction, for example—a pressure-temperature explosion limit curve of the type shown in Figure 3 is observed. The abrupt change in slope of the explosion limit curve at β and γ, together with the appearance of multiple explosion limits, is completely incomprehensible from the point of view of the thermal theory of explosions. The chain-branching theory of Semenoff accounts for this phenomenon. Hence, the existence of upper explosion limits is considered to be unequivocal evidence for a branching chain explosion. Equation 11 indicates that the activation energy, E, can be obtained from the slope of a $\ln (P_{cr}/T_o^{1+2/N})$ vs. $1/T_o$ plot for a constant composition mixture. The linearity and slope of such a plot is little affected by the exponent of T_o in the ln term.

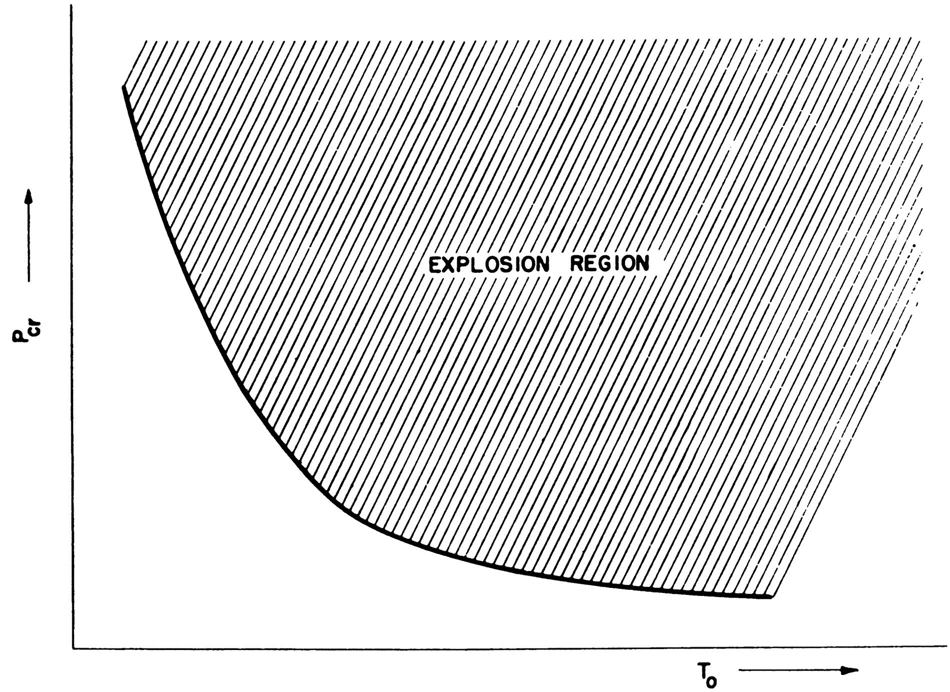

Figure 2. P_{cr} – T_o limit for thermal explosion

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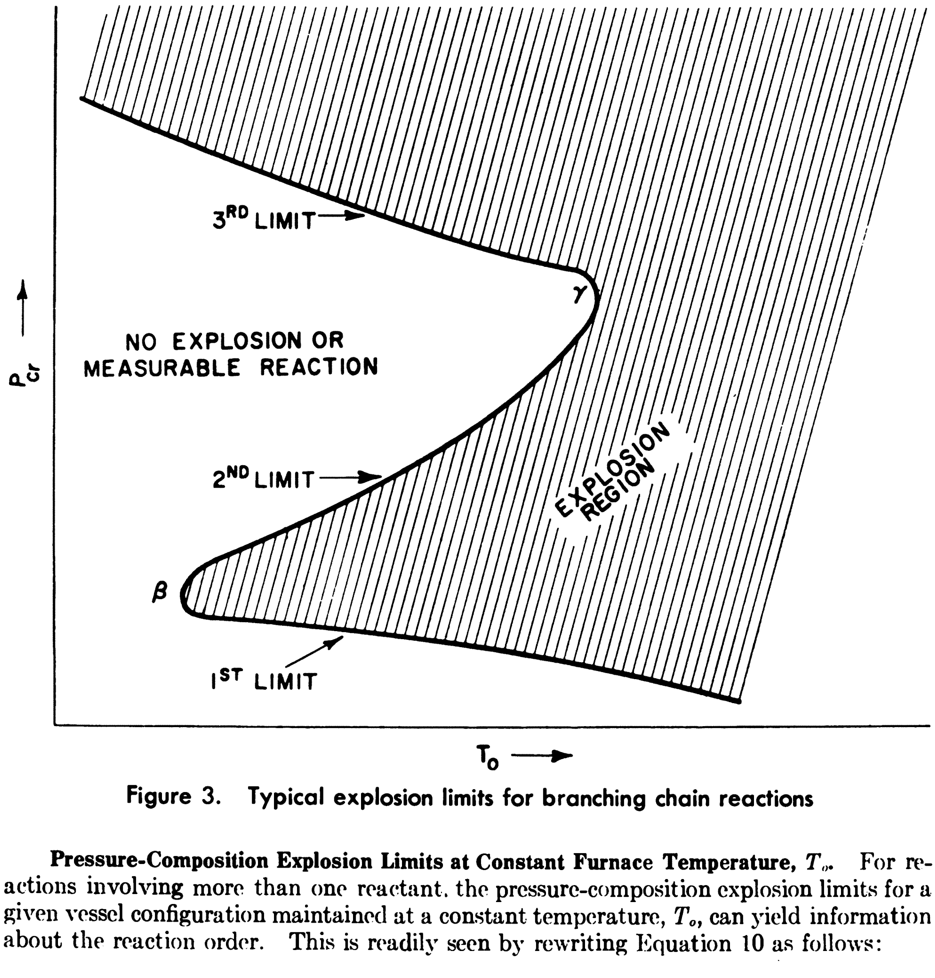

Figure 3. Typical explosion limits for branching chain reactions

Pressure-Composition Explosion Limits at Constant Furnace Temperature, T_o. For reactions involving more than one reactant, the pressure-composition explosion limits for a given vessel configuration maintained at a constant temperature, T_o, can yield information about the reaction order. This is readily seen by rewriting Equation 10 as follows:

$$\frac{1}{P_{cr}} = \left(\frac{QCEe^{-E/RT_o}}{fhT_o(RT_o)^{N+1}}\right)^{1/N} X_o^{m/N}(1 - X_o)^{n/N} \qquad (12)$$

As T_o and f are constants for such a series of experiments, and to the approximation that $h^{1/N}$ is independent of pressure and composition, Equation 12 can be rewritten as

$$\frac{1}{P_{cr}} = BX_o^{m/N}(1 - X_o)^{n/N} \qquad (13)$$

where B is constant. Differentiating P_{cr} with respect to the mole fraction, X_o, yields

$$\frac{dP_{cr}}{dX_o} = -\frac{BP_{cr}}{N}\left[mX_o^{m/N-1}(1 - X_o)^{n/N} - nX_o^{m/N}(1 - X_o)^{n/N-1}\right] \qquad (14)$$

Examination of Equation 14 shows that an extreme value X_{oo}, exists in the $P_{cr} - X_o$ plane, as when $dP_{cr}/dX_o = 0$,

$$mX_{oo}^{m/N-1}(1 - X_{oo})^{n/N} = nX_{oo}^{m/N}(1 - X_{oo})^{n/N-1}$$

or (15)

$$X_{oo} = \frac{m}{m + n} = \frac{m}{N}$$

In order to ascertain whether the extremum is a maximum or a minimum, we evaluate

$$\left|\frac{d^2P_{cr}}{dX_o^2}\right|_{X_o=X_{oo}=m/N}$$

$$= \frac{BP_{cr}^2 mn}{N^2}\left[\left(\frac{m}{N}\right)^{m/N-2}\left(\frac{n}{N}\right)^{n/N} + 2\left(\frac{m}{N}\right)^{m/N-1}\left(\frac{n}{N}\right)^{n/N-1} + \left(\frac{m}{N}\right)^{m/N}\left(\frac{n}{N}\right)^{n/N-2}\right]$$

As B, m, n, and N, are positive quantities,

$$\left|\frac{d^2P_{cr}}{dX_o^2}\right|_{X_o=X_{oo}=m/N}$$

is positive. Consequently the extremum must be a minimum, as is shown schematically in Figure 4.

Effect of Vessel Diameter and Surface upon Thermal Explosion Limit. For mixtures of a given composition initially at temperature T_o, a change in vessel diameter will result in a change in the limiting explosion pressure. This can be made clear by rearranging Equation 10 in the following manner.

$$P_{cr}^N = \frac{T_o(RT_o)^{N+1}e^{E/RT_o}}{QCEX_o^m(1-X_o)^n}fh \tag{16}$$

As T_o and X_o are constants, Equation 16 can be written as

$$P_{cr}^N = Dfh \tag{17}$$

where D is constant. For spherical vessels of diameter, d, $f = 6/d$. For a quiescent mixture the heat transfer coefficient, h, is given (*17*) by $h = 5.9K/d$. K is the thermal

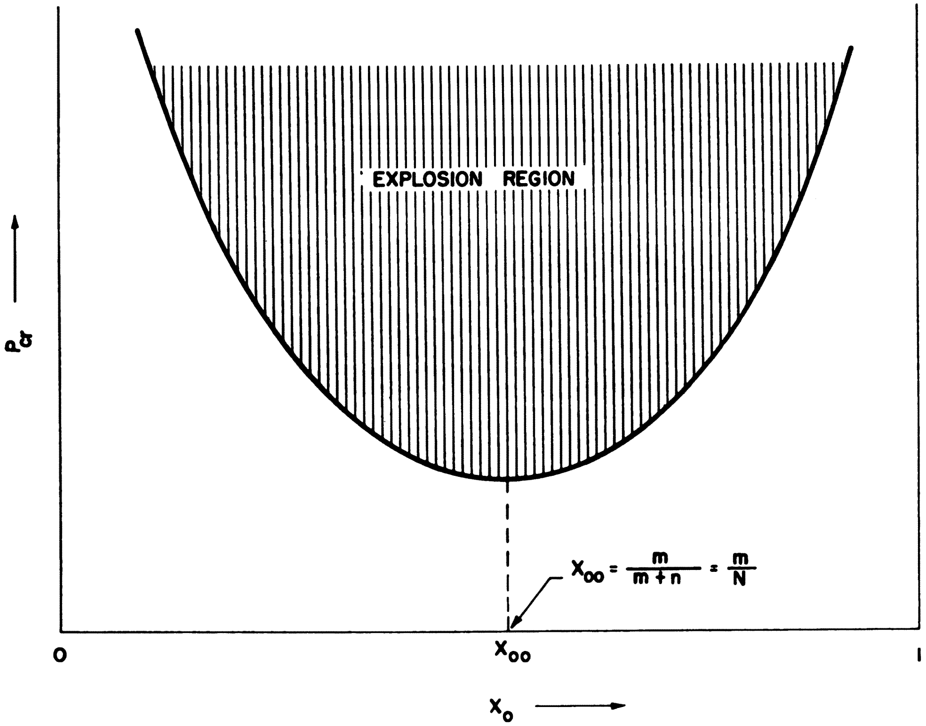

Figure 4. Pressure-composition explosion limit

conductivity of the mixture, which for ideal gases at moderate pressures is independent of the total pressure (*37*). Equation 17 can therefore be written in the form

$$P_{cr}^{N}d^{2} = 35.4\,KD = \text{constant} \tag{18}$$

or

$$\ln P_{cr} = -\frac{2}{N}\ln d + \text{constant}' \tag{19}$$

Equation 19 shows how the over-all reaction order, N, may be obtained from the dependence of explosion limit pressures upon vessel diameters for mixtures of constant initial composition, X_o, at a given initial temperature, T.

Examination of Equation 16 clearly shows that for a thermal explosion the limiting explosion pressure is independent of the nature of the vessel surface. In general, this is not the case for branching-chain explosions. The presence of surface effects in explosion limit experiments strongly suggests that a chain mechanism containing a heterogeneous step is operative. For if such a reaction were nonchain and occurred predominantly at the vessel walls, acceleration of the rate could not occur. The heat would be liberated at the vessel wall and therefore tend to be rapidly conducted away, and the rate of diffusion of unreacted gas to the catalytic surface would place a limit upon the reaction rate. Whether or not the reaction chain includes branching steps can be decided only in light of additional evidence such as the existence of a second explosion limit.

Time Factor Prior to Occurrence of a Thermal Explosion (Induction Periods). In the study of spontaneous explosions occurring in closed vessels, a well defined induction period frequently elapses prior to the development of an actual explosion. The length of this time interval has been observed to be anywhere from a few seconds to several minutes, depending upon the experimental conditions employed. Such observations are not surprising, in view of the fact that in order for an explosion to occur a build-up either of the internal energy or of chain carriers is first required. The rate of such a nonstationary process would then be expected to determine the duration of these pre-explosion times. For the case of a purely thermal explosion, the over-all rate of heat release, dq/dt, prior to explosion is given by

$$\frac{dq}{dt} = QVr - Sh(T - T_o) \tag{20}$$

where r is the rate of reaction, and in general is a function of concentration, temperature, and time. If $\bar{C}_v$ is the mean molar heat capacity at constant volume of the initial mixture, and $(n_A)_o$ and, $(n_B)_o$ are the initial number of moles of reactants, then

$$\frac{dT}{dt} = \frac{1}{[(n_A)_o + (n_B)_o]\bar{C}_v}\frac{dq}{dt} = \frac{RT_o}{PV\bar{C}_v}\frac{dq}{dt}$$

or

$$\frac{dT}{dt} = \frac{RT_o}{P\bar{C}_v}[Qr - fh(T - T_o)] \tag{21}$$

The thermal diffusivity σ, of the mixture is given by, $\sigma = \bar{M}K/\rho\bar{C}_v = (RT_o/P\bar{C}_v)K$, where $\bar{M}$, ρ, and, K are the mean molecular weight, mixture density, and mixture thermal conductivity, respectively. For spherical vessels of diameter d, fh can be approximated by $35.4K/d^2$, so that Equation 21 can be written as

$$\frac{dT}{dt} = \frac{RT_oQr}{P\bar{C}_v} - \frac{35.4\sigma}{d^2}(T - T_o) \tag{22}$$

The integral of this differential equation for an arbitrary reaction order has not been obtained. Several specific cases are considered (*4*, *48*, *60*).

ZERO ORDER REACTIONS. The assumption of a zero-order reaction can be justified for explosions which develop in so short a time that the initial reactant concentrations do not change appreciably during the induction period. For this case, r is independent of concentration and time. It is a function of the temperature only—namely, $r = k = Ce^{-E/RT}$—so that Equation 22 becomes

$$\frac{dT}{dt} = \frac{RT_oQC}{P\bar{C}_v e^{E/RT}} - \frac{35.4\sigma}{d^2}(T - T_o) \tag{23}$$

Integration of this equation can be readily obtained for the case where the heat conduction term can be neglected (adiabatic approximation). This is not too bad an approximation, as $T - T_o$ is small during the induction period. With this approximation in mind, Equation 23 becomes

$$\frac{P\bar{C}_v}{RT_oQC}\int_{T_o}^{T} e^{E/RT}\,dT = \int_o^{\tau} dt = \tau \tag{24}$$

where τ is the induction period. The end of the induction period is reached when $T = T_o + RT_o^2/E$ (Equation 9). As $E \gg RT_o$, the integral in Equation 24 is given to a good approximation, by

$$\int_{T_o}^{T_o+RT_o^2/E} e^{E/RT}\,dT \approx \frac{RT_o^2}{E}\cdot e^{E/RT_o} \tag{25}$$

The expression for the induction period, τ, is therefore

$$\tau = \frac{P}{RT_o}\,\frac{\bar{C}_vRT_o^2}{QCE}\,e^{E/RT_o} = \frac{n_o}{V}\,\frac{\bar{C}_vRT_o^2}{QCE}\,e^{E/RT_o} \tag{26}$$

Where n_o is the total number of reactant moles present initially. Equation 26 gives an independent method for determining the activation energy for systems with small amounts of transformation during the induction period—i.e., $\ln \tau = E/RT_o +$ constant for mixtures of constant initial composition and total pressure.

FIRST-ORDER REACTIONS. In order for Equation 21 to be accurately valid beyond the very first stages of reaction, the variation of concentration with time must be taken into account. For a first-order reaction

$$r = \frac{dy}{dt} = k\left(\frac{P}{RT_o} - y\right)$$

where y is the decrease in reactant concentration as the reaction proceeds. Integrating this equation with the initial conditions, $y = 0$, when, $t = 0$, yields:

$$y = \frac{P}{RT_o}(1 - e^{-kt})$$

or

$$r = k\left(\frac{P}{RT_o}e^{-kt}\right) = \frac{PC}{RT_o}\exp\left[-\frac{E}{RT} - Cte^{-E/RT}\right]$$

Substituting this expression back into Equation 21, we then have

$$\frac{dT}{dt} = \frac{QC}{\bar{C}_v}\exp\left[-\frac{E}{RT} - Cte^{-E/RT}\right] - \frac{RT_o}{PC_v}fh(T - T_o) \tag{27}$$

This equation has been numerically integrated by Rice and his associates (*48*). The results of their rather tedious calculations are in good agreement with the experimental data which they have obtained for azomethane and ethyl azide explosions. These calculations, together with the measured induction periods and explosion conditions, allowed these authors to make reasonable estimates of Q, the heat of reaction.

αTH-ORDER REACTIONS. The general case of an αth order ($\alpha \neq 0$ or 1) reaction is simplified if one considers only equimolar initial concentrations of the reactants—i.e., if m is the reaction order with respect to reactant, A, and N is the over-all order, then the equimolar fraction of A is m/N. Under these circumstances, the reaction rate is given by

$$r = \frac{dy}{dt} = \frac{k}{\alpha}\left(\frac{P}{RT_o} - \alpha y\right)^{\alpha} \tag{28}$$

where a is a factor dependent upon the exact nature of the reaction. For example, for the processes:

$$2A \rightarrow \text{products}, \ a = 1 \text{ and } \alpha = 2$$

$$A + B \rightarrow \text{products}, \ a = 4 \text{ and } \alpha = 2$$

$$A + 2B \rightarrow \text{products}, \ a = 27/4 \text{ and } \alpha = 3$$

Integrating Equation 28 then yields, for the initial conditions, $y = 0$, when $t = 0$.

$$\left(\frac{P}{RT_o} - \alpha y\right)^{\alpha} = \left[\frac{\alpha(\alpha - 1)}{a} kt + \left(\frac{RT_o}{P}\right)^{\alpha - 1}\right]^{\alpha/(1-\alpha)}$$

so that

$$r = \frac{Ce^{-E/RT}}{a}\left[\frac{\alpha(\alpha - 1)}{a} Cte^{-E/RT} + \left(\frac{RT_o}{P}\right)^{\alpha - 1}\right]^{\alpha/(1-\alpha)}$$

and Equation 21 becomes

$$\frac{dT}{dt} = \frac{RT_o}{P\bar{C}_v}\left\{\frac{QCe^{-E/RT}}{a}\left[\frac{\alpha(\alpha - 1)}{a} Cte^{-E/RT} + \left(\frac{RT_o}{P}\right)^{\alpha - 1}\right] - fh(T - T_o)\right\} \qquad (29)$$

No attempt to integrate this equation has ever been made. However, the availability of modern high speed digital computing devices brings its numerical integration within the realm of possibility. However, up to the present time, few clear cut cases of high order thermal explosions have been reported in the literature.

Effect of Addition of Inert Diluents. The addition of inert gases to an explosive mixture will have two major effects. It will increase the heat capacity of the mixture, and depending upon the nature of the added gas, it will change the mixture thermal conductivity. Equation 26 shows that an increase in the heat capacity of the mixture will tend to increase the induction period. The addition of a high thermal conductivity gas such as helium will increase the limiting pressure. Rearranging Equation 18 shows that for a given vessel diameter, reactant concentration, and furnace temperature, the ratio

$$\frac{P_{cr}{}^{N}}{K} = \text{constant} \qquad (30)$$

For mixtures containing varying quantities of inert diluent, K, the thermal conductivity of the mixture is readily calculated (*37*) and P_{cr} *is the partial pressure of the reactants only.*

Examples of Thermal Explosions

Rice, Allen, and Campbell have studied the explosions of azomethane (*2*), ethyl azide (*10*), and ethyl azide in the presence of diethyl ether (*49*). The decomposition of azomethane in a spherical bulb was found to exhibit a well defined explosion limit at pressures between 20 and 200 mm. of mercury in the temperature range 340° to 390° C. From the dependence of P_{cr} upon vessel diameter (Equation 19), the reaction order was found to increase slightly from 1.1 to 1.5 as the temperature was raised from 353° to 384° C. A plot of log $P_{cr}/T_o{}^3$ *vs.* $1/T_o$ yielded an activation energy of about 50 kcal. per mole. This agrees with the observations of Rampsperger (*46*), who found that the slow thermal decomposition was first-order in the temperature range 290° to 330° C. with an activation energy of 51 kcal. per mole. Later work by various authors (*43*, *47*, *55*, *59*) has shown that this reaction is a chain of over-all order somewhat larger than one, involving methyl radicals as chain carriers. As a second limit has not been observed and the chain lengths are short (*44*), the existence of chain branching is unlikely. Further agreement with the thermal theory was shown by the observed (*2*) increase in P_{cr} upon the addition of helium as an inert diluent. Essentially analogous results were found in the studies of ethyl azide (*10*) and ethyl azide–diethyl ether explosions (*49*). By numerically integrating Equation 27, Rice, Campbell, and Allen (*48*) were able to calculate induction periods for the azomethane and ethyl azide explosions which were in good agreement with their observed data. These calculations also allowed these authors to estimate the heats of reaction. They found 43 and 42 kcal. per mole for the heats of the azomethane and ethyl azide decompositions, respectively.

The explosive and slow decomposition of methyl nitrate vapor was studied by Appin, Chariton, and Todes (*4*). Agreement with the predictions of the thermal theory of explosions is not as clear-cut as for cases previously mentioned. In the temperature range 210° to 240° C., the decomposition is slow, homogeneous, and first order. The specific rate constant for this slow decomposition is $2.5 \times 10^{14}e^{-39.500/RT}$ second^{-1}. In the temperature region 245° to 324° C. a well defined explosion limit was observed in the pressure range 4 to 163 mm. of mercury. In a plot of log P_{cr}/T_o^3 *vs.* $1/T_o$ only the high temperature points fell on a straight line whose slope corresponded to an activation energy of only 23 kcal. per mole. A fivefold increase in the ratio of vessel surface to volume resulted in a fivefold increase in P_{cr}, as required by Equation 17. Measurements of the induction period as a function of temperature (Equation 26) yielded an activation energy of 35 kcal. per mole, in agreement with the slow decomposition kinetics. Todes and coworkers therefore conclude that the methyl nitrate explosion is essentially thermal in nature. In a review of these data, Rice and Campbell (*49*) point out that this reaction

$$CH_3ONO_2 \rightarrow \tfrac{1}{2}CH_2O + \tfrac{1}{2}CH_3OH + NO_2$$

is only about 6 kcal. per mole exothermic, while their analysis of the induction period data yields a heat of reaction in the neighborhood of 70 to 80 kcal. per mole. This discrepancy, together with the nonlinearity of log P_{cr}/T_o^3 *vs.* $1/T_o$ plot, leads these authors to doubt the thermal character of this explosion. More recent investigations of the slow and explosive decomposition of alkyl nitrates by Gray and Yoffe (*21*, *24*, *25*) show conclusively that complex chain reactions are involved. The possibility of the simultaneous occurrence of both chain branching and thermal effects should not be overlooked for this type of explosion.

Harris and Egerton (*27*, *28*) have studied the slow and explosive decomposition of diethyl peroxide. They found that the slow decomposition was homogeneous and first order in the temperature range 130° to 190° C. The specific rate constant, k, is given by $5 \times 10^{14}e^{-31,700/RT}$ second^{-1}. A well defined explosion limit was observed in different vessels (spheres and cylinders) in the range 170° to 210° C. at pressures of 2 to 100 mm. of mercury. A plot of log P_{cr}/T_o^3 *vs.* $1/T_o$ for seven different vessels all gave good straight lines with the same slope. This slope corresponded to an activation energy of 28.3 kcal. per mole, which compares well with the value of 31.7 kcal. per mole obtained in the slow decomposition kinetics. The effect of vessel diameter was found to be as predicted by the thermal theory (Equation 19), but the addition of the inert diluents hydrogen and helium resulted in an increase in P_{cr} which was only ½ to ⅓ that required by the theory (Equation 30). These authors attribute this discrepancy to an inefficient energy transfer between the diluent and the reaction products. The explosion of diethyl peroxide, therefore, probably occurs predominantly by way of a thermal mechanism.

Gray and Lee studied the explosion of oxygen-hydrazine mixtures (*22*, *23*). In a study of the slow oxidation, Bowen and Birley (*8*) showed that the reaction is homogeneous, involves short radical chains, and is approximately first order with respect to each component. Well defined explosion limits were obtained by Gray and Lee in the temperature range 370° to 540° C. A plot of log P_{cr}/T_o^2 *vs.* $1/T_o$ gave straight lines with slopes independent of vessel diameter, corresponding to an activation energy of 24.5 kcal. per mole. Variation of vessel diameter at constant temperature gave explosion limit pressures as predicted by Equation 18 for $N = 2$. The addition of the inert diluents helium, argon, and nitrogen at a given furnace temperature resulted in explosion limit pressures in agreement with Equation 30. The minimum in the $P_{cr} - X_o$ plane, however, occurred at a hydrazine mole fraction 0.35 instead of 0.50 as required by the approximate order ($N = 2$) of the reaction. A potassium chloride-coated surface was found to hinder explosion slightly. The authors conclude, therefore, that while these explosions are undoubtedly due to thermal causes, the reaction mechanism involves a complex chain with heterogeneous steps. At temperatures above 420° C., but at pressures lower than that required for the explosive combustion described above, a feeble ignition was observed after long induction periods. This process exhibited both lower and upper pressure limits. From analyses of the reaction products during the induction period and from explosions observed with artificial mixtures of hydrazine, ammonia, nitrogen, hydrogen, and oxygen, these authors conclude that this delayed ignition effect is due to the chain-branching hydrogen-oxygen reaction. The hydrogen, ammonia, and nitrogen are products of the thermal decomposition of the hydrazine which presumably occurs during the rather lengthy induction periods.

Vanpee (*62*) has studied the explosion of formaldehyde-oxygen mixtures. The dependence of explosion pressure upon temperature, vessel diameter, and the addition of inert diluent is in agreement with the thermal theory and consistent with studies of the slow reactions (*54, 61*). Typical of other reactions which have been reported to exhibit thermal explosion limits are the decomposition of nitrous oxide (*75*), the reaction between nitrous oxide and hydrogen (*38*), and cyanogen-air (*32*).

Branching Chain Explosions

The explosion phenomena which are most readily interpreted in terms of reaction mechanisms are known as the upper and lower or first and second pressure limits of explosion. These limits define a peninsular region in the $P_{cr} - T_o$ plane, within which ignition is spontaneous and outside of which there is generally no measurable reaction. Occasionally, there is a narrow zone lying just outside the limits within which a slow reaction takes place, sometimes accompanied by feeble light emission having a relatively long life. The boundaries within which this effect occur are known as glow limits. Figure 3 illustrates a typical explosion peninsula. Systems unambiguously exhibiting this type of behavior are oxygen with:

Reactant	References	Reactant	References
H_2	(*3, 6, 12, 31, 35, 36, 42, 52*)	COS	(*52*)
CO	(*3, 5, 15, 19, 29, 30, 31, 36, 52, 70, 71*)	N_2H_4	(*22, 23*)
CH_4	(*29, 31, 36, 39, 52, 58, 63, 64, 65, 66, 68*)	H_2S	(*1, 52, 73, 74*)
C_2H_6	(*20, 31, 36, 52*)	PH_3	(*52, 57*)
CS_2	(*26, 31, 33, 41, 52*)	B_2H_6	(*45, 50, 51, 72*)
SiH_4	(*52, 56*)		

Explosion peninsulas have never been found for any systems not containing oxygen as a reactant. In a number of systems, a continued increase of pressure results in a turning of the explosion boundary and the formation of a third limit (*1, 36*), having the negative slope characteristic of a thermal limit. The designation "third limit" refers to a limit that is a kinetic consequence of reactions in the gas phase, which occur predominantly on the vessel surface at the lower pressures of the second limit. Experimentally, it is difficult to distinguish between such a third limit and a thermal limit which may intersect the second limit at high pressures. Under certain conditions of vessel surface and geometry, a thermal limit may even intersect the explosion peninsula at a low enough pressure so as to mask the latter entirely.

This phenomenon of multiple pressure limits of explosion can be explained on the basis of branching chain reactions. For example, a series of reactions comprising a branching chain may be illustrated by resort to the well-known hydrogen-oxygen reaction (*13, 31, 36, 52*).

Thus,

		ΔH_{298}, Kcal./Mole
$O + H_2 = OH + H$	(31)	3.0
$H + O_2 = OH + O$	(32)	17.2
$OH + H_2 = H_2O + H$	(33)	−15.8

Heats of reaction have been included for later reference. Reactions 31 and 32 are chain branching steps and Reaction 33 merely carries the chain. A simple calculation by Pease (*44*) illustrates the rates of reaction which may be encountered in branching-chain reactions. If a single chain carrier is introduced into 1 cc. of reaction mixture ($\sim 10^{19}$ molecules) and is regenerated at each collision, then for species of an average molecular weight of 30, a collision frequency calculation indicates that approximately 10^7 molecules react per cubic centimeter per second. As there are 10^{19} molecules, 10^{12} seconds or 30,000 years would be required for complete reaction. If the chain branches, producing one additional carrier per collision, then in n collisions $1 + 2 + 2^2 + \cdots 2^n = (2^{n+1} - 1)$ molecules will have reacted. To consume 10^{19} molecules ($2^{n+1} - 1 = 10^{19}$ or $n \approx 62$ collisions) would take about 6×10^{-7} seconds. Even if the branching efficiency were only 1%,

$$1 + 1.01 + (1.01)^2 + (1.01)^3 + \cdots = \frac{(1.01)^{n+1} - 1}{1.01 - 1} = 10^{19},$$

so that $n \approx 3934$ collisions, taking about 4×10^{-5} seconds. These explosively rapid rates indicate how explosion limits of a nonthermal nature may occur. For a sharp boundary to exist between a region of very slow reaction and one of explosive reaction, there must be one or more processes in competition with the chain-branching process—namely, the occurrence of one or more chain-breaking reactions. For example, the branching chain presented above includes as a chain-breaking step, the reaction,

$$H + O_2 + M = HO_2 + M \tag{34}$$

where M is any third body and hydroperoxy is assumed to be unable to continue the chain. A steady state must exist at the explosion limit where the rate of chain branching is equal to the rate of chain breaking and the chain-carrier concentrations are constants. This limit law may be applied to the branching chain (Reactions 31 to 34), to indicate how three distinct limits may arise. Thus, the steady-state free radical concentrations may be expressed as

$$d(O)/dt = -k_{31}(O)(H_2) + k_{32}(H)(O_2) = 0 \tag{35}$$

$$d(H)/dt = k_{31}(O)(H_2) - k_{32}(H)(O_2) + k_{33}(OH)(H_2) - k_{34}(H)(O_2)(M) = 0 \tag{36}$$

$$d(OH)/dt = k_{31}(O)(H_2) + k_{32}(H)(O_2) - k_{33}(OH)(H_2) = 0 \tag{37}$$

The limiting explosion pressure is obtained from the condition that the determinant of the coefficients of the chain-carrier concentrations is equal to zero. The result is an expression from which the free radical concentrations have been eliminated:

$$(M) = 2k_{32}/k_{34} = P_{cr}/RT_o \tag{38}$$

where (M) now stands for total concentration, as any molecule may act as a third body in Reaction 34. This expression describes the second explosion limit which results when both branching and breaking reactions occur predominantly in the gas phase. The order of the breaking reaction must be higher than that of the branching reaction for a limit to exist and, in order to be competitive, branching and breaking reactions must be of the same order with respect to chain carriers. Equation 38 may be expanded to

$$\frac{P_{cr}}{RT_o} = \frac{2C_{32}e^{-E_{32}/RT_o}}{C_{34}e^{-E_{34}/RT_o}}$$

and

$$\ln (P_{cr}/T_o) = A/T_o + B \tag{39}$$

where $A = (E_{34} - E_{32})/R$. Equation 39 gives the P_{cr}—T_o relationship for the explosion limit. Because branching and breaking occur in the gas phase, variation of the explosion vessel diameter should have no effect on the position of the limit. Experimentally, this is generally the case for the second explosion limit. Second explosion limits approximate Equation 39. This expression, however, is not a criterion for determining whether a particular limit is a second limit. First limits and thermal limits are described by similar equations (Equation 11). The P_{cr}—T_o variation of the second explosion limit may be explained qualitatively in another way. The chain-breaking reaction is third-order, whereas branching is second-order. Therefore, the breaking rate will increase as the cube of the pressure, while the branching rate will increase only as the square of the pressure. An increase in initial pressure, therefore, will lead to the nonexplosive condition, chain-breaking rate ≫ chain-branching rate. However, if the activation energy of the branching reaction exceeds that of the breaking reaction, an increase in T_o will eventually overcome the inequality. Therefore, in agreement with observation, as the limit pressure increases, the limit temperature must also increase.

The rate constant, k_{34}, in Equation 38 is dependent on the nature of the third body, M. Therefore, an averaged rate constant, $\Sigma k_{34,M}X_M$ where X_M are mole fractions of components of the reaction mixture, must be used. Equation 38 then becomes,

$$\frac{P_{cr}}{RT_o} = \frac{2k_{32}}{k_{34.\mathrm{H_2}}X_{\mathrm{H_2}} + k_{34.\mathrm{O_2}}X_{\mathrm{O_2}} + \sum_{M_i} k_{34.M_i}X_{M_i}} \tag{40}$$

or at constant temperature,

$$P_{cr}\left(X_{\mathrm{H_2}} + \frac{k_{34.\mathrm{O_2}}}{k_{34.\mathrm{H_2}}}X_{\mathrm{O_2}} + \sum_{M_i}\frac{k_{34.M_i}}{k_{34.\mathrm{H_2}}}X_{M_i}\right) = \text{constant} \tag{41}$$

Therefore, at constant temperature, the second explosion limit pressures for a series of mixture compositions can be used to obtain ratios of rate constants. In addition, Equation 41 serves as a check on the validity of the proposed reaction scheme. Alternatively, explosion-limit temperatures at constant pressure may be compared. Equation 40 can be rewritten as

$$T_o \exp\left[\frac{E_{34} - E_{32}}{RT_o}\right] = \text{constant}\left(X_{\mathrm{H_2}} + \frac{k_{34.\mathrm{O_2}}}{k_{34.\mathrm{H_2}}}X_{\mathrm{O_2}} + \sum_{M_i}\frac{k_{34.M_i}}{k_{34.\mathrm{H_2}}}X_{M_i}\right) \tag{42}$$

If the activation energy difference, $(E_{34} - E_{32})$, is known, rate constant ratios may be evaluated. Conversely, if the latter are known, $(E_{34} - E_{32})$ may be evaluated. If second explosion limits for a series of undiluted mixtures of hydrogen and oxygen are compared, Equation 42 becomes

$$\frac{X_{\mathrm{O_2}}}{X_{\mathrm{H_2}}} = \text{constant}\left(\frac{T_o}{X_{\mathrm{H_2}}}\exp\left[\frac{E_{34} - E_{32}}{RT_o}\right]\right) - \frac{k_{34.\mathrm{H_2}}}{k_{34.\mathrm{O_2}}} \tag{43}$$

and a family of straight lines should be obtained when X_{O_2}/X_{H_2} is plotted against $T_o/X_{H_2} \exp\left[(E_{34} - E_{32})/RT_o\right]$ for various assumed values of $(E_{34} - E_{32})$. The intercepts are $-k_{34,H_2}/k_{34.O_2}$ and as the rate constant ratio must be positive, only negative intercepts are meaningful. Therefore, the value of $(E_{34} - E_{32})$ which gives a line with an intercept of zero is a maximum value. Similarly, a limit may be set for $(k_{34,H_2}/k_{34,O_2})$ by assuming $(E_{34} - E_{32})$ equal to zero.

Equations 40, 42, and 43 have been found to apply to the second explosion limit for diborane-oxygen (*50, 51*) in addition to hydrogen-oxygen (*31, 36*). In mixtures diluted with inert gases, it has been found that the relative chain breaking efficiencies as determined experimentally from the k_{34} ratios are in agreement with the relative ternary collision frequencies for both the hydrogen-oxygen and diborane-oxygen systems.

The endothermicity of Equation 32 is sufficient to prevent explosion at room temperature, even when hydrogen atoms are introduced into the system. Reaction 34 is of interest in that hydroperoxy is a free radical, and may participate in the chain depending upon the reflectivity of the vessel surface to hydroperoxy radicals. Thus, in potassium chloride coated vessels all of the hydroperoxy is destroyed at the wall

$$\mathrm{HO_2} \xrightarrow{\text{KCl wall}} \text{destruction} \tag{44}$$

However, in clean silica or boric oxide coated vessels, the hydroperoxy may be efficiently reflected from the wall and may reenter the gas phase to react as follows:

$$\mathrm{HO_2} + \mathrm{H_2} = \mathrm{H_2O_2} + \mathrm{H} \tag{45}$$

$$H_2O_2 + HO_2 = H_2O + O_2 + OH \qquad (46)$$

$$H_2O_2 + M = 2OH + M \qquad (47)$$

$$H + HO_2 = 2OH \qquad (48)$$

The occurrence of Reactions 45 through 48 will modify the second explosion limit. This has been offered in explanation of the observed dependence of the hydrogen-oxygen second-explosion limit on the nature of the vessel surface.

The role of hydroperoxy at the second limit leads directly to an explanation for the occurrence of a third limit (*13*, *36*). The hydroperoxy radical, which is predominantly destroyed at the vessel wall at the second limit, will, at higher pressures, undergo an increasing number of collisions in the gas phase before reaching the wall. Thus, Reaction 45 may predominate in the gas phase over Reaction 44. This will result in a pressure-dependent increase in the number of chain carriers and lead to the formation of another limit, as shown in Figure 3. It is experimentally difficult to distinguish between such a third limit and a thermal explosion limit. It would be necessary to distinguish between thermal conduction and diffusion effects.

The first explosion limit has been shown, by detailed theoretical treatment, to exist as a result of a competition between chain branching in the gas phase and chain breaking at the vessel wall (*31*, *36*, *52*). At the low pressures of this limit, diffusion to the wall becomes the controlling factor in chain breaking. A simplified treatment, based on the diffusion equation, will suffice to show the properties of this limit. As the explosion limit mechanism for the hydrogen-oxygen reaction is the most substantiated of those systems exhibiting first and second limit phenomena, it will again be used illustratively. Thus, chain breaking will occur by diffusion of radicals to the wall, where they will be adsorbed and recombine. The mechanism will therefore consist of Reactions 31, 32, 33, and the chain-breaking steps

$$\left.\begin{array}{l} H \\ O \\ OH \end{array}\right\} \longrightarrow \text{wall recombination} \qquad \begin{array}{r} (49) \\ (50) \\ (51) \end{array}$$

The solution of the diffusion equation in one dimension serves as a good approximation to the pressure and diameter dependence of the rate of diffusion, as the functional dependence on these parameters will be the same for any coordinate system chosen. Thus, for Reactions 49, 50, and 51, the rates are equal to

$$\frac{k_{49}(H)}{P_{cr}d^2}, \quad \frac{k_{50}(O)}{P_{cr}d^2}, \quad \text{and} \quad \frac{k_{51}(OH)}{P_{cr}d^2},$$

respectively, where P_{cr} is the total pressure, d is the vessel diameter and the k's are constants containing accommodation coefficients and diffusion coefficients stripped of their pressure dependence. When the steady-state condition is applied to Reactions 31, 32, 33, 49, 50, and 51, the following limit expression is obtained.

$$2k_{31}(H_2)P_{cr}d^2 = k_{49}\left[\frac{k_{31}(H_2) + \dfrac{k_{50}}{P_{cr}d^2}}{k_{32}(O_2)}\right] + \frac{k_{51}}{P_{cr}d^2}\left[\frac{k_{50} + k_{49}\left(\dfrac{k_{31}(H_2) + \dfrac{k_{50}}{P_{cr}d^2}}{k_{32}(O_2)}\right)}{k_{33}(H_2)}\right] \qquad (52)$$

Inasmuch as the diffusion coefficient for hydrogen atoms is very much greater than that for oxygen atoms or hydrogen, we may say that $k_{49} \gg k_{50}$ and k_{51}. Equation 52 may then be simplified to

$$2k_{31}k_{32}(H_2)(O_2)P_{cr}d^2 = k_{49}\left[k_{31}(H_2) + \frac{k_{50}}{P_{cr}d^2}\right] \qquad (53)$$

For a given vessel diameter, reactant concentration and temperature Equation 53 may be approximately represented by

$$\frac{P_{cr}}{k_{49}} = \text{constant} \qquad (53a)$$

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This is of the same form as Equation 30, but involves the mixed diffusion coefficient, k_{49}, instead of the thermal conductivity of the mixture. However, as seen from the kinetic theory of gases, the thermal conductivity is proportional to the diffusion coefficient. Therefore agreement of experimental results with either Equation 30 or 53a is not an adequate criterion for distinguishing between first explosion limits in branching chain reactions and purely thermal limits. It has been reported (*52*), that, empirically,

$$(P_{H_2})(P_{O_2})d^2 = \text{constant} \tag{54}$$

However, reproducibility of lower limit results has been poor, owing principally to changes in the nature of the surface, so that Equation 54 cannot be regarded as accurate. For certain mixture compositions, the first limit pressure is independent of hydrogen concentration and is dependent solely upon oxygen concentration, as Equation 53 would predict (*52*).

As the rate of diffusion has an exponential temperature dependence of the Arrhenius type, it can readily be seen that the equating of chain branching and diffusion chain breaking will yield an equation similar to Equation 39 for the P_{cr} to T_o relationship of the first limit.

From the foregoing discussion of first, second, and third limits it is apparent that the second limit studies have been most fruitful for the elucidation of the reaction mechanism because of their relative independence of vessel factors.

Induction Periods in Branching Chain Explosions. Induction periods in the case of chain-branching explosions are often observed (*22*, *23*, *40*, *41*) and may be interpreted in any one of the following ways:

1. An inhibitor—e.g., an efficient chain breaker—is initially present and its concentration is slowly reduced to a critical level, below which its inhibition becomes unimportant. At constant pressure, then, the induction period, may be given by an Arrhenius expression, $\tau = Ae^{E/RT}$, where E is the activation energy of the process involving removal of the inhibitor.

2. The reaction mixture is initially outside the explosion peninsula. However, a sensitizer, which shifts the peninsula, may be produced at a relatively slow rate. Explosion would then occur when the shift was sufficient to enclose the mixture temperature and pressure within the peninsula. The induction period would then have the same temperature dependence as above.

For cases 1 and 2, the pressure dependence of τ would be a function of the order of the reaction removing inhibitor or producing sensitizer. In general, however, τ, decreases with increasing pressure.

3. One of the branching steps may be relatively slow, so that development of the chain takes a measureable time. The rate of production of chain carriers, n, may be expressed by

$$dn/dt = n_o + (f - g)n$$

where n_o is the initial rate of chain carrier production, f is the branching probability and g, the breaking probability. The solution of this equation is

$$n = \frac{n_o}{f - g}\,[e^{(f-g)t}\,(1 + f - g) - 1]$$

or since $(f - g) \ll 1$ in the vicinity of limit conditions

$$n = \frac{n_o}{f - g}\,[e^{(f-g)t} - 1]$$

Provided $(f - g) > 0$, the chain carrier concentration, and hence, the reaction velocity will increase exponentially with time. However, $(f - g)$ may be small enough so that t, corresponding to the induction period, τ, may be very long. If $(f - g) < 0$, a true explosion never develops. A slow change from − to + values of $(f - g)$ has been observed for hydrocarbon-oxygen systems. These phenomena are sometimes referred to as degenerate chain-branching explosions or cool flames (*44*, *52*).

Carbon Monoxide and Hydrocarbon Oxidative Explosions. At the second limit of the carbon monoxide-oxygen system the reaction is apparently considerably more complex than the hydrogen-oxygen reaction and a completely satisfactory mechanism has not been developed. A recent reinvestigation of this problem (*70*) has resulted in the development of two alternative but kinetically equivalent mechanisms (*9*, *18*, *34*). The reactions involved are:

$$O + O_2 + M = O_3 + M \tag{55}$$

$$O + CO + M = CO_2^* + M \tag{56}$$

$$O_3 + CO = CO_2 + 2O \tag{57}$$

$$CO_2^* + O_2 = CO_2 + 2O \tag{58}$$

$$CO_2^* + O_2 = CO_2 + O_2^* \tag{59}$$

$$CO_2^* + O_2 + M = CO_2 + O_2 + M \tag{60}$$

$$O_2^* = 2O \tag{61}$$

$$O_2^* + M = O_2 + M \tag{62}$$

(Asterisks indicate electronically excited states.)

One mechanism consists of Reactions 55, 56, 57, 58, and 60 and leads to the limit expression

$$(M) = \frac{k_{58}}{k_{60}} \left\{ \frac{1 + \left(\dfrac{k_{55}(O_2)}{k_{56}(CO)}\right)}{1 - \left(\dfrac{k_{55}(O_2)}{k_{56}(CO)}\right)} \right\} \tag{63}$$

The alternative mechanism consists of Reactions 55, 56, 57, 59, 61, and 62, and leads to Equation 63 with k_{61}/k_{62} substituted for k_{58}/k_{60}. Equation 63 is consistent with the experimental observation that the limit pressure increases with mole fraction of oxygen and finally becomes infinite. Furthermore, evidence for Reaction 59 is found in the fact that in the emission spectrum of the carbon monoxide–oxygen explosion flame the Schumann-Runge oxygen bands begin to appear and increase in intensity while the carbon dioxide bands and continuum decrease in intensity as the oxygen–carbon monoxide ratio is increased (*36*). It has been found that replacement of portions of a given carbon monoxide–oxygen mixture with nitrogen has no effect on the second limit. This can be explained only by assuming that the third-body collision efficiencies of carbon monoxide, oxygen, and nitrogen are approximately equal. In order for experimental results to fit Equation 63, k_{55}/k_{56} must be less than unity, whereas experiments indicate a value one or two orders of magnitude greater than unity. However, if the reaction

$$O_3 + CO = CO_2 + O_2 \tag{64}$$

is competitive with Equation 57, then k_{55}/k_{56} in the limit expression is multiplied by $(k_{57} - k_{64})/(k_{57} + k_{64})$ and a result less than unity may be obtained.

The addition of hydrogen or water vapor to the carbon monoxide–carbon dioxide system results in even greater complexity (*19*, *36*). There are some indications that water vapor has no effect on the second limit. However, the reason for this cannot be the same as that given for the lack of a nitrogen effect.

The oxidation mechanisms of some of the simpler hydrocarbons are of great interest in petroleum combustion processes. It is unfortunate that the pressure explosion limits of methane–oxygen and ethane–oxygen have not been more thoroughly investigated. Each system exhibits three limits and explosion occurs only after an induction period (*12*, *40*) which becomes shorter as the pressure is raised. The production of carbon monoxide occurs rapidly during the induction period and it has been suggested that the explosions observed are those of the carbon monoxide–oxygen system. This suggestion appears to have deterred further investigation of these explosive reactions. This view is inconsistent, however, with the following facts:

At high pressures, the induction period is short (5 to 10 seconds). Production of

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carbon monoxide could not have reached a point where an explosive carbon monoxide-oxygen mixture is formed.

Three limits exist at pressures below 1 atm. Only two limits have been observed for carbon monoxide-oxygen.

It has been reported (*52*) that addition of 10% methane to a carbon monoxide-oxygen mixture raises the ignition temperature by 100° C. However, the limits for carbon monoxide-oxygen and methane-oxygen lie in about the same temperature range. A similar inhibition of the second limit of hydrogen-oxygen by ethane has been observed (*6*, *7*).

Formaldehyde is produced in the early stages of methane oxidation. It has recently been found that formaldehyde induces ignition in methane-oxygen mixtures (*67*).

It would seem worth while, therefore to restudy the explosion limits of methane-oxygen and ethane-oxygen and also to study the effects of these hydrocarbons on the carbon monoxide-oxygen limits, with a view toward establishing whether these systems are connected in any way. In any case, valuable clues to the mechanisms of combustion of hydrocarbons can probably be obtained.

Experimental Techniques

There are many methods of obtaining explosion-limit data. In general, they involve rapid heating of a mixture, rapid mixing at a known temperature, or changing the mixture pressure at a constant temperature. The results are in most cases self-consistent but rarely agree from method to method. Jost (*31*) discusses most of the methods and compares results obtained with some of them. Here, only those methods most commonly used in kinetics studies are discussed and critically evaluated.

We may rule out all methods which depend upon ignition of the gases with electrically heated wires, heated spheres, or heated rods. These are kinetically unreliable, as they depend strongly on convective heat and mass transfer, they often act catalytically, and accurate temperature measurement is difficult. The following methods have found wider use in the plotting of explosion limits.

1. An evacuated vessel at a known temperature is rapidly filled with a mixture to a known pressure. It is noted whether explosion occurs (*56*).
2. A vessel is filled to a known pressure at room temperature and is then rapidly heated by immersion in a furnace until explosion occurs. The temperature and pressure just prior to explosion are measured. This is commonly referred to as the "heating method" (*50*, *70*).
3. A vessel is filled at room temperature to a pressure above the explosion limit. The temperature is then raised to a known value and the mixture is slowly withdrawn until explosion occurs. The pressure just prior to explosion is measured. This is commonly referred to as the "withdrawal method" (*45*, *56*), and is applicable only to situations where upper (or second) explosion limits exist.
4. Measured quantities of the reactants are heated separately to a known temperature and mixed rapidly, one generally flowing into the other. In a modification of this method the reactants are heated to slightly less than the explosion limit temperature and heating to explosion is continued after mixing. Observation is made of whether or not explosion occurs (*72*).
5. A mixture flows through a tube. Inlet and outlet valves are adjusted so that a constant pressure is maintained in the chamber. The chamber is then heated until explosion occurs.

Each method suffers from one or more inherent sources of error. Method 1 is not readily adaptable to the determination of second explosion limits. If temperature equilibrium is reached very quickly by the gas flowing into the vessel, as the continued flow causes the pressure to increase, the system must first intersect the lower explosion limit. Method 2 can lead to large errors if explosion is preceded by an induction period. In the carbon monoxide-oxygen reaction, for example, it was found that the heating rate could considerably affect the results owing to the existence of a zone of slow reaction adjacent to the second limit and inhibition of the reaction by the product, carbon dioxide

(*14*, *70*). If heating is too slow, significant amounts of carbon dioxide may be produced before the limit is reached and may alter its position. The heating rate should not exceed the rate at which the temperature-measuring device can follow the change. In Method 3, similar difficulties arise. Withdrawal must be rapid enough to avoid accumulation of products and again induction periods during which appreciable amounts of reaction occur can lead to large errors. Methods which involve mixing in situ—e.g., Method 4—are subject to large errors when incomplete mixing occurs.

During mixing at a constant temperature, explosion will occur when any homogeneous volume element attains the composition most easily ignitable at the given temperature and pressure. This composition may not correspond to that of the completely mixed gases. For example, in the carbon monoxide–oxygen system, the second explosion limit for the stoichiometric mixture ($CO + 2O_2$) lies at the pressure minimum of the pressure-composition curve. It is possible to obtain ignition at pressures above the upper limit for $CO + 2O_2$ if, during mixing, a leaner mixture should be attained in a sufficiently large volume element. Complete mixing in a carbon monoxide–oxygen mixture at 1000° K. and about 300 mm. of mercury may take on the order of 10 seconds in a spherical vessel 5 cm. in diameter. Mixing may be hastened by allowing one gas to stream into the other. However, the order of addition should always be reversed as a check on the completeness of mixing. Method 5 has the advantage of minimizing wall reactions. Sources of error are the same as for Method 2.

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Role of Vaporization Rate in Combustion of Liquid Fuels

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This review covers the literature pertaining to rate of fuel vaporization and the time required for vaporization of droplets in a gas stream. It excludes detailed coverage of the injection of larger droplets of low-grade fuels which crack on overheating to produce a radiant flame. Although fundamental information on combustion systems is ever increasing, much more study is needed, especially on combustion efficiency. Thus a singular criterion for prediction of combustor performance cannot be obtained from application of a vaporization literature survey. However, such application can provide some very pertinent performance limits, as regards operating ranges and combustion efficiency values.

Vaporization of liquid hydrocarbon fuel is a prerequisite to combustion. Any fuel unvaporized at the combustor exit is obviously wasted. In addition, it may have the detrimental effects of eroding or depositing upon metal surfaces. Fuel barely vaporized at the combustor exit may have insufficient time to burn. Again there is wastage, plus possible deposition or endothermic decomposition. When fuel is intended to vaporize substantially upstream of the flamefront position, the degree of vaporization may have a pronounced influence upon the ignitability characteristics of the combustor and its operating limits of fuel-air ratio (*1, 9, 54, 91, 119*). Finally, turbulent distribution of fuel in a moving air stream depends upon the fuel state (*2, 79*), while the fuel distribution in turn has marked influence upon ignitability (*75, 90, 110*), operating limits of fuel-air ratio (*6, 16, 66*), and reaction rate (*80*).

This paper reviews the available literature pertinent to fuel vaporization rate and the residence time required for vaporization of droplets in a gas stream. The author's particular point of view is that of air-breathing, jet-propulsion engines, but this review is, in general, of broad applicability. However, one fundamental distinction exists: In some furnace applications of combustion a highly radiant flame is desired. Then it may be desirable not to maximize vaporization rate, but instead to inject rather large droplets of low-grade fuels, which crack appreciably upon overheating, leading to formation of incandescent carbon (*38, 49, 114*). Details of this aspect are outside the scope of this paper.

The fundamentals of combustion systems are yielding to treatment at the present time, but interrelationships of their effects in a real combustor require much additional study, particularly in regard to combustion efficiency. Full-scale engine performance has not been explained in terms of fuel vaporization effects (*44*), and a survey of vaporization literature cannot be applied to a real combustor as the sole criterion for performance prediction. Rather, such application can provide some approximate answers and very useful limits.

Vaporization Rate Equations

Other factors being constant, the rate of vaporization from a large exposed liquid surface is proportional to the area of the surface. This may also be true for droplets (*67*, *96*) if radiant heat transfer is predominant (*17*). Under normal circumstances, however, the rate of vaporization of a droplet at rest with respect to its environment is proportional to the droplet diameter (*3*). This comes about because the vaporization rate is controlled by the rate of conduction of heat or of mass through the gas film surrounding the droplet. The appropriate equation is:

$$\frac{-dm}{dt} = \frac{\pi}{4}\rho\lambda x \tag{1}$$

where λ is the evaporation constant determined by a combination of physical constants and by the Nusselt number of the droplet. For a given droplet, granting constancy of λ and of ρ,

$$x_t^2 = x_0^2 - \lambda t \tag{2}$$

Equations 1 and 2 in the forms stated are attributable to Probert (*98*), and derivations for the case of heat transfer controlling are given by Kumm (*70*), Marshall and Seltzer (*87*), Godsave (*37–39*), and Goldsmith and Penner (*42*). The case of mass transfer controlling is derived by Fuchs (*31*) and compared by Gilbert, Howard, and Hicks (*36*) to isothermal evaporation into a maintained vacuum.

Many investigators (*17*, *37*, *39*, *41*, *55*, *68*, *69*, *92*) have reported test data for single droplets which verify Equation 2 by showing x^2 decreasing linearly with t. However, in many of these cases a droplet heating-up period is involved, so that λ becomes constant some time after the start of measurements, and graphs of x^2 *vs.* t yield straight lines of slope λ only over the higher ranges of t (*41*, *55*, *68*, *92*). Similarly, failure to allow for variation of Nusselt number and thus of λ during a droplet acceleration or deceleration period will also yield lines of x^2 *vs.* t which are not straight, as shown theoretically by El Wakil, Uyehara, and Myers (*117*).

A number of investigators (*59*, *60*, *82*, *83*, *108*, *120*) have conducted experiments with so-called model droplets. A porous solid sphere is used, and means are provided for feeding fresh liquid to the sphere continuously, so as to maintain a wetted surface. Actually these models generally are far too large to fit the droplet classification, and instead simulate large drops, with diameters of several millimeters. Nevertheless, model droplets have yielded data which show a vaporization rate proportional to droplet diameter, being still small enough for the resistance film thickness to be proportional to droplet diameter. Liquid particles of the sizes formed by normal fuel atomization procedures are designated generally as droplets in this discussion. A rather extreme upper size limit is 1000 microns (1 mm.), while a definitely restricted upper limit would be 100 microns (0.1 mm.). A range of raindrop diameters of practical interest is established as 0.1 to 3.5 mm. (*62*). Considering the potential overlap of one order of magnitude, it appears reasonable to set 300 microns (slightly more than 0.01 inch) as the dividing point between drop and droplet classifications. A graphic series of pictures of "secondary atomization" (*88*) shows a 0.10-inch drop being converted to droplets by aerodynamic forces (*34*). Pictures for a range of disrupting forces are given by Hinze (*52*).

Comprehensive treatment of the evaporation constant λ is given by Spalding (*109*), and a comprehensive examination of Nusselt numbers for droplets is presented by Ranz and Marshall (*102*). The first work in the field is that of Froessling (*29*), after whom the appropriate equations are named. According to the combined treatments of Spalding and of Ranz and Marshall, when diffusion is controlling at relatively low vaporization rates

$$\lambda = \frac{4D\rho_g}{\rho_l}\ln(1+B)\,\mathrm{Nu} = \frac{4D\rho_g}{\rho_l}\ln(1+B)(2+0.60\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}) \tag{3}$$

When heat transfer is controlling at relatively high vaporization rates,

$$\lambda = \frac{4k}{c_p \rho_l} \ln (1 + B) \text{ Nu} = \frac{4k}{c_p \rho_l} \ln (1 + B)(2 + 0.60 \text{ Re}^{1/2} \text{ Pr}^{1/3}) \qquad (4)$$

The parameters $(2 + 0.60 \text{ Re}^{1/2}Sc^{1/3})$ and $(2 + 0.60 \text{ Re}^{1/2}\text{Pr}^{1/3})$ represent the Nusselt numbers for mass and heat transfer, respectively (*87*). Equation 3 derives from Froessling directly, while Spalding substituted thermal diffusivity for molecular diffusivity to establish the basis for Equation 4.

The transfer number B in Equations 3 and 4 is Spalding's contribution. It is the driving force for mass transfer in dimensionless form. With diffusion controlling (Equation 3):

$$B = \frac{m_{jg} - m_{js}}{m_{js} - 1} \qquad (5)$$

where m_j is the fractional mass concentration of component j, g refers to the main gas stream, and s refers to the vaporizing surface. In general, m_{jg} will be negligible in combustion applications and the equation becomes:

$$B = \frac{p_{js}}{p_{is}} \qquad (6)$$

where p is partial pressure and i denotes the system constituents other than j.

When heat transfer is controlling (Equation 4) and combustion is taking place:

$$B_{\text{comb.}} = \frac{\frac{m_{O_g}H}{r} + c_p(T_g - T_s)}{Q} \qquad (7)$$

m_{O_g} is the fractional oxygen concentration in the main gas stream, r the stoichiometric oxygen-fuel ratio, and H the heat of combustion. [Wise, Lorell, and Wood have shown (*120*) that data which correlate burning rate of droplets as a function of oxidant concentration in the gas phase verify the use of stoichiometric proportions as the basis of droplet burning analysis.] Q is either the latent heat of vaporization alone, or this plus the enthalpy increase of the liquid between the initial and the surface temperatures. When combustion does not occur, the first term of the numerator drops out:

$$B_{\text{no comb.}} = \frac{c_p(T_g - T_s)}{Q} \qquad (8)$$

The remainder of this survey is concerned with verifications of Equations 3 and 4, evaluation of values of λ therefrom, and application to actual cases of vaporizing droplets.

Experimental Verification of Basic Equations

Most of the data available to substantiate Equations 1 to 4 pertain to single droplets in still air. Therefore, in most cases, the Nusselt number is 2, and Froessling's correlation for the Nusselt number in terms of the Reynolds and Schmidt numbers is neither verified nor cast in doubt. Data of Ranz and Marshall (*102*) do afford substantiation; in particular, they verify Equation 4.

Ranz and Marshall obtained a rounded-off coefficient of 0.30 in their Nusselt number expressions instead of Froessling's value of 0.276. Discussion of variation with Reynolds number of the coefficient is given by Tverskaya (*116*) for water vapor. Hsu, Sato, and Sage (*57*) substantially checked the Froessling value, obtaining 0.272 as the coefficient. The bulk of their effort, however, was concerned with showing that nonsphericity of the droplet has an important effect upon the vaporization rate, as compared to the rate for a sphere of the same diameter.

The expressions of Ranz and Marshall were used by El Wakil, Uyehara, and Myers (*117*) in extensive theoretical calculations for vaporization during the droplet heating-up period under a variety of conditions. They were careful to point out that they had

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extrapolated the data correlations of Ranz and Marshall to small droplet sizes far below the experimental conditions.

El Wakil, Uyehara, and Myers assumed isothermal droplets. Apparently (*71*) this is the actual case for droplets of relatively nonviscous liquids, conducive to internal circulation. Ranz and Marshall (*102*) measured droplet temperatures substantially equal to the calculated surface temperatures. High-speed motion pictures of salt solution droplets vaporizing in a hot air stream, taken by Marshall and his associates (*86*), indicated extreme internal circulation. For cold droplets, on the other hand, Langstroth, Diehl, and Winhold (*73*) reported internal temperatures less than calculated surface temperatures. Topps (*114*) conducted tests with kerosine, gas oil, and residual fuel. The results for kerosine indicate that evaporation took place at the same rate as a pure hydrocarbon boiling at the normal bubble point. Some fractionation or cracking occurred with the gas oil. Residual fuel droplets tend to swell at temperatures of approximately 600° to 800° C.; at higher ambient temperatures small cokelike residues are obtained. This indicates that in the more viscous droplets the high-boiling fractions remained in the surface layer, became overheated, and cracked. Swelling occurred upon subsequent evolution of vapor from the droplet interior beneath this scum forming on the surface. Short of cracking, Hartwig showed theoretically (*48*) that the assumption of isothermal droplets provides a reasonable approximation to the case of nonisothermal droplets.

At high values of Reynolds number, such as may pertain to model droplets, the value of the constant 2 becomes less significant (*102*), and Equations 3 and 4 may be converted to the *j*-factor equations of Chilton and Colburn (*12, 14*). Maisel and Sherwood (*82, 83*) employed the *j*-factor equations in their data presentation, but the same data were applied successfully by Ranz and Marshall in their own analysis in support of the Froessling equation.

Gohrbandt's data for camphor spheres (*40, 97*) afford comparison of rates with diffusion controlling and with heat transfer controlling. Extrapolation to low temperatures of the heat transfer portion indicates sufficient heat transfer but inadequate diffusion. Similarly, extrapolation to high temperatures of the diffusion portion indicates sufficient diffusional driving force but inadequate heat transfer to maintain the surface temperature.

While the basic equations for Nusselt number have not been proved for small droplets, there is ample demonstration that Equations 3 and 4 apply to small droplets when Reynolds number is zero and Nusselt number is 2. Such discrepancies as arise may be attributed to uncertainties in the necessary physical property values and in the particular experimental data. Pertinent investigations are those for burning droplets performed by Godsave (*37–39*), Goldsmith and Penner (*42*), and Graves (*44*), with analysis by Spalding (*109*).

Godsave introduced a complication in the analysis in order to account for heat loss in the evolving vapor (as superheat) when the gas temperature is high, a criterion which Marshall (*84*) establishes as 600° F. Godsave's treatment, based on observations of the luminous flame diameter, leads to sizable disagreement between reported data for the effective vaporization constant and computed values according to Equation 4 or its variations. This aspect has been treated by Marshall (*85*). On the other hand, Goldsmith and Penner (*42*), predicting precisely, have checked experimental data for a number of fuels rather successfully.

Values of Evaporation Constant

Because there still are discrepancies, and appropriate physical properties are often unavailable, values of λ actually reported or easily computed from other reported data can be of considerable benefit. A summary of applicability of a number of references appears as Table I.

Data predictions for droplets moving freely in turbulent gas streams are confounded by the problem of ballistics of droplets. Until the droplet is essentially accelerated or decelerated to the gas stream velocity, Reynolds number, thus Nusselt number, and thus λ are changing constantly, and precise calculations require very small steps. The drag coefficient is of considerable importance. El Wakil, Uyehara, and Myers (*117*) em-

Table I. Actual Data for λ

Reference	Fuel	Type of Drop or Droplet	Relative Air Velocity	Air Temp.	Type of Data Presented
(*73*)	Various	Suspended	Nil	Cold	Vaporization rate
(*82*)	Benzene	Model	Appreciable	Cold	Vaporization rate
(*105*)	Kerosine	Free (spray)	Slight	Cold	Vaporization rate
(*40*)	Camphor	Suspended	Appreciable	Hot	Correlating parameter on graph
(*17*)	Various	Burning—free and suspended	Slight	Hot	Combustion lifetimes
(*27*)	Hexane	Free (spray)	Slight	Cold	Droplet size distribution data *vs.* time
(*59*)	Various	Model	Appreciable	Cold, hot	Vaporization rate
(*102*)	Aniline, benzene	Suspended	Appreciable	Cold	λ values
(*37–39*)	Various	Burning—suspended	Slight	Cold	λ values
(*44*)	Iso-octane	Burning—suspended	Slight	Cold	λ values
(*57*)	*n*-Heptane	Suspended	Appreciable	Cold	Vaporization rate
(*109*)	Various	Burning—model	Appreciable	Cold	λ values
(*42*)	Various	Burning	Slight	Cold	Comparison of theoretical λ with Godsave's data (*37, 39*)
(*117*)	Various	...	...	...	Physical properties for calculation of λ
(*61*)	Iso-octane	Free (spray)	Slight	Cold	Slopes of graphs are λ values
(*55*)	Heavy fuel oil	Burning—free	Appreciable	Hot	Slopes of graphs are λ values
(*69*)	*n*-Heptane	Burning—suspended	Vibrating suspension	Cold	λ values
(*120*)	Ethanol-water solutions	Burning—model	Slight	Cold	Vaporization rate
(*68*)	Various	Burning—suspended	Slight	Hot	Slopes of graphs are λ values
(*92*)	Various	Burning—suspended	Slight	Hot	Slopes of graphs are λ values
(*41*)	Various	Burning—suspended	Slight, appreciable	Cold, hot	λ values
(*103*)	Various	Burning—suspended	Slight	Cold	λ values

ployed a standard graph of drag coefficient for solid spheres as a function of Reynolds number. While pointing out that the drag coefficients for solid spheres and droplets are not equal, they estimated from the work of Hughes and Gilliland (*58*) that the correction for their particular calculations was minor. Hughes and Gilliland showed that the drag of an accelerating body differs from that at steady-state conditions, and that with droplets, distortions occur which affect the drag. At high vaporization rates, the evolution of vapor may also affect the drag. Thus Ingebo (*61*) calculated on the basis of his observations a family of drag coefficient curves, for various values of relative air velocity, as functions of Reynolds number. These crossed over the basic correlation line for solid spheres.

Very little work has been reported on vaporization under conditions of turbulent gas flow. Ingebo (*61*), for example, took pains to minimize approach stream turbulence. Two exceptions are the investigations of Maisel and Sherwood (*83*) and Fledderman and Hanson (*27*). Neither went so far in analysis as insertion into the Nusselt number equations of allowance for the additional relative velocity between droplet and air stream occasioned by turbulence. In the case of Maisel and Sherwood's investigation with model droplets at fixed positions, the effect would not be expected to be extreme, because at all times there was appreciable relative velocity, discounting turbulence. However, in Fledderman and Hanson's experiments the relative velocity, discounting turbulence, fell away as the droplets accelerated up to stream velocity. Thus turbulence would eventually provide the only appreciable relative velocity. The results indicate a substantial increase in vaporization rate because of the turbulence and provide some basis for gross engineering estimates.

The obvious question arises as to how much influence two droplets in a spray may have upon one another as regards vaporization. Directly, on a statistical approach, they should not have much. For reasonable fuel-air ratios and reasonable air temperatures, complete vaporization is far short of saturation of the air. In addition, for equal droplet spacing, the droplets must be rather far apart from one another. For example, kerosine droplets of uniform size and uniform dispersion in a stoichiometric quantity of room temperature air would have center-to-center spacing of more than 17 diameters.

Admittedly, when a cloud of droplets is burning in stoichiometric proportions in air, the last traces of the burning droplets must burn in atmospheres almost depleted of oxygen. Thus the reaction rate may be very poor, if high gas temperature does not more than offset low oxygen concentration. Nevertheless, the droplet at least will be exposed

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to gas of very nearly stoichiometric flame temperature and should vaporize about as well as if it were burning, even if only pyrolysis is possible after vaporization.

Present work at California Institute of Technology (*103*) is concerned with interactions of two or a few droplets, suspended in close proximity and burning in air. The results are more germane to rocket engines than to air-breathing combustion systems, as absence of diluent nitrogen can result in much closer packing of droplets of any given size and make radiative effects more important. In any application, however, some trajectories will actually cross, and physical property values based upon oxidant plus fuel vapor should then instead be based upon fuel vapor plus fuel vapor or reaction products plus fuel vapor. In the experiments themselves, the effect of adjacency of droplets upon convection currents must be considered. From continuance of this program and detailed analysis of results should come more reliable procedures for assigning appropriate physical property values, more advanced treatment of the fractional heat loss as superheat to the evolving vapor, and better understanding of ballistics of adjacent droplets.

Vaporizing Time Considerations

In any spray of droplets there is a statistical distribution of sizes dependent upon the conditions of atomization. Some particular types of fuel injectors can create nearly uniform sizes, but generally a fairly wide range of droplet diameters results. According to Equations 2, 3, and 4, individual droplets of a fuel spray will complete vaporization over a range of elapsed times. Consequently analysis becomes complicated (*85*).

Very few investigations have been reported which combine experimental and analytical work on vaporization of sprays. Probert's classic paper (*98*) is wholly analytical. From the standpoint of λ, the report of Fledderman and Hanson (*27*) is wholly experimental. The first complete study to be noted is that of Ingebo (*61*), which represents much work encompassing a number of aspects of the problem. However, the large amount of analysis reported involves only two operating points. It would be unreasonable to apply Ingebo's conclusions and equations far beyond the experimental work to which they apply in attempting to predict vaporization rates. On the other hand, several of the concepts might prove useful if an attempt were made to analyze the data of Fledderman and Hanson (*27*) so as to evaluate allowance for turbulence.

Tanasawa (*111*) investigated burning droplets from a swirl spray nozzle in an essentially quiescent atmosphere. Again the results are limited and preclude broad application. At this point one may wonder, therefore, how the equations for vaporization rate can be utilized. The solution is to deal with some particular droplet size which is representative of the point of interest. Usually this will be a size considerably greater than average for the spray; when it has diminished to zero, substantially all of the spray will have vaporized.

Order-of-magnitude estimates can be made for the vaporizing path length required, if the droplet is up to gas velocity, for various conditions within the conceivable range of interest for combustion in ducts. Roughly speaking, droplets of 1000-micron diameter (1 mm.) are huge (actually drops), 100-micron droplets are large, 10-micron droplets small, and 1-micron droplets tiny. For combustion in ducts, a low gas velocity would be 31.6—i.e., $10^{1.5}$—feet per second, a moderately low value would be 100 feet per second, a moderately high one 316—i.e, $10^{2.5}$—feet per second, and a high value 1000 feet per second.

The range of values of λ to be considered is from 10^4 to 10^7 sq. microns per second, 10^4 corresponding to vaporization of a still droplet with diffusion controlling, and 10^7 to a burning droplet with appreciable velocity relative to the air stream. The lower limit is based upon a value of 0.55×10^4 sq. microns per second for a still toluene droplet in cold air (*73*). Godsave's data (*37–39*) for still, burning droplets of various fuels range around 10^6 sq. microns per second (Nusselt number of 2). The upper limit is based upon a value of 22.5 for the Nusselt number, calculated according to Equation 4 for a 100-micron droplet with a velocity relative to the gas stream of 1000 feet per second and with physical property values (*117*) for 50° F. benzene droplets commencing vaporization in a 1000° F. air stream.

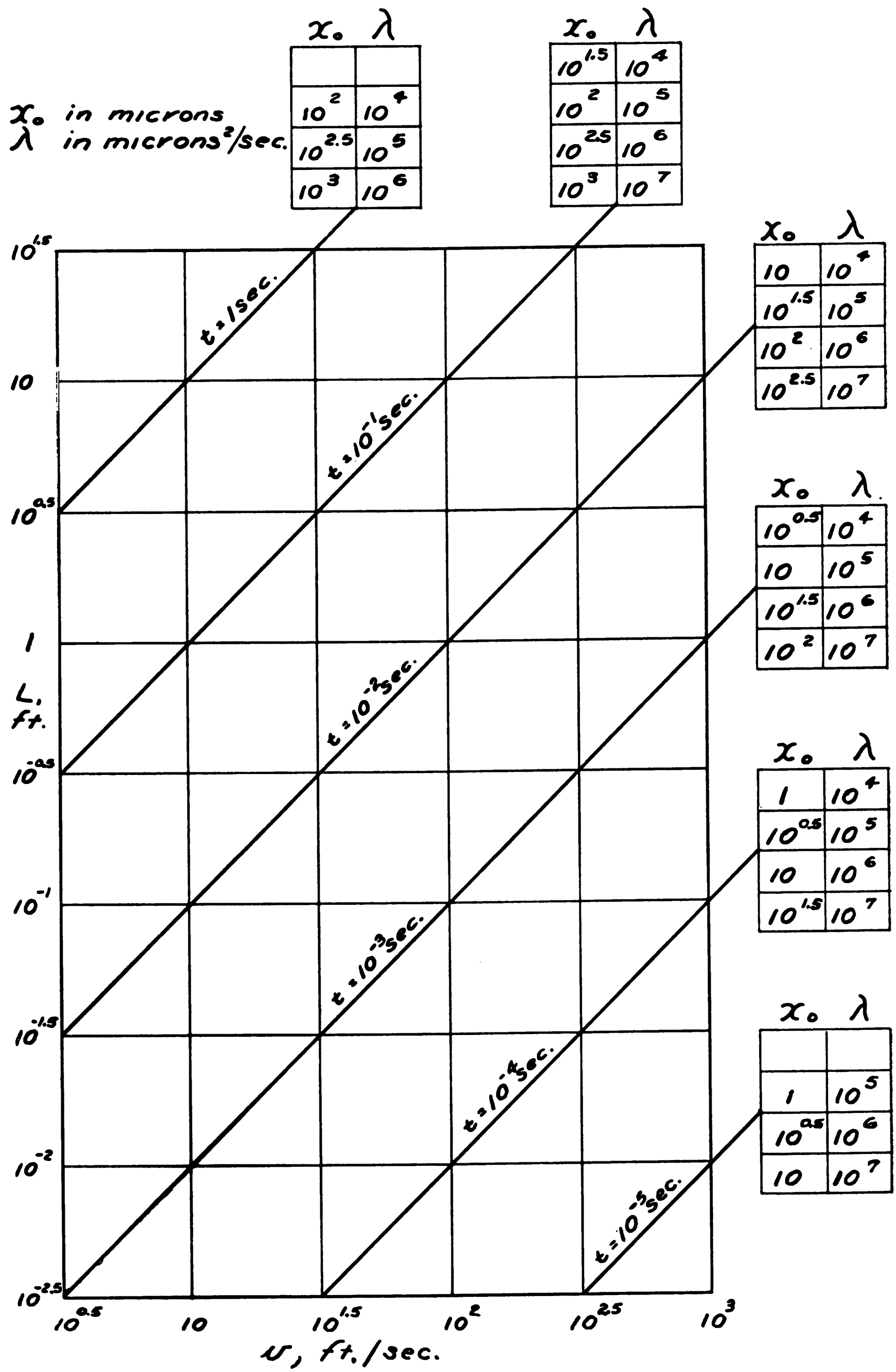

Figure 1. Representative solutions of vaporization time equation

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The minimum value for vaporizing path length from this collection of possible parameters is $10^{-5.5}$ foot and the maximum value is 10^5 feet. Reasonable intermediate solutions, displaced by factors of $10^{3.5}$, are 10^{-2} and $10^{1.5}$ feet. These are demonstrated by Figure 1, which is simply a plot of Equation 2 for a large number of pairs of values of x_0 and λ.

The solution $L = 0.01$ foot corresponds, as an example, to a 10-micron droplet, with $\lambda = 10^6$ sq. microns per second, traveling along with the air stream at 100 feet per second. This solution implies explanation for direct flamefront vaporization reported by Wolfhard and Parker (*121*) and, for smaller droplet sizes, by Burgoyne and Cohen (*10*). The solution $L = 31.6$ feet corresponds, as an example, to a 100-micron droplet, with $\lambda = 10^5$ sq. microns per second, traveling along with the air stream at 316 feet per second. As the gas velocity normally is fixed, the advantages are obvious for retarding the time when the droplet gets up to speed, for making Nusselt number and thus λ as large as possible, and particularly for minimizing droplet size.

Droplet Size Prediction

Treatment of droplet size distribution invites controversy. The mere fact that the normal frequency distribution equation does not apply should make one skeptical that any other equation determined empirically will be universally applicable; something more than pure chance is involved in droplet formation.

Various comparisons have been made (*4, 27, 28, 61, 74, 89, 106, 111*). For a particular task of fitting data, the recognition of an actual upper size limit leads to the modified logarithmic representation of Mugele and Evans (*89*). However, for pure mathematical ease the Rosin-Rammler distribution employed by Probert (*98*) is preferable from a vaporization point of view.

The Rosin-Rammler equation has two empirical constants, $\bar{x}$ and n:

$$R = e^{-(x/\bar{x})^n} \tag{9}$$

Probert set the value of n as lying generally between 2 and 4. A large variety of fuel injector types yield sprays for which $n = 3$ is a reasonable approximation. In the absence of specific data to the contrary, this value is recommended for any fuel injector which is not specifically designed to produce nearly uniform droplet size. [Spinning disk and spinning cup atomizers lead to much more nearly uniform sprays, and Burgoyne and Cohen (*10*) produced "areosols which were almost monodisperse" by condensing fuel vapor from a nitrogen atmosphere.]

For fixed value of the vaporization constant, regardless of droplet size, a graph presented by Probert (*98*) shows fraction vaporized as a function of n, $\bar{x}$, λ, and t. When λ is not constant with change of droplet size, this graph does not apply. Nevertheless, its significance in development of vaporization analysis techniques has been great.

Whereas few actual values of n for sprays from various fuel injectors are reported, it is usually possible to obtain a fairly reliable estimate of $\bar{x}$. This is so because $\bar{x}$ is uniquely related to various mean droplet diameters solely in terms of n, and data for Sauter mean diameter are rather frequently reported. Sauter mean diameter (SMD) is that diameter representative of the surface area per unit volume which is characteristic of the actual spray.

$$\frac{\bar{x}}{\text{SMD}} = \Gamma\left(1 - \frac{1}{n}\right) \tag{10}$$

When $n = 3$, $(x/\text{SMD}) = 0.7384\ (x/\bar{x})$.

Values of x/SMD for $n = 3$ are given in Table II. If time is allowed for droplets of size $(x/\text{SMD})(\text{SMD})$ to vaporize, all of R fraction of the spray will have vaporized, and some portion of $(1 - R)$ fraction as well. In view of the extreme range of Figure 1, it seems rather pointless to quibble over small differences in R. Assuming $n = 3$, if time is allowed for droplets of size 1.2285 SMD to vaporize, more than 99% of the spray is accounted for, which is substantially all of it, while if time is not allowed even for droplets

Table II. Rosin-Rammler Equation Characteristics When n Equals 3

R	$x/\bar{x}$	x/SMD
0.99	0.2158	0.1593
0.975	0.2934	0.2166
0.95	0.3716	0.2744
0.90	0.4723	0.3487
0.75	0.6601	0.4874
0.50	0.8850	0.6535
0.25	1.1150	0.8233
0.10	1.3205	0.9751
0.05	1.4416	1.0645
0.025	1.5451	1.1409
0.01	1.6637	1.2285

of size 0.1593 SMD to vaporize completely, then substantially none of the spray will have vaporized. With these limiting values for droplet size, Figure 1 furnishes a convenient index with which to establish whether an operating point provides practically zero vaporization, practically complete vaporization, or sizable partial vaporization to be analyzed in the manner indicated by Marshall (*85*).

Actual values of SMD (or some other mean droplet size) for various types of fuel injectors are given for orifice injectors (*23, 25, 45, 47, 61, 95, 107, 113*); swirl injectors (*8, 18, 20, 26, 34, 46, 63, 76–78, 81, 87, 93, 99, 100, 104, 112, 115, 118, 123*); air-blast atomizers (*5, 13, 33, 50, 64, 74, 94, 101*); impinging-jet atomizers (*30*); rotating-element atomizers (*7, 28, 53*); and droplet formation caused by collapse of gas bubbles rising through a liquid surface (*32, 91*). Maximum values of x are reported for orifice injection (*88*) and for air-blast atomization (*72*). [The air-blast atomization mechanism may be controlling when the "air blast" is in reality only a high relative velocity between the air and the injected liquid (*61*).]

Additional data for a particular type of fuel injection might be discovered by means of comprehensive bibliographies available (*15, 22, 35, 84*). Most current work is eventually noted in one or more of the following publications: *Aeronautical Engineering Review*, *Aircraft Engineering*, *Jet Propulsion*, *NACA Research Abstracts* (unclassified and confidential), *Title Announcement Bulletins* of the Armed Services Technical Information Agency (unclassified and confidential), *U. S. Government Research Reports*.

Sample droplet size distribution data are given for orifice injectors (*11, 65*); swirl injectors (*19, 21, 27, 43, 111, 122*); air-blast atomizers (*43, 56*); rotating-element atomizers (*51*); and natural clouds and fogs (*43*). These might be plotted on graph paper laid out with scales according to the Rosin-Rammler equation in order to determine $\bar{x}$ and n. The last few points probably will deviate from the line and must be dealt with separately according to the calculation objective. The remaining droplets from a partially vaporized spray of a particular distribution function do not constitute a spray of that same distribution function themselves, even when λ is held independent of droplet size (*85*).

Nomenclature

All equations are dimensionally consistent.

B = transfer number
c_p = heat capacity of vapor
D = molecular diffusivity of vapor
H = heat of combustion of fuel
h = heat transfer coefficient
k = thermal conductivity of gas or vapor
m = fractional mass concentration
dm = differential change of droplet mass
Nu = Nusselt number, hx/k
n = droplet distribution constant in Rosin-Rammler equation
Pr = Prandtl number, $c_p\mu/k$
p_i = partial pressure of components other than j
p_j = partial pressure of component j
Q = enthalpy increase of vaporizing fuel, measured from initial liquid temperature
R = volume or mass fraction of droplets larger in diameter than x according to Rosin-Rammler equation

Re = Reynolds number, $xv\rho_g/\mu$
r = stoichiometric oxygen-fuel ratio
Sc = Schmidt number, $\mu/\rho_g D$
SMD = Sauter mean diameter, surface-to-volume mean diameter of a spray
T = gas or vapor temperature
t = elapsed time for vaporization to proceed
dt = differential change of vaporization time
v = gas velocity (with droplet at gas velocity)
x = droplet diameter
$\bar{x}$ = droplet size constant in Rosin-Rammler equation
Γ = gamma function
λ = evaporation constant, defined as $d(x^2)/dt$
μ = gas or vapor viscosity
ρ = density (of liquid, if without subscript)

Subscripts

g = main gas stream
i = components other than j
j = component j
l = liquid
O = oxygen
0 = time zero
s = vaporizing surface
t = time t

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Burning of a Liquid Droplet

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The wide use of spray injection for the introduction of reactants into combustion chambers has pointed to the need for an analysis of the processes which govern combustion of liquid aerosols. This review presents the theoretical and experimental aspects involved in the burning of a single droplet. The application of the results obtained for a single droplet to the burning characteristics of liquid sprays remains a problem of fundamental importance in combustion research.

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In general, two cases of droplet combustion are of interest. A heterogeneous monopropellant flame involves a single reactant system in which a single component evaporates from the liquid surface and then decomposes exothermically at a rate which is a function of temperature and composition. On the other hand, a bipropellant flame requires the interaction of two reactants, fuel and oxidizer, one of which evaporates from the droplet surface and diffuses into the gas phase containing the other reactant. As a result of the interdiffusion of the reactants, a flame is established at some distance from the droplet. Experimental measurements have shown that the mechanism of droplet vaporization at high heat flux, such as prevails during combustion, is different from that observed at low temperature gradients near the liquid surface. Under the latter conditions the evaporation rate is governed by diffusional processes (*4*, *5*), whereas at high temperatures the rate of heat transfer from the flame to the liquid has been found to play a dominant role. Based on a mechanism of heat conduction through a stagnant film between concentric spherical shells, a useful approximation of the burning process may be devised. Thus it can be shown that the mass burning rate is proportional to the droplet radius and inversely proportional to the heat of vaporization. It is apparent, however, that such a model neglects the mass-diffusional process which occurs during the combustion of a liquid droplet and thereby modifies the rate of energy transfer. The approximate derivation also implies knowledge of the location of combustion radius with respect to the liquid surface. Such considerations stimulated a new approach to the problem of droplet combustion during the past few years (*7–9*, *11*, *17*, *20*, *23*, *25*, *37*, *42*, *44*, *46*, *51*, *52*, *54*, *59*, *60*, *62*).

Theoretical Analysis

Heat Transfer by Conduction. In the theoretical analysis of steady state, heterogeneous combustion as encountered in the burning of a liquid droplet, a spherically symmetric model is employed with a finite cold boundary as a flame holder corresponding to the liquid vapor interface. To permit a detailed analysis of the combustion process the following assumptions are made in the definition of the mathematical model:

The droplet and flame surfaces are represented by concentric spheres.

Combustion occurs under isobaric, steady-state conditions.

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The reactants yield product gases by exothermic reaction at a rate governed by the chemical kinetics.

The source of one reactant is a liquid surface at its boiling point, and that of the other is located in the gas phase at an infinite distance from the liquid sphere where the weight fraction of gaseous reactant and temperature are specified.

The heat released by chemical reaction is removed by thermal conduction and mass transport—i.e., radiation and thermal diffusion are neglected. The effect of radiation has been considered in some detail (*23*).

The transport parameters and the specific heat of the system are considered to be independent of temperature and composition. Average values are used for these parameters and the ratio of Schmidt to Prandtl number is taken as unity throughout the system.

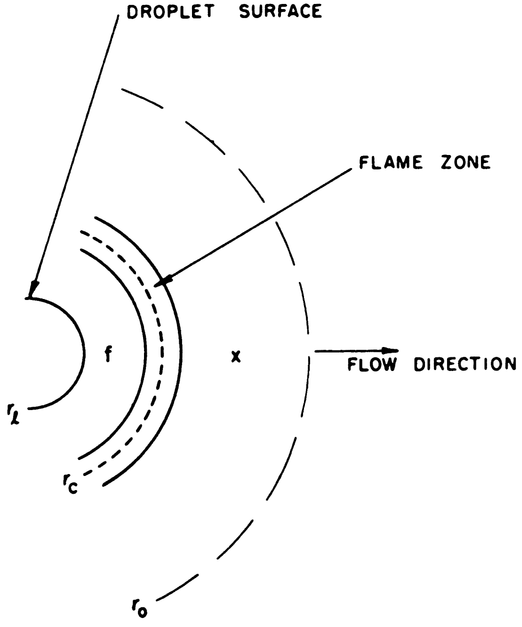

Figure 1. Model of burning droplet

Dynamic effects on the droplet and interaction between droplets are neglected.

As shown schematically in Figure 1, the gases flow from a cold boundary r_l outward towards infinity r_o in a coordinate system fixed with respect to the cold boundary. A steady state is established in which fuel vaporizes from the liquid surface and flows toward the flame zone while oxidizer diffuses against the flow of products into the flame front. Because the bipropellant system involves the material transfer of two reactants interdiffusing from opposite directions, the exothermic chemical reaction is limited to a region in which both reactants are present. Although a small weight fraction of the oxidizer diffuses to the liquid surface, where the weight fraction of fuel is high, the extent of chemical reaction in this region is very small because of the low temperatures prevailing near the liquid surface. The transport of matter and enthalpy in such a system is given by the equations for conservation of mass and energy; conservation of momentum is implied in the assumption of an isobaric process. In generalized form (*36*) these equations may be written as

$$\dot{m}_j = \dot{M}_j + \dot{m}z_j = A\rho v(Y_j - D_j Y_j'/v) \qquad j = 1, 2, 3, \cdots n \tag{1}$$

$$\sum_{j=1}^{n} \dot{m}_j h_j - A\lambda t' = \text{constant} \tag{2}$$

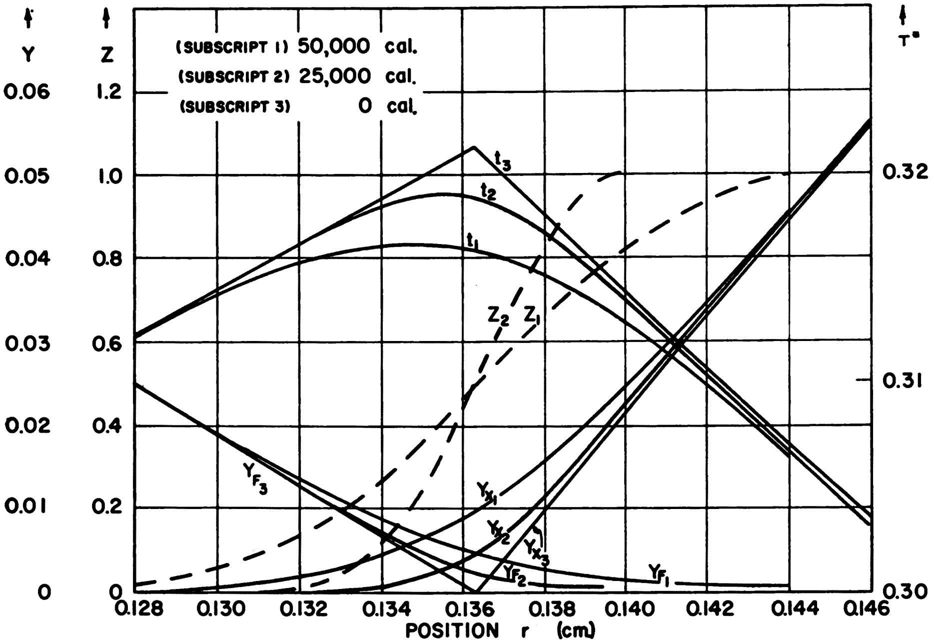

Figure 2. Flame structure surrounding fuel droplet burning in oxygen at various activation energies

where M_j, the mass flow rate of species j at the liquid surface, represents a constant characteristic of the system of equations and the boundary conditions. The notation used is given in the section on nomenclature (the prime notation refers to time derivatives and the dashed quantities are space derivatives). The parameter z_j represents the contribution by chemical reaction to component j; thus

$$z_j = \int_{r_l}^{r} (R_j/v)\, dr \tag{3}$$

For a four-component system composed of fuel, oxidizer, products, and inert gas, four conservation-of-mass equations describe the mass flow rate of each component. The mass flow rate of inert gas is zero because no "sink" exists within the system for this species of molecules. With the appropriate boundary conditions (*36*), the solution of the resulting differential equation constituting a fourth-order system for the bipropellant, heterogeneous flame requires numerical integration (*38*). From such a computation detailed information may be obtained concerning the temperature and composition profiles surrounding the burning droplet. A series of solutions for a representative fuel-oxidizer system is shown in Figure 2. The values of the parameters used in the numerical

Table I. Parameters for Fuel-Oxygen System (36, 38)[a]

C (cal./gram° K.)	0.38
D (sq.cm./second)	0.8
i	2.09
L (cal./gram)	238
q (cal./gram)	6694
λ (cal./cm.second° K.)	1.2×10^{-4}
ρ (gram/ml.)	0.4×10^{-3}
R	$10^{13}\rho Y_F Y_X \exp.[-E/K(t + T_l)]$

Boundary Conditions

$r_l = 0.02$ cm.

$T_l = 351.5°$ K.

$T_o = 291.5°$ K.

$Y_{X_o} = 1.00$ (pure oxygen)

Averaged at 1500° K.

integration are listed in Table I. Of special interest is the effect of the reaction rate on the structure of the flame zone. A decrease in the activation energy of the process is associated with a diminution in the flame-zone thickness (Table II) until the system attains the flame structure observed in the limit for zero activation energy. At the same time the maximum temperature in the flame zone increases slightly; the highest temperature gradient occurs at the liquid surface. This heat sink absorbs energy for vaporization and heating of the liquid phase.

Table II. Thickness of Flame Front (38)

Activation Energy *E*, Kcal.	Flame Thickness, Mm.
0	0
25	0.047
50	0.099

Under the conditions of zero activation energy a flame zone of infinitesimal thickness results at which the weight fractions of both fuel and oxidizer attain zero. The mass flow rates of oxidizer and fuel into this mathematical surface are taken to be of stoichiometric mixture ratio—i.e., $\dot{m}_X/\dot{m}_F = -i$. The system is thereby divided into two regions, denoted by f and x (Figure 1) separated by a step function. In the f-region the extent of chemical reaction is zero ($z = 0$); in the x-region, reaction has gone to completion ($z = 1$). Such a simplified analysis of the combustion process which neglects the contribution of chemical kinetics has been applied in the early theories of heterogeneous combustion (*7, 17, 20, 23, 42, 51, 62*). The analysis is of particular interest because it gives rise to a system of first-order differential equations which may be integrated in closed form. Thus explicit solutions may be obtained for the mass flow rate of fuel, the temperature of the combustion surface, the radius of the combustion surface, and the weight fraction of fuel at the liquid surface, as shown by Equations 4 through 7.

$$\dot{M} = 4\pi r_l \rho D \ln (1 + B) \tag{4}$$

$$t_c = \frac{q - L}{C}\left[\frac{1}{1 + \frac{i}{Y_{X_o}}}\right] + \left[\frac{t_o}{1 + \frac{Y_{X_o}}{i}}\right] \tag{5}$$

$$\frac{r_c}{r_l} = \ln (1 + B)/\ln \left(1 + \frac{Y_{X_o}}{i}\right) \tag{6}$$

$$Y_{Fl} = 1 - \left[\left(1 + \frac{Y_{X_o}}{i}\right)\Big/ (1 + B)\right. \tag{7}$$

The parameter B is given by

$$B \equiv \frac{1}{L}\left(\frac{qY_{X_o}}{i} + Ct_o\right) \tag{8}$$

and has been termed the transfer number (*51*). For a large number of solid and liquid hydrocarbon fuels burning in air the value of this number varies over a narrow range. As a result, the mass burning rates of these fuels show little variation. For solid fuels burning in air, such as carbon, which have a reaction zone in close proximity to the solid surface, an increased surface temperature results. Consequently the value of t_o in Equation 8 is greatly reduced, leading to very low transfer numbers.

The assumption of a reaction rate sufficiently fast to prevent the passage of oxidizer and fuel through the reaction surface appears a satisfactory approximation for the calculation of a parameter such as the mass burning rate, because the heterogeneous combustion process is governed by heat transfer from the flame to the liquid surface. The calculations show that the maximum temperature attained by the system and the location of the maximum are not materially affected by the reaction kinetics (Figure 2). However, a detailed analysis of the structure of the diffusion flame surrounding the droplet must take into account the rate of chemical transformation in the region of interdiffusion of reactants. Although the combustion rate occurring in such a diffusion flame is determined by physical mixing processes, the limits of combustion rate are governed by chemical considerations. Thus the theoretical calculations including chemical kinetics indicate that the width of the flame zone may reach a value at which steady-state combustion is no longer feasible. Increases in activation energy may result in such a flat temperature profile, caused by the broadening of the reaction zone, that the heat flux into the liquid is not sufficient to sustain stable combustion (*38*).

This observation supports Spalding's interpretation of the phenomenon of flame extinction in droplet combustion under conditions of forced convection (*56*). An increase in relative air velocity is associated with a thinner boundary layer and higher mass transfer rate. To accommodate the increased transport rate of fuel and oxidizer, the reaction zone thickens. This effect causes a decrease in the temperature prevailing in the reaction zone which in turn is associated with a decrease in the rate of reaction occurring in this region. Ultimately a condition is reached when, because of the decreased temperature, the weight fraction of reactants present in the reaction zone can no longer be consumed, and unburned (or partially burned) material passes through the zone. Further reduction in temperature and reaction rate results until finally the flame is extinguished.

The theoretical analysis based on the spherico-symmetrical model (Figure 1) elucidates the effect of total pressure on the combustion of a fuel droplet involving a bimolecular reaction. The differential equations show that an increase in total pressure will cause a rise in the reaction rate accompanied by a narrowing of the flame zone without change in the location of the temperature maximum with respect to the droplet surface. As a result the mass burning rate remains essentially unaffected by changes in pressure, as shown by the theoretical equation which shows that $\dot{M}$ is proportional to the product ρD, which is pressure-insensitive. Consequently, for the sphericosymmetrical model changes in pressure do not result in any major variation in heat flux to the droplet surface because the location of the flame front remains unaffected and the rise in maximum temperature with decreasing flame thickness is relatively small. These conclusions do not apply to steady-state combustion in the presence of convective heat transfer.

Free and Forced Convection. Considerable deviations from spherical symmetry of the flame front surrounding the droplet are produced by convection effects. Under the conditions of free convection a simple heat-transfer analysis based on the Grashof-Nusselt correlations suggests that the mass burning rate of the droplet should vary with pressure. The theory predicts a mass burning rate which is proportional to the square root of the total pressure and a position of the maximum in the temperature profile—i.e., the location of the flame zone—inversely proportional to the square root of the total pressure (*62*). It is apparent that in experimental measurements of droplet combustion spherical symmetry cannot be realized because of convection effects. Quantitative comparison of the predicted flame characteristics with experimental determinations must take into account the contribution of free convection on droplet combustion. Spalding has applied the concept of a boundary layer to the problem of heterogeneous combustion with natural and forced convection (*51*). The following relationships were obtained (*51, 58*) from the boundary layer theory for heterogeneous combustion from a vertical plane surface with natural convection and for both a plane surface and the forward stagnation point of a sphere with forced convection:

Natural convection, vertical flat plate

$$\frac{\dot{M}}{yD\rho B} = f_1(B, \mathrm{Pr}) \sqrt[4]{\frac{gy^3}{\nu^2}} \tag{9}$$

Forced convection, flat plate

$$\frac{\dot{M}}{yD\rho B} = f_2(B, \mathrm{Pr}) \sqrt{\mathrm{Re}} \tag{10}$$

Forced convection, forward stagnation point of sphere

$$\frac{\dot{M}}{r_1 D\rho B} = f_3(B, \mathrm{Pr}) \sqrt{\mathrm{Re}} \tag{11}$$

The parameter B, the transfer number, is defined by Equation 8.

These relationships have been used by Spalding in the dimensionless presentation both of theoretical values obtained in his approximate solution of the boundary layer equations (*58*) and of the experimental data (*51, 55, 60*). Emmons (*3*), who has solved the problem of forced convection past a burning liquid plane surface in a more rigorous fashion, shows graphically the rather close correspondence between values obtained from his exact solution and that of Spalding, and between the calculated values for flat plates and the experimental values for spheres.

The case of combustion of an entire spherical surface with forced convection has not yet been solved. Frössling (*4*) originally proposed a semi-empirical relation for the low-temperature evaporation of droplets in motion. Spalding (*60*) has applied the equation to his heterogeneous combustion data with some success by including the term containing the transfer number:

$$\frac{\dot{M}}{4\pi r_l D\rho \ln (1 + B)} = 1 + 0.276\ \mathrm{Re}^{1/2}\ \mathrm{Sc}^{1/3} \qquad (12)$$

At a Reynolds number of zero this expression reduces to Equation 4. Hottel, Williams, and Simpson (*23*) suggest that a term accounting for chemical reaction rate in relation to momentum transfer should be included in Equation 12.

The subject of flame extinction at the forward stagnation point of the liquid sphere under forced-convection conditions has also been analyzed in some detail (*56*). Basing his conclusion on theoretical considerations of the chemical kinetics and the hydrodynamics at the forward stagnation point, Spalding stated that for specified physical conditions the flame extinction velocity is proportional to the sphere diameter. This relationship was confirmed by his experimental observations but not by work performed subsequently (*1*).

Dynamics of a Burning Droplet. The influence of mass transfer on the drag coefficient of spheres has not been analyzed theoretically. However, the problem of the flat plate has been attacked by Mickley and coworkers (*39*), Spalding (*58*), Emmons (*3*), and others. In all cases a pronounced decrease in drag coefficient is indicated as a result of mass transfer. Spalding (*60*) states that at moderate Reynolds numbers the ratio of frictional drag coefficients both with and without mass transfer is of the order of $\ln(l + B)/B$. Emmons presents a curve showing the change in velocity distribution over a flat plate effected by mass transfer.

Experimental Techniques

The experimental techniques employed in the fundamental studies of the burning rate of a liquid droplet fall into three groups: (a) The process of stationary, non–steady-state combustion in which the combustion rate of a droplet suspended in a reacting medium is determined from the variation of droplet size with time; (b) the process of stationary, steady-state combustion in which the geometric dimensions of a supported droplet are maintained constant during combustion; and (c) the process of nonstationary, non–steady-state combustion in which a freely-moving droplet is allowed to come in contact with a gaseous reactant.

Godsave (*7, 10, 11*), Hall and Diederichsen (*22*), Kumagai, Kimura, and Isoda (*30–33*), Kobayasi (*27, 28*), Nishiwaki and Haghi (*42, 43*), Graves (*19, 20*), Goldsmith and Perkins (*18*), and Kiley (*35*) all studied the burning of liquid fuel drops (700 to 1700 microns in diameter) suspended from fused silica filaments with natural convection accounting for the motion of ambient gas past the burning surface. In each case the progress of combustion was recorded photographically, and the change in size of the burning droplet was noted as a function of time.

Godsave examined the burning of drops in unconfined air. Ignition was accomplished by momentarily exposing the droplet to a small gas flame. Kumagai and Isoda carried out their tests in essentially the same manner. In some of their later tests they introduced a vibrating air field for investigation of its effect on droplet combustion. Kobayasi and Nishiwaki both studied the combustion of individual drops in a horizontal,

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cylindrical furnace (550° to 1000° C.). In each case the furnace, mounted on wheels, was rolled into position to surround the drop suspended from a filament. The spontaneous ignition and the progress of combustion of the droplet were photographed through windows in the side wall of the furnace. Hall and Diederichsen used a small cylindrical vessel to enclose their droplets to study combustion over the pressure range of 1 to 10 atmospheres. Ignition was produced by a small gas jet which initially was ignited by a spark. Goldsmith and Perkins, and Graves, similarly enclosed their droplets to study the effect of oxygen concentration in the ambient gas.

The second, less direct method applied to droplet combustion with natural convection involves the use of a spherical model covered with a continually replenished film of fuel. Rigid models are employed readily under conditions of forced convection, where the velocity of the ambient gas relative to the model is varied over a broad range. Khudyakov (*24*), in his study of the drag of burning droplets in air streams, used a metal sphere (1.57 cm. in diameter) covered with liquid fuel introduced to the surface through a 1-ml. hole approximately at the forward stagnation point. In an investigation of burning rates of a liquid sphere (3.8 cm. in diameter) under natural convection conditions, Spalding (*51, 53, 55*) employed a similar procedure in providing a wetted surface with excess fuel. From measurements of the liquid consumed he was able to compute the burning rate. To produce an adhering liquid film under forced convection conditions, Spalding employed a sphere (2.54 cm. in diameter) grooved at the leading surface and covered with a tightly fitting fabric. Wise, Lorell, and Wood (*62*) used porous Alundum spheres of several sizes (0.36 to 1.26 cm. in diameter). Fuel fed to the center of the porous sphere flowed to the surface, forming a thin liquid film. A mechanically driven syringe delivered the fuel at controlled rates of flow.

The third experimental technique employs drops which are projected or allowed to fall freely through a reactive gas contained in a high-temperature furnace. In this manner, Chang (*2, 50*) and Gerald (*6, 50*) investigated the combustion of fuel oil drops (267 to 384 microns in diameter) at furnace temperatures of 800° to 1100° C. The velocity of fall of each drop was evaluated from photographs taken at different points along the path. The extent of combustion was determined from the weights of the residues of drops of initially known size. Application of their method to still smaller sizes was thwarted by furnace convection effects. Streed attempted to surmount this difficulty by allowing the droplet to fall into a hot stream of air moving down through the vertical furnace (*50*); however, the recovery of droplet residues from the stream constituted a serious problem. Topps (*61*) studied the weight change of drops (300 to 600 microns in diameter) of several pure fuels, kerosine, and fuel oil falling through a vertical furnace. At the operating conditions chosen with temperatures below 800° C. ignition was not generally obtained during residence in the furnace.

Hall and Diederichsen (*22*) projected a stream of droplets (diameters 150 to 170 microns) from the periphery of a spinning disk up into a vertical furnace maintained at a sufficiently high temperature for ignition, 710° C. The spinning disk atomizer employed was capable of producing droplets of uniform, predetermined size. Drum photographic records were obtained of the luminous portion of the droplet trajectory and drop burning times were estimated therefrom.

Hottell, Williams, and Simpson (*23*) report a study employing a similar technique. Droplets of heavy heated fuel oils and pure liquids (350 to 650 microns in diameter) were introduced from a spinning disk into a furnace maintained at various temperature levels (900° to 1100° C.) and on leaving the furnace were extinguished and caught on a weighing dish. The residence time of the droplets was measured individually by photoelectric means. The extent of combustion in each test was determined from the combined weights of residues of 50 to 100 drops of a given initial size.

Each of the above experiments possesses features which facilitate study of particular aspects of the complex process of droplet combustion. However, all suffer from the shortcoming that the drops or model diameters investigated are appreciably greater than the sizes most commonly experienced in modern propulsion systems and industrial furnace applications. On the basis of the results obtained, only extrapolations and estimates can be made for droplet combustion mechanics in practical situations. The method of the filament-supported droplet possesses the advantage of simplicity of equipment. One inherent disadvantage is that the shape of the droplets studied sometimes departs significantly from the spherical shape. The method allows, on the other hand, a means of observing at close quarters ignition near the drop surface, spattering of fluid from the drop surface, and frothing and caking of heavy hydrocarbon fuels.

The use of a wetted spherical model affords the opportunity of studying combustion under steady-state conditions. Forced convection of the ambient gas may be employed without distortion of the object. Sufficiently large models may be employed when it is desired to probe the gas zones surrounding the burning sphere. It is apparent that the method is restricted to conditions where polymerization products and carbonaceous residues are not formed. In the application of such models, the conditions of internal circulation, radiant heat transmission, and thermal conductivity of the interior are somewhat altered from those encountered in a liquid droplet. Thus the problem of breakup of the droplet as a result of internal temperature rise cannot be investigated by this method.

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Experimental Results

After injection into a combustion zone, a fuel droplet may pass through as many as three distinct phases during its lifetime (*23*). In the first stage the droplet is preheated to a point where sufficient vapors are evolved to support a flame (ignition). During the second stage single component fuels generally vaporize and continually feed the diffusion flame enveloping the droplet until the liquid phase disappears. Simultaneously, in the case of residual fuel oils, surface polymerization and internal vaporization may occur during the second step. For fuel oils there is generally a third step—i.e., that of the heterogeneous combustion of the cokelike residue. Hottel, Williams, and Simpson (*23*) present data from which the relative times of duration of these three steps may be compared. For drops of Type A production oil (initially 410 to 608 microns in diameters) injected into a furnace at 1000° C., it was shown that the preheat time was of the order of 200 milliseconds, the second step required from 125 to 250 milliseconds (increasing with droplet size), and, from an extrapolation, the third combustion phase is estimated to require on the order of 500 milliseconds. Thus it is evident that the time interval for the third step may be significant in many combustion systems.

Stage I—Preignition Period. Quantitative data specifically on droplet preignition heating are rather fragmentary. Much pertinent information may be found in the general heat transfer literature. Inasmuch as the intent in this paper is to review references treating the subject of drop burning subsequent to ignition, only ignition observations made in connection with drop combustion studies are mentioned here.

In experiments with both suspended drops and drops in free motion it has been noted that on exposure to elevated temperatures in a furnace, there is little change in volume prior to ignition. Following ignition, the change in drop diameter with time is considerably more rapid. The moment of ignition can be detected readily at the intersection of straight lines obtained by plotting the square of diameter, or (droplet mass)$^{2/3}$, *vs.* residence time in the furnace. In Table III estimated preheat times are listed from several sources.

Kobayasi (*26–28*) and Nishiwaki (*42*) also present curves showing change in diameter of their drops with respect to time. The preheat times (in this case the residence time of a suspended drop in the furnace prior to ignition) taken from their curves are presented in Table III. Nishiwaki detects an intermediate transition point during the preignition period which he interprets as defining two regimes: a heating time during which the droplet is raised in temperature to a level where appreciable evaporation begins, and an evaporation period leading to ignition. His data indicate that the evaporation period for α-methylnaphthalene decreases with increasing initial drop diameter at furnace temperatures of 550° and 680° C.; at 716° C. the evaporation period is relatively independent of diameter. In all cases, the sum of the preignition heating and evaporation periods—i.e., the preignition time—increased with initial drop diameter. In addition,

Table III. Preheat Time Preceding Drop Ignition

Fuel	Drop Size, μ	Furnace Temp., °C.	Preheat Time, Msec.	Exptl. Method	Reference
Cetane	461	1000	170	Projected drops	*23*
	554		165		
	679		150		
n-Eicosane	466		140		
	564		170		
	675		210		
Wax	534		210		
m-Terpheny	442		140		
	541		175		
	636		200		
Phrenanthrene	453		170		
	549		175		
	653		180		
Acenaphthene	416		60		
	501		100		
	621		100		
Type A production oil	410	900	160		
	410	1000	190		
	410	1100	225		
	502	900	140		
	502	1000	200		
	502	1100	220		
	608	900	160		
	608	1000	210		
	608	1100	240		
Benzene	1277	740	900	Suspended drops	*27*
	1216		800		
Motor gasoline (density = 0.742 gram/ml.)	1136	700	800		
	1010	800	300		
Light Diesel oil (density = 0.828 gram/ml.)	1183	700	560		
	1140	700	490		
Heavy oil (density = 0.918 (gram/ml.)	1072	700	1000		
	1130	695	930		
α-Methylnaphthalene	1323	713	1515		
	1183		1510	Suspended drops	*42*
	1049		1500		

increasing the ambient oxygen concentration (furnace temperature, 680° C.) was found to cause a decrease in the preignition evaporation period but not to affect the heating period for cetane and α-methylnaphthalene droplets (1010 to 1210 microns in diameter). Kumagai and Kimura (*34*) observed that the droplet preignition period is composed of a heating stage without chemical reaction followed by a stage where chemical reactions occur. Nishiwaki also reported information on the effect of proximity of two like droplets (about 1000 microns in diameter) on their ignition. The shortest preignition residence times were obtainable when the droplets were 4 to 5 mm. apart. This optimum distance appeared to increase slightly with temperature over the ambient temperature range 560° to 730° C.

Kobayasi (*27*) presents photographs showing the transient state from ignition to steady combustion for a suspended benzene droplet. The flame originating at some point in the vapor mixture spreads throughout the diffusion zone, producing soot in the case of fuels having a high carbon content. As a result of heat liberation, natural convection sets in and a stable flame front is ultimately formed.

Stage II—Period of Liquid Combustion. The subject of combustion following ignition has been pursued rather extensively. The linear relationship between the square of the diameter and time, which is predicted theoretically to hold for the combustion of a spherical drop surrounded concentrically by a spherical flame, has been found to apply generally to the evaporation period in the combustion of pure compounds.

The slope, $-\,d(2r_l)^2/d\theta$, of the straight lines which characterize combustion of various compounds as well as the lighter petroleum fractions during the evaporation stage has been termed the "evaporation constant"—i.e., $r_l^2 = r_{l\,\theta=0}^2 - \epsilon\theta/4$ and $\epsilon = 2\dot{M}/(\pi\rho^0 r_l)$ (*7–11, 48*). Experimentally determined values of this constant are presented in Table IV. The burning lifetimes of fuel drops initially at the boiling point—i.e., with no preheat period—can be calculated by dividing the square of the initial drop diameter by the evaporation constant.

Evaporation constants have been calculated from the published data of Hall and Diederichsen (*22*) and are given also in Table IV. From the luminous tracks on their photographic records these investigators estimated the burning times of drops projected

Table IV. Evaporation Constants

Liquid	Ambient Pressure, Atm	Ambient Gas Composition, Vol. %	Ambient Temp., °C.^{a}	Evapn. Constant, ϵ, Sq. Cm./Sec.	Exptl. Method	Reference
Ethyl alcohol	1	Air	20	0.0081	Suspended drop	7
		Air	20	0.0086		16
		34% O_2–66% N_2	20	0.0111		16
		47% O_2–53% N_2	20	0.0150		16
		67% O_2–33% N_2	20	0.0184		16
		89% O_2–11% N_2	20	0.0204		16
Ethyl alcohol, 95.5% by weight	1	Air	20	0.0096	Porous sphere	62
		34% O_2–66% N_2	20	0.0137		62
		47% O_2–53% N_2	20	0.0171		62
		67% O_2–33% N_2	20	0.0214		62
		89% O_2–11% N_2	20	0.0240		62
		100% O_2	20	0.0242		62
		21% O_2–79% He	20	0.0128		62
		34% O_2–66% He	20	0.0189		62
		47% O_2–53% He	20	0.0214		62
		56.2% O_2–43.8% He	20	0.0229		62
Ethyl Alcohol, water 83.9% by weight	1	Air	20	0.0085	Porous sphere	62
75.5%		Air	20	0.0043		62
59.1%		Air	20	0.0036		62
83.9%		100% O_2	20	0.0195		62
75.5%		100% O_2	20	0.0155		62
59.1%		100% O_2	20	0.0123		62
Ethyl alcohol,		Air	700	0.0099	Suspended drop	27
n-Heptane		Air	20	0.0097	Suspended drop	7
		Air	20	0.0084		16
		34% O_2–66% N_2	20	0.0138		16
		47% O_2–53% N_2	20	0.0150		16
		67% O_2–33% N_2	20	0.0186		16
		89% O_2–11% N_2	20	0.0223		16
		Air	135	0.0114		16
		Air	700	0.0116		27
		Air	800	0.0124		27
2,2,4-Trimethylpentane (isooctane)	1	Air	20	0.0095	Suspended drop	7
		17% O_2–83% N_2	20	0.0107		20
		Air	20	0.0114		20
		24.9% O_2–75.1% N_2	20	0.0125		20
		34.9% O_2–65.1% N_2	20	0.0143		20
		Air	700	0.0090		27
		Air	900	0.0130		27
		Air	995	0.0135		27
Benzene	1	Air	20	0.0097	Suspended drop	7
		Air	20	0.0099		16
	2	Air	20	0.013		16
	5	Air	20	0.018		16
	1	Air	730	0.0101		27
		Air	740	0.0106		27
		Air	750	0.0095		27
		Air	800	0.0127		27
		Air	995	0.0140		27
Methyl alcohol	1	Air	800	0.016	Suspended drop	27
Toluene	1	Air	20	0.0066	Suspended drop	7
		Air	20	0.0077		16
		Air	735	0.0091		27
o-Xylene	1	Air	20	0.0079	Suspended drop	7
p-Xylene	1	Air	20	0.0077	Suspended drop	7
Ethyl benzene	1	Air	20	0.0086	Suspended drop	7
Isopropylbenzene	1	Air	20	0.0078	Suspended drop	7
n-Butylbenzene		Air	20	0.0086		7
tert-Butylbenzene		Air	20	0.0077		7
tert-Amylbenzene		Air	20	0.0078		7
Pseudocumene		Air	20	0.0087		7
Nitrobenzene		Air	700	0.0102		27
		Air	800	0.0100		27
		Air	600	0.0105		27
Cetane	1	Air	700	0.0144	Suspended drop	27
		Air	800	0.0155		27
		Air	900	0.0240		27
		Air	990	0.0260		27
		Air	1000	(0.0133)	Projected drop	23
Cyclohexane	1	Air	700	0.0102	Suspended drop	27
		Air	800	0.0150		27
Methylnaphthalene	1	Air	700	0.0097	Suspended drop	27
		Air	800	0.0111		27
		Air	713	0.0120		42
Furfuryl alcohol	1	Air	20	0.0072	Suspended drop	22
	4	Air	20	0.0086		22
	6.7	Air	20	0.0093		22
	10	Air	20	0.0105		22
	15	Air	20	0.0133		22
	20	Air	20	0.0151		22

Table IV. Evaporation Constants (*Continued*)

Liquid	Ambient Pressure, Atm	Ambient Gas Composition, Vol. %	Ambient Temp., °C.[a]	Evapn. Constant, ε, Sq. Cm./Sec.	Exptl. Method	Reference
Tetralin	1	Air	20	0.0076	Suspended drop	*22*
	4	Air	20	0.0084		*22*
	6.7	Air	20	0.0121		*22*
	15	Air	20	0.0153		*22*
	20	Air	20	0.0168		*22*
	1	Air	710	0.0209	Projected drop	*22*
Decane	1	Air	20	0.0101	Suspended drop	*22*
	2	Air	20	0.0097		*22*
	4	Air	20	0.0105		*22*
	6	Air	20	0.0130		*22*
	10	Air	20	0.0163		*22*
	20	Air	20	0.0192		*22*
Amyl acetate	1	Air	20	0.0080	Suspended drop	*22*
	2	Air	20	0.0110		*22*
	4	Air	20	0.0121		*22*
	6	Air	20	0.0134		*22*
	10	Air	20	0.0164		*22*
	20	Air	1020	0.0356		*22*
n-Eicosane	1	Air	1000	(0.0153)	Projected drop	*23*
m-Terphenyl	1	Air	1000	(0.0119)	Projected drop	*23*
Phenantherene	1	Air	1000	(0.0117)	Projected drop	*23*
Acenaphthene	1	Air	1000	(0.0091)	Projected drop	*23*
Wax	1	Air	1000	(0.0177)	Projected drop	*23*
Paraffin (Abel flash: 164° C.)	1	Air	1000	0.0143	Projected drop	*22*
Petroleum ether (100°-120° C.)	1	Air	20	0.0099	Suspended drop	*7*
Kerosine (ρ = 0.805)	1	Air	20	0.0096	Suspended drop	*7*
Kerosine (ρ = ?)	1	Air	650	0.0103		*27*
		Air	700	0.0112		*27*
		Air	740	0.0128		*27*
		Air	790	0.0147		*27*
Kerosine (164°-280° C.)	1	Air	710	0.0309	Projected drop	*22*
Gasoline (ρ = 0.742)	1	Air	700	0.0106	Suspended drop	*27*
		Air	800	0.0149		*27*
Diesel oil (ρ = 0.850)	1	Air	20	0.0079	Suspended drop	*7*
Diesel light oil (ρ = 0.828)	1	Air	700	0.0109	Suspended drop	*27*
Nitric acid	1	Ammonia 100%	20	0.0184	Porous sphere	*62*
(10% H_2O)	1	Ammonia 100%	20	0.0149		*62*
(13% NO_2, 1% H_2O)	1	Ammonia 100%	20	0.0238		*62*
Hydrazine	1	Air	20	0.0212	Suspended drop	*35*
Nitromethane	1	Air	20	0.0109		*35*

[a] Room temperatures are recorded as 20° C.

into a furnace. They also measured the burning rate of drops suspended on silica fibers. Evaporation constants based on their suspended drop data are closer in value to those obtained by other investigators.

Included in Table IV are drop evaporation constants determined for some commercially important fuels. To conserve space the data of Kobayasi (*27*) are tabulated here in the form of averaged values at various temperature levels.

Kobayasi observed that at 700° C. light diesel oil burns in a manner similar to gasoline or pure compounds, yielding a linear relationship between the square of diameter and time. At 750° and 800° C. the data patterns are no longer linear and liquid phase cracking is observed. With heavy oil it was noted that the lighter components evaporate first, yielding a viscous residue which froths, splashes, and swells because of internal vaporization and cracking. With such fuel oils the linear behavior was not observed. Gerald (*6*, *50*) reported that with ambient air at 1100° C. the diameter of Bunker C fuel drops increases about 1.5 times the original diameter of the drop before collapsing to low density carbonaceous residues. At 800° C., drops of the same fuel swell to twice the original size yielding a hollow lattice-like cenosphere. Kobayasi (*27*) appears to have obtained a similar residue by exposing a drop of heavy oil B in a nitrogen atmosphere at 700° C. In explanation of the differences in appearance of the residues obtained at the end of Stage II, it is suggested that polymerization can occur to a greater extent at 800° C. than at 1100° C. because the constituents available for polymerization do not vaporize

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as readily (*6*, *50*). At 800° C. the flame surrounding the droplet was not luminous; it became luminous (particularly in the wake) for an increasing fraction of the evaporation period as the furnace temperature was increased. Soot was noted in the wake of the droplets, suggesting cracking and polymerization in the vapor phase. Goldsmith (*16*) reports that in the combustion of droplets of benzene and toluene (but not of ethyl alcohol and *n*-heptane) a carbonaceous product was formed in the wake gases which collected on the droplet-supporting silica filament. The effect of molecular structure on carbon formation was noted by Godsave (*10*) who made comparisons with gas diffusion flames.

Hottel, Williams, and Simpson (*23*) present their data in the form of $(\text{mass})^{2/3}$ *vs.* residence time. The slopes of the straight lines drawn through the plotted points can be converted simply to the evaporation constant. This conversion has meaning only for fuels which do not crack in the liquid phase with resulting frothing and swelling. The tabulated values enclosed by parentheses (Table IV) have been calculated from slopes of curves presented by Hottel, Williams, and Simpson, disregarding the occurrence of liquid phase cracking. Plotting data in the manner employed by these investigators possibly has general utility because the linear relation between $(\text{mass})^{2/3}$ and time in Stage II is obtained not only for the pure fluids but also for Type A production oil which burned in a manner typical of the heavier petroleum fractions. The value of the slope, $-\,d(\text{mass})^{2/3}/d\theta$, noted for Type A production oil drops (410, 502, and 608 microns) injected into a furnace at 900°, 1000°, and 1000° C., was substantially constant at 0.0077 $(\text{gram})^{2/3}$ per second. This is numerically equal to the average value obtained for a series of substances (cetane, *n*-eicosane, wax, *m*-terphenyl, phenanthrene, and acenaphthene) which are considered representative of those found in fuel oils. It is of particular interest to note that the values of the evaporation constants for the large number of fuels studied varies over a very small range. This fact lends further support to the heat-transfer controlled mechanism of droplet combustion. Thus the mass burning rate is determined primarily by the physical properties of the fuel and its environment rather than by chemical reaction kinetics. For a given weight fraction of oxygen the magnitude of the ratio of the heat of combustion to the heat of vaporization has the major influence on the mass burning rate.

The distance between the outer edge of the luminous zone of the flame and the base of a suspended drop burning in air has been measured (see Table V) and found to be essentially independent of diameter (*22*, *33*). This experiment was also performed with ethyl alcohol–wetted porous spheres of different sizes (0.36 to 1.25 cm. in diameter) and again a constant flame distance was obtained (*62*). This observation points to a defect in the theoretical analysis of droplet combustion based on the spherico-symmetrical model. As indicated in Equation 5 the ratio of the flame to droplet diameter is expected to remain constant rather than to show the difference $(r_c - r_l)$ as found experimentally. Calculations also indicate that the computed value of r_c for a representative fuel-oxidizer system is far in excess of the experimental value. Such a disagreement between theory and experiment is not surprising because the spherico-symmetrical model chosen does not satisfactorily approximate the prevailing conditions of free convection encountered during the droplet-burning experiments.

Table V. Flame Distance (Natural Convection)[a]

Liquid	Flame Distance, Mm.	Surface	Reference
Benzene	0.40	Suspended drop	*7*
Tetralin	1.2		*22*
Furfuryl alcohol	0.95		*22*
Ethyl alcohol	2.3	Wetted porous sphere	*62*

[a] Air at 1 atm. pressure and room temp.

EFFECT OF GAS TEMPERATURE ON BURNING RATE. It has been common practice in certain industrial applications to preheat the air before it enters the combustion region. The theoretical analysis of the droplet combustion process indicates that such an increased air temperature does not change materially the mass burning rate, because the increase in transfer number produced by heating the air stream enters in the logarithmic term of the expression for $\dot{M}$ (Equation 4). Thus for a representative fuel droplet such as benzene, a 20% increase in $\dot{M}$ for a rise in air temperature from 300° to 1300° K. is calculated. Experimental measurements tend to confirm this minor influence of ambient air temperature on mass burning rate as evidenced by the evaporation constants determined by several investigators (Table IV). A 20 to 50% increase in burning rate has been reported for most fuels when the ambient air temperature was raised from room temperature to 1273° K. Hottell, Williams, and Simpson (*23*) present a diagram indicating the influence of drop diameter and ambient temperature on the relative amounts of heat transferred to the drop surface by thermal radiation and by thermal conduction.

Table VI. Pressure Exponent[a]

Liquid	Pressure, Atm.[b]	Pressure Exponent	References
Furfuryl alcohol	4–20	0.30	*22*
Tetralin	1–20	0.29	*22*
Decane	1–6	0.17	*22*
Amyl acetate	1–6	0.17	*22*
Benzene	1–5	0.41	*16*

[a] Air at 1 atm. pressure and room temp.
[b] Pressure range over which pressure exponent was obtained.

EFFECT OF PRESSURE ON BURNING RATE. Hall and Diederichsen (*22*) show that in the pressure range of 1 to 20 atmospheres the lifetime of a burning drop is proportional to its initial diameter. The evaporation constants calculated from data on the combustion of suspended drops of furfuryl alcohol, tetralin, decane, and amyl acetate are presented in Table VI. Their data indicate that $\dot{M}$ is proportional to the ambient pressure, raised to the ¼th power. In addition these investigators noted that the distance between the flame front and the liquid surface was inversely proportional to the square root of the pressure. Goldsmith (*16*) measured the burning rate of benzene drops at 1, 2, and 5 atmospheres (Tables IV and VI). He reports that at higher pressures there appeared to be no increase in soot deposition on the supporting silica filament.

EFFECT OF GAS PHASE COMPOSITION ON BURNING RATE. Several investigators have added oxygen to air to study the effect of the oxygen-nitrogen ratio on drop combustion (Table IV). Values for evaporation constants representing the ethyl alcohol–oxygen–nitrogen data of Wise, Lorell, and Wood (*62*) are presented to enable direct comparison with the reported values of Goldsmith (*16*) (Table IV). At oxygen concentrations less than 17 wt. %, an ethyl alcohol flame could not be supported (*62*). Graves (*20*) made similar observations on the burning of 2,2,4-trimethylpentane (isooctane) drops. Goldsmith (*16*) reports that at oxygen concentrations exceeding 23%, benzene and toluene (but not ethyl alcohol and *n*-heptane) drops burn with the formation of soot which collects on the supporting silica filament. When nitrogen was replaced by helium—i.e., helium-oxygen mixtures—the burning rate of ethyl alcohol wetted spheres increased 30 to 50% (*62*) because of the higher molecular and thermal diffusivity of the gas mixture.

The increase in burning rate with rising weight fraction of gaseous oxidizer manifests itself in the gradual approach of the luminous flame region towards the liquid surface. As a result the rate of heat transfer per unit area becomes greater and the attainment of steady-state combustion becomes more difficult. Similar considerations apply to the increase in heat flux associated with decreasing droplet size, since Q is inversely proportional to the droplet radius. This effect, together with the gradual heating of the interior of the droplet, may be responsible for the disruptive boiling and shattering of the droplet observed during the course of burning of certain liquids (*62*).

EFFECT OF LIQUID PHASE COMPOSITION ON BURNING RATE. Many of the evaporation constants for drops of pure organic compounds burning in air at 20° C. are in the range 0.0070 to 0.0110 sq. cm. per second (Table IV). Values for some of the lighter petroleum fractions also fall in this range.

The effect of an inert material on $\dot{M}$ was observed in a series of tests on the burning rates of aqueous ethyl alcohol solutions from a wetted porous sphere (*62*). As is to be expected, the burning rate decreased as the water content increased up to about 60% by weight where combustion no longer proceeded at a steady rate. It is suggested that with high water concentrations, the heat flux is low and equilibrium distillation is favored, thereby allowing water to accumulate on and finally drip from the spherical surface. At lower water concentrations, the higher flame temperature yields a heat flux sufficiently large to effect nonequilibrium vaporization (*62*).

The effect of liquid composition has also been noted in the combustion of nitric acid in ammonia (*62*). Striking color changes in the flame delineate three distinct luminous zones in the flame. The composition of the liquid phase was varied to observe its effect on burning rate (Table IV). Addition of water to the acid produced a stable flame and a lower burning rate. With the addition of nitrogen dioxide to the acid, an increased burning rate and also spattering from the liquid surface were noted. The ejection of liquid from the surface may have been caused by very fast vaporization of the nitrogen dioxide.

Kiley (*35*) attempted to burn liquid monopropellants in nitrogen by the method of suspended droplets and by the technique of a porous Alundum sphere (7 mm. in diameter). These experiments did not yield stable combustion in an inert gaseous atmosphere. For combustion in air he reports the evaporation constants for hydrazine and nitromethane (Table IV).

In their trace photographs of projected droplets in a furnace, Hall and Diederichsen (*22*) observed that large kerosine drops (600 to 700 microns) showed a momentary brightening of the flame just prior to extinction. Smaller drops of kerosine (350 to 500 microns) produced a small auxiliary tongue of flame close to the top of the droplet trajectory. It is suggested by the investigators that the latter is due to convection effects. The flame phenomenon observed with the larger drops is explained on the basis of formation of unstable products in the liquid phase which explode when their concentration becomes sufficient. This explanation had support from certain tests which they performed on tetralin. Peroxide-free tetralin drops burned without explosion. Drops of peroxidized tetralin (in excess of 500 microns in diameter) burned with a brilliant flash at the end of their visible burning life. The explosion was made to occur prior to the extinction of the flame trace (as in the case of kerosene) by the addition (30%) of a heavy oil.

EFFECT OF AMBIENT GAS FLOW ON BURNING RATE. In all of the experiments reviewed, ambient gas flow plays an important role. In general, combustion of suspended drops took place under conditions of natural convection. In the steady-state tests with porous spheres, a slight upward stream of ambient gas was superimposed on natural convection to replenish the oxygen consumed in the confined test zone. Although small, this flow may partly account for the somewhat higher values of the evaporation constant (Table IV). Projected drops experienced a varying degree of influence of natural and forced convection in their trajectories. Here again the occasionally higher evaporation constants may be attributable to the added influence of forced convection.

Spalding (*51, 55, 60*) presents, in dimensionless form, data on natural convection for kerosine, gas oil, petrol, and heavy naphtha burning from a 1.5-inch sphere. He suggests the following empirical relation (see Equation 8) for a range of transfer numbers, B, of 0.25 to 3:

$$\frac{\dot{M}}{2\pi r_l \lambda} = 0.45B^{3/4} \sqrt[4]{\frac{g(2r_l)^3}{\nu^2}} \tag{14}$$

Spalding obtained additional information with forced air convection past 0.5-, 0.75-, and 1-inch spheres, with kerosine, petrol, ethyl alcohol, and benzene as fuels. For the range $B = 0.6$ to 5 and Reynolds number (based on sphere diameter and ambient gas conditions) ranging from 800 to 4000 he found the following to apply (see Equations 9 and 10):

$$\frac{\dot{M}}{2\pi r_l \mu} = 0.53B^{3/5} \sqrt{\text{Re}} \tag{15}$$

The data were also plotted in the form $\dot{M}C/2\pi r_l\lambda\ln(1 + B)$ *vs.* Re on logarithmic coordinates and were found to fall slightly below the line predicted by the Frössling equation (Equation 12). Spalding performed a similar study of burning rates for cylinders wetted with kerosine (*57*). On the basis of Equation 15 the mass burning rate of a droplet becomes proportional to the 3/2 power of the droplet radius at high Reynolds numbers. Also, because at high relative velocities the mass burning rate becomes proportional to the square root of the Reynolds number, a dependency on pressure is to be expected.

Goldsmith (*16*) subjected suspended droplets to an upward stream of air. Effective evaporation constants obtained from a plot of the square of the droplet diameter *vs.* time are presented in Table VII. Forced convection produced burning rates as high as 36% above the corresponding natural convection values.

Table VII. Effect of Forced Convection on Burning Rate (16)[a]

Fuel	Air Velocity, Cm./Sec.	Effective Evapn. Constant, Sq. Cm./Sec.	Increase in Evaporation Constant, %
n-Heptane	0	8.4 × 10^3	...
	11.8	10.2	22
	26.9	11.0	32
	34.5	11.4	36
Ethyl alcohol	0	8.6	...
	11.8	9.0	5
	26.9	9.6	12
	39.4	10.7	25
Benzene	0	9.9	...
	11.8	10.4	6
	26.9	11.5	17
	34.5	13.1	33

[a] Air at 1 atm. pressure and room temp.

Kumagai and Isoda (*30*) observed the combustion of suspended *n*-heptane droplets in a vibrating air field above a vertically operated dynamic speaker. Under these conditions they found the same linear relationship between the square of the diameter and time as that observed in the absence of vibration. The evaporation constant was noted as a function of amplitude (range 0 to 1.8 mm.) and of frequency (range 0 to 435 cycles per second). The maximum value of evaporation constant was 15% above that measured in still air. At small amplitudes, as in still air, the flame was oval shaped. With increasing amplitude the flame was disturbed, and the distance between flame zone and liquid surfaces decreased (with sharply increasing burning rate). Recent studies show that high intensity turbulence in the air stream flowing past wetted porous spheres has no effect on the mass burning rate of a droplet (*1*).

FLAME EXTINCTION FROM THE UPSTREAM PORTION OF A DROP IN MOTION. In his studies of the influence of relative air velocity on the combustion of liquid fuel spheres, Spalding (*51, 56*) noted a critical velocity above which flame could not be supported at the upstream portion of the sphere. He observed that the flame blew off and resided solely in the sphere's wake. In tests with kerosine, the air (20° C.) velocity at extinction varied linearly with sphere diameter (range 0.7 to 2.6 cm.), and the ratio $U_{b/2r_l}$ was about 100 seconds^{-1}. A similar result is obtained from the data on flame extinction of burning camphor spheres (*15, 59*). The near proportionality between extinction velocity and diameter was taken as supporting evidence for a theory on flame extinction advanced by Spalding (*59*). More recent experimental work with porous spheres and *n*-butyl alcohol as fuel does not support this relationship (*1*), because it was found that the extinction velocity is proportional to the square root of the drop diameter.

When the flow of air past a burning liquid sphere is increased, the distance of the luminous portion of the flame from the forward stagnation point of the sphere decreases. Spalding (*51*) reports that at flame extinction the flame distance is a constant (0.9 mm.) for kerosine-wetted spheres (0.7 to 2.6 cm. in diameter). Recently the same constant value has been obtained with ethyl- and *n*-butyl alcohol–wetted porous spheres (*1*).

No comprehensive experimental work has been reported yet on the probably important influence of ambient temperature on flame extinction. Spalding (*51, 56*) presents a small amount of data indicating a definite increase of extinction velocity with temperature (5° to 32° C.). In the high temperature tests of Chang (*2, 50*), Gerald (*6, 50*), and Hottel, Williams, and Simpson (*23*), flame extinction was not encountered at the speeds at which their drops were moving.

Increasing the oxygen concentration of the ambient gas has a profound effect in increasing the extinction velocity of wetted spheres (*1*). In the same work, the scale and intensity of turbulence in a gas stream have been found to have a strong influence on the extinction velocity.

Table VIII. Drag Coefficients of Burning Spheres (24)[a]

Air stream Velocity, Meter/Sec.	Air stream Temp., °C.	Fuel	Drag Coeff. Unignited	Drag Coeff. Ignited	Ratio of Drag Coeff. Ignited/Unignited	Reynolds No.[b]
5	200	Gasoline	0.54	0.48	0.89	2,200
8.5	200	Gasoline	0.52	0.40	0.77	3,700
10.2	210	Gasoline	0.54	0.38	0.70	4,200
15.3	207	Gasoline	0.49	0.32	0.65	6,500
18.9	200	Gasoline	0.50	0.32	0.64	8,300
24.3	200	Gasoline	0.49	0.30	0.61	10,600
7.2	225	Kerosine	0.63	0.58	0.92	2,800
11.3	230	Kerosine	0.59	0.55	0.93	4,400
15.3	230	Kerosine	0.61	0.52	0.85	6,300
19.1	230	Kerosine	0.62	0.518	0.84	7,400
23.9	232	Kerosine	0.62	0.513	0.83	9,400

[a] Pressure, 1 atm.
[b] Reynolds No. is based on air-stream conditions and on diameter of sphere, which is taken as 1.61 cm. to allow for fuel film thickness.

DRAG COEFFICIENT OF BURNING DROPS. Drag coefficient of burning drops is an important parameter in the calculation of their trajectories. Khudyakov (*24*) measured the drag coefficient of a metal sphere (1.57 cm. in diameter) wetted with fuel. Under burning conditions in his tests, flame was present only in the wake of the sphere—i.e., the flame extinction velocity was exceeded. The presence of the wake flame accounted for an appreciable decrease in drag coefficient (see Table VIII). Khudyakov measured the pressure in the burning wake and found it to be slightly greater (0.2 to 1 mm. of water) than when there was no combustion. Form drag, which accounts for a large portion of the total drag of the sphere, is reduced when the wake pressure is increased (*60*). No information is available on the effect of drag of a flame totally enveloping a droplet or sphere. Spalding (*57*) in similar work with flame in the wake of kerosine-wetted cylinders found that the ratio of drag with flame to drag without flame decreases from 0.9 to 0.78 when the Reynolds number is increased from 1300 to 5300. He found that the static pressure in the burning wake of rods was approximately equal to the static pressure in the free stream.

Application of Burning-Rate Measurements

Theoretical and experimental considerations of heterogeneous combustion have demonstrated that the rate of burning of a fuel droplet in an oxidizing atmosphere is governed by transport phenomena, whereas chemical rate processes governed by activation energy and concentration of reactants set the limits between which steady-state combustion can occur. Major variations in the burning rate of a fuel droplet can be attained by changes in the physical properties of the system. Special consideration has to be given to multicomponent fuels encountered in some industrial applications because of a wide range of volatilities.

The assumption of steady-state combustion as used in the preceding theoretical development is a good approximation for those fuel droplets which exhibit a short life time so that the average temperature in the interior of the liquid lags sufficiently. For slow burning droplets, on the other hand, the temperature pattern within the droplet may show large variations with time. Therefore, the heat required to vaporize a unit weight of fuel will also be a function of time. But even more important are the chemical phe-

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nomena associated with internal heating, such as thermal cracking and polymerization as well as physical instability of the liquid sphere leading to droplet breakup. The solution of the heat-conduction equation for the radial flow of heat in a spherico-symmetrical system with a moving outer boundary is based on a surface temperature maintained at the boiling point of the liquid (*29*). Such a calculation has been carried out (*23*) for a representative fuel droplet and it was found that the interior of the droplet reaches the boiling point before the droplet has burned completely. This phenomenon may be responsible for the thermal decomposition and polymerization observed during the combustion of certain hydrocarbon fuels containing high-boiling fractions. Such thermal cracking may result in the accumulation of less volatile constituents in the droplet during the combustion process. Also, because the heat flux increases with diminishing droplet diameter, the tendency for decomposition of thermally labile liquids is further enhanced. This subject has received considerable attention by Godsave and the workers at Massachusetts Institute of Technology (*12–14, 50*) who have examined the combustion of multicomponent liquid systems and the residues formed from fuels containing large concentrations of asphaltenes (a black, high molecular weight fraction found in residual fuel oils). During the latter stages of droplet burning the process resembles that of the combustion of a solid fuel such as carbon and powdered coal. Because the flame zone is stabilized near the fuel surface, which is at a relatively high temperature, the combustion rate becomes relatively insensitive to variations in ambient gas temperature (Equation 4) except at very high gas temperatures at which the contribution of radiative heat transfer becomes pronounced. The rate of diffusion of oxygen to the surface of the residue begins to play a dominant part under these conditions.

The complex problem of the formation of solid deposits of carbonaceous residue during the combustion of certain fuels has been the subject of several studies. The conditions prevailing during the combustion of a liquid droplet particularly favor such thermal degradation and polymerization reactions. In addition to heating of the liquid phase during droplet burning, the fuel molecules leaving the liquid surface enter a precombustion zone which is characterized by a high temperature gradient and a very low value of the weight fraction of oxygen near the liquid surface, because the flame zone offers an effective barrier for diffusion of oxygen into this region. (As shown above the detailed analysis, including chemical kinetics, demonstrates that a relatively small amount of oxygen does reach the liquid surface.) The fuel vapor diffusing from the liquid surface may thus undergo a series of endothermic reactions which are the basis for carbon formation with acetylene as an intermediate, according to Porter (*47*). The appearance of polymers in the precombustion zone followed by solid-phase dehydrogenation is favored by Parker and Wolfhard (*45*) as a mechanism of carbon formation.

Some attempt has been made to correlate the combustion characteristics of fuel sprays with the burning rate measurements of single droplets. Although the processes of mass transfer present in the combustion of liquid fuels are fairly well elucidated, the numerous component processes associated with droplet sprays require further investigation. Burning rate measurements for single droplets are always carried out with excess oxygen with little depletion of the oxygen available, a condition which may not prevail in the combustion of spray. In a recent publication the interference effects of one droplet upon another during combustion have been investigated (*49*). These measurements demonstrated that in a symmetrical array of stationary droplets with fixed spacing between their centers, the linear relationship between mass burning rate and droplet radius continues to apply as observed for a single droplet. However, the magnitude of the evaporation constant, ϵ, as a function of distance between droplets exhibited a maximum. This behavior was interpreted to be the result of two opposing factors: the reduction in heat loss as the droplets approach each other and the decrease in available oxygen under these conditions. In addition, consideration must be given to the dynamics of droplet sprays. Neglect of the effects of relative gas velocity, flame extinction, droplet-droplet interaction, and heterogeneous combustion instability (*40, 41*) in a complex aerodynamic system makes Probert's analysis (*48*) of questionable validity when it is applied to the combustion of a fuel cloud in a turbojet combustor (*19, 21*). Additional research is required before the complex processes associated with the burning of a fuel cloud can be analyzed in every detail.

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Nomenclature

A = area of section normal to flow
B = transfer number (see Equation 8)
C = isobaric heat capacity per unit mass, gas
D = diffusion coefficient, gas
E = activation energy
g = acceleration due to gravity
h = enthalpy per unit mass of specified component relative to boiling point of liquid reactant
i = stoichiometric mixture ratio = $(Y_X/Y_F)_{\text{stoich.}}$
K = universal gas constant
L = latent heat of vaporization plus enthalpy of liquid reactant
m_j = mass of component j in vapor phase
$\dot{m}$ = total mass flow rate
$\dot{m}_j$ = mass flow rate of species j in vapor phase
$\dot{M}$ = mass flow rate of vapor leaving liquid surface
Pr = Prandtl number
q = heat of reaction per unit mass of fuel vapor
Q = heat flux
r = radial distance
R = reaction rate
Re = Reynolds number
R_j = rate of production of component j by chemical reaction
Sc = Schmidt number
T = temperature
T_l = boiling point of liquid reactant
T^* = dimensionless temperature = $Ct/(q - L)$
t = relative temperature with respect to T_l—i.e., $t = T - T_l$
U = ambient gas velocity relative to surface
v = flow velocity normal to surface
Y = weight fraction of specified component at any point
y = distance along flat plate
z = weight fraction of specified component generated by chemical reaction in the region from r_l to any point
ρ = density, gas
ρ° = density, liquid
γ = thermal conductivity, gas
μ = viscosity, gas
ν = kinematic viscosity, gas
θ = time
ϵ = evaporation constant

Subscripts

b = flame extinction conditions
c = flame front
j = component j
l = liquid surface
o = outer boundary
F = fuel
X = oxidizer
x = region x
f = region f

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Production and Measurement of Single Drops, Sprays, and Solid Suspensions

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Experimental methods presented in the literature may prove of value in combustion studies of both solid and liquid suspensions. Such suspensions include the common liquid spray. Uniform droplets can be produced by aerosol generators, spinning disks, vibrating capillary tubes, and other techniques. Mechanical, physicochemical, optical, and electrical means are available for determination of droplet size and distribution. The size distribution, aggregation, and electrical properties of suspended particles are discussed as well as their flow and metering characteristics. The study of continuous fuel sprays includes both analytical and experimental procedures. Rayleigh's work on liquid jet breakup is reviewed and its subsequent verification and limitations are shown.

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The experimental investigation of the combustion of sprays is complicated by the many variables involved. Common sprays are composed of a wide range of droplet sizes distributed unevenly in the spray cone. Turbulence of the air and the relative motion of the droplets through the air are poorly defined. The burning of an isolated droplet itself presents a difficult problem, although much progress has been made in this field in the past few years. To study the effect of any single variable on the combustion characteristics of a spray, other variables must be held constant. This paper reviews those fields of effort in which work has been done to simplify the complex physical aspects of this problem.

The literature has been divided into two main headings: (1) production and (2) size measurement of both single particles and sprays (including uniform clouds of droplets and solid suspensions). In many instances a single reference may give important information in each category.

No attempt has been made to include all the literature, as many excellent reference sources are available. Periodic publications (*1A, 3A, 4A, 7A, 8A, 10A*) keep the investigator informed of current literature. Detailed bibliographies are also available (*2A, 6A, 11A, 12A, 15A–18A*).

Several papers give excellent introductions to the problems of spray combustion (*5A, 9A, 13A, 14A, 19A*). Lloyd (*14A*) includes a diagrammatic sketch of the physical and chemical factors influencing combustion. The fuel used, method, and degree of atomization, and the many combustion parameters all affect the final combustion efficiency.

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Production

Single Droplets and Streams of Uniform Droplets. It is comparatively simple to produce drops larger than a few hundred microns. A microburet for producing drops of known size is discussed by Lane (*17E*) and Levvy (*18E*). When such relatively large drops have once been made, their evaporation and combustion may be studied in several different ways. Richardson (*20E*) has conducted experiments on drops falling inside a 110-foot tower and on drops suspended in a wind tunnel. Savic (*21E*), using a vertical wind tunnel, has been able to keep the drop centered in the stream by the clever technique of electroplating the calming screen in its center portion. Wood and Charvonia (*27E*) and Gregory and Calcote (*10E*) have studied the combustion of large droplets dropping vertically through a closed oxidizing medium isolated from atmospheric air. A sliding valve arrangement allowed the drop to enter the chamber.

Bolt, Boyle, and Mirsky (*2E*) discuss and evaluate different techniques of producing droplets. Their work includes photographing drops falling through a vertical furnace. They have successfully suspended drops in a vertical wind tunnel, using a stationary ultrasonic field to center the drop.

The evaporation from large spheres and shapes with subsequent combustion cannot be studied without the use of an artifice. Gohrbandt (*7E*) has investigated the evaporation from large surfaces by emersing a camphor sphere in a hot air stream. Another technique has been used by Ingebo (*13E*) and Wise, Lorell, and Wood (*26E*), who continuously inject the liquid into a porous sphere. The liquid passes to the outer surface of the sphere, where it is evaporated. Spalding (*22E*) allows the liquid to pass upward through a hollow sphere and spill over the outer surface. Excess fuel is collected in a trough at the base. A variation of this method was adopted for forced convection experiments, after it became apparent that fuel was being blown away from the leading surface. A silk sheath covers the entire sphere, while grooves cut in the leading surface increase liquid flow rates to this area.

A large portion of the literature discusses the use of suspended drops on fine filaments. This technique has been used with visual and photographic observation (*5E, 6E, 8E, 9E, 11E, 16E*). Results show the mass rate of change of size due to evaporation to be proportional to the first power of the diameter. Kobayasi (*14E, 15E*) first suspends the droplet on a silica filament and then moves a heated furnace to surround the droplet. Nishiwaki (*19E*) uses a similar experimental device. Instead of a filament to support the drop, Wakil, Uyehara, and Myers (*25E*) use a fine thermocouple.

Droplets ranging from 10 to 300 microns can be made in a rather simple manner. Dimmock (*4E*) discusses the use of a glass capillary tube, to which is attached a small piece of iron. The tube is forced to vibrate in an alternating magnetic field. When 50 cycles are used, the tube will throw off 100 droplets per second so regularly that stroboscopic analysis is possible. A variation of the same method has been used by Vonnegut and Neubauer (*23E*). Compressed air at high velocity strikes the capillary tube to supply the driving force for vibration. In each case the length of the tube, the diameter of the capillary hole, and the amplitude of the oscillations may be controlled to give the desired droplet size.

Vonnegut and Neubauer (*24E*), using liquids of low conductivity, have produced two types of droplet distributions by means of high voltage; 5000 volts direct current produces a uniform stream of droplets of 100 micron diameter at the rate of about 100 per second. A cloud of fine particles which are so uniform in size that Tyndall spectra are apparent, is also produced.

A unique method of producing droplets down to 1-micron radius has been proposed by Blanchard (*1E*). Air bubbles are allowed to break through the surface of a mass of water. The resulting bubble cavity collapses, producing an upward moving jet which disintegrates into several small droplets. Droplets of the same size always rise to the same height above the liquid surface. Droplet size appears to be proportional to the original air bubble size.

Hottel, Williams, and Simpson (*12E*) and Hall and Diederichsen (*11E*) have been able to produce streams of droplets by use of a spinning disk. A small portion of the total number of droplets produced by such a disk can be made to travel in a single trajectory by means of a collimating slit. These droplets are introduced into a furnace for further study.

Spinning Disk Atomization. The spinning disk produces a continuous spray which spreads radially outwards from the periphery of the disk. A major difference of this technique in comparison with pressure atomization of liquids is mentioned by Marshall and Seltzer (*5F*), who give a detailed theory of atomization for both smooth and vaned disks. High velocities are achieved without a pressure increase.

May (*6F*), using a spinning top apparatus, has found that when the smaller satellite drops are removed, and when the fluids used wet the surface of the disk, the diameter of 90% of all drops falls within a band of 5% of the mean. Bolt, Boyle, and Mirsky (*2E*) have used disks ranging from 1.3 to 3.0 inches in diameter, and have shown their results graphically. They also present the results of combustion experiments in which the spinning disk is used as a source of uniform droplets ranging from 70 to 150 microns, depending on disk speed. These droplets are burned in the form of a concentric ring about the disk in the horizontal plane. The analysis of the burning spray is based upon a series of photographs taken vertically downward through the flame. The results indicate that the uniformity of size and velocity of the spray in the flame zone is considerably diminished as burning proceeds.

Adler and Marshall (*1F*) have conducted a comprehensive program to determine the drop-size distribution from seven different types of disks operated at one feed rate and peripheral speed. Results show that disk design has a negligible influence on drop-size distribution. An equation for estimating power requirements of disk atomizers is given. Adler and Marshall give an excellent bibliography covering disk design, drop size distribution, mechanism of atomization, drop-sampling techniques, power requirements, and liquid velocitiy. Friedman, Gluckert, and Marshall (*2F*) present a similar type of study.

Using a rotating cup, Hinze and Melborn (*4F*) have determined the necessary conditions for producing a uniform spray. The centrifugal acceleration must be much greater than that of gravity. Rotation must be free of vibration. The supply of fluid must proceed at a uniform rate. The disk surface must be smooth, particularly if the liquid layer is thin. Three general types of liquid disintegration into droplets are noted. The first is the formation of droplets directly from the main body of liquid. An increase in flow rate or cup velocity changes the mechanism to that of the formation of ligaments, which later break into droplets. Highest values of rotation produce a film of liquid prior to the formation of ligaments.

Tanasawa (*8F*) has found that the use of a flat disk or cup makes little difference in the resulting spray. A sharp edge on the disk gives slightly smaller droplets than a thicker edge. A sawtooth edge gives the smallest sizes.

Pilcher and Rodman (*7F*), using an air-powered turbine at rotational speeds as high as 60,000 r.p.m., have produced droplets as small as 20 microns. They suggest a technique making use of a rotating disk to produce a uniform air-fuel mixture which can be fed into a conventional Bunsen tube for flame investigation.

An equation linking the size of drop produced by a rotating disk is presented by Walton and Prewett (*9F*):

$$d = 3.8 \left(\frac{T}{D\rho}\right)^{1/2} \Big/ w$$

where d = drop diameter, D = disk diameter, w = angular velocity of disk, T = surface tension of liquid, and ρ = density of liquid.

Small satellite droplets, which are produced along with the uniform size larger droplets when ligaments break, can easily be removed. Droplet sizes from 15 microns to 3 mm. have been produced. The proportion and size of satellite droplets increase with increased liquid flow rates until a flow is reached where separation is no longer possible. Liquid viscosity plays a negligible role.

Herring and Marshall (*3F*) have sprayed the droplets into cells containing a fluid in which all droplets are allowed to settle to a common plane. Later investigations of drop distributions indicate that drop size varies with the 0.82-power of disk speed and the 0.85-power of disk diameter.

Pressure Atomization. Pressure atomization consists of forcing a liquid through an orifice. It is by far the most common means of forming sprays. Although a large number of references are available, little progress has been made in the experimental use of sprays to verify basic combustion theory. For example, studies such as those which have determined the rate of evaporation of singly suspended drops cannot be directly correlated to spray systems, because of the motion of such droplets and the lack of an infinite air source. However, the literature gives detailed information concerning the over-all phenomenon of spray combustion.

Hagerty (*8C*) presents an excellent summary of the work on continuous fuel spray conducted at the University of Michigan. Five major problems closely related in the field of spray research include the stability of the liquid phase, drop-size factors, spray distribution, metering characteristics, and the effect of all these on the resulting combustion. Hagerty discusses these factors in relation to theoretical and experimental studies of the process of spray formation.

Giffen and Muraszew (*7C*) have published a very complete text on the atomization of liquid fuels, which includes an excellent bibliography. Among other topics they discuss the mechanism of jet breakup, atomizer and spray characteristics, effect of physical properties on the spray, and experimental techniques.

Problems pertinent to the combustion of sprays are discussed by Gerstein (*5C*). He places special emphasis on the distribution, dynamics, trajectories, and evaporation of droplets, and includes an additional section on drag coefficients. His list of references includes much of the latest work done in the field of spray combustion.

Prior to World War II the majority of experimental work in the field of sprays concerned itself with Diesel engine injection problems. Sauter (*21C*) has suggested that the efficiency of atomization is determined by its fineness and uniformity. De Juhasz (*2C*) has determined the effect of many different variables on the process of spraying. The more important physical factors tested include the pressure drop across the orifice, the viscosity of the liquid, and the density of the air. For the many different nozzles tested, the ratio of orifice length to diameter has little effect. To determine the effect of the density of the air into which the liquid was sprayed, the nozzles were allowed to discharge into an evacuated chamber. Under these conditions good results are still obtained, suggesting little influence of air friction on jet breakup.

Schweitzer (*22C*), using ratios of orifice length to diameter less than 4 to 1, finds the relationship $V = c\sqrt{(2g\Delta P)/\rho}$ for the velocity of the liquid jet, where equation c is a velocity coefficient, ΔP is the pressure drop, and ρ is the specific gravity of the oil being tested. The viscosity plays no role in the liquid jet velocity for low L/D ratios. Poiseuille's formula applied for long orifices.

The rate of depth of penetration of a spray tip into a chamber is found by Gelalles (*4C*) to be a function of the ratio of length to diameter. Using pressures ranging from 2000 to 8000 pounds per square inch and a plain stem ahead of the orifice, maximum penetration rates have been obtained for L/D ratios between 4 and 6. The spray cone angle increases with the ratio of the orifice area to the groove area. Others who have conducted detailed investigations on spray formation include Doble (*3C*), Lee (*9C, 10C*), and Rothrock and Waldron (*20C*).

With the advent of gas turbine and rocket engines has come a major shift in experimental emphasis. The extremely high pressures used in Diesel engines have been reduced greatly. A trend away from the collection of a wealth of empirical data has resulted. In fact, research in seemingly diverse fields is of direct importance to the combustion field. Marshall and his associates at the University of Wisconsin have made large contributions as a result of spray drying investigations. Tate and Marshall (*24C*) have studied the effect of liquid jet tangential velocities on both the atomization and cone angles of sprays. Beneficial results are obtained in both cases by the use of tangential nozzles.

Giffen (*6C*) and Mock and Ganger (*15C*) present the effect of various operating parameters on fuel atomization in sprays. Applications of dimensional analysis to spray-nozzle performance data are discussed by Shafer and Bovey (*23C*).

Perhaps the most significant work in the field of pressure atomization has been in the field of jet instability. The liquid flowing through an orifice forms a jet. The breakup of this jet into the eventual formation of the spray droplets has long presented a challenge. The stability of such jets was studied by Rayleigh (*19C*), who employed the method of small disturbances. The potential energy of the unstable system was determined by considering the capillary force to be of major importance. His theory predicts that the disintegration wave length is a function only of the jet radius, and is independent of other physical properties of the jet or the surrounding air.

Tyler (*26C*) verified the work of Rayleigh. He assumes that the droplets formed by jet breakup are of a volume equal to that of a discontinuous cylinder of the jet of length equal to the wave length of the most rapidly growing disturbance. The studies of both Rayleigh and Tyler are applicable for those liquid jets experiencing little frictional drag from the surrounding medium. However, for high-pressure sprays predicted drop sizes are much too large.

It is now known that a liquid jet under conditions of high surface friction does not immediately break up according to Rayleigh's theory. Rather, according to Castleman (*1C*), the jet first breaks into fine ligaments which later experience Rayleigh breakup. The life of these ligaments is extremely short; thus, their existence could not be experimentally verified until the advent of high-speed photography.

Using a low-velocity jet of one liquid passing into another, Tomotika (*25C*) has studied the case when the viscosity ratio is of prime importance. He predicts that the disintegration wave lengths should be small for viscosity ratios near unity, with increasing wave lengths for ratios approaching either zero or infinity. This theory holds well for the portion of the jet close to the nozzle (*14C*).

Secondary atomization, the breakup of the drops first formed, has been studied by Littaye (*11C*), who assumes a necessary criterion that the drag forces exceed the inertia forces. Ohnesorge (*17C*) makes use of the principles of mechanical similarity by introducing dimensionless coefficients to help explain jet breakup. Above certain well defined numbers, the jet completely atomizes at the nozzle. Lower values indicate the formation of a jet which disintegrates, owing to helical vibrations which later change into Rayleigh vibrations.

Panasenkov (*18C*) has studied the influence of turbulence of the liquid jet on its atomization. With the onset of turbulence the jet becomes shorter and begins to break up. He correlates the drop diameter as a function of the orifice diameter and the Reynolds number. Miesse (*12C, 13C*) has made a careful investigation of the effect of time lag of jet breakup on combustion stability and has correlated the influence of ambient pressure oscillations on the liquid jet.

York, Stubbs, and Tek (*27C*) have developed a theory for the breakup of thin liquid sheets as produced by tangential nozzles. A force balance between the interfacial tension and aerodynamic forces is the basic concept, and the criteria for stability and instability are determined from it. Wave formation at the interface is of major importance in the subsequent breakup.

Two major contributions give an excellent view of the development of spray technology plus detailed summaries of current knowledge. Marshall (*15A*) presents such topics as jet breakup, performance characteristics of atomizers, and drop-size distributions. Miesse (*14C*) traces the theories of jet instability and has performed four series of experiments to verify them.

Mullins has conducted an extensive program to determine the spontaneous ignition of fuels injected into hot air streams. His experimental apparatus is discussed (*16C*).

Airstream Atomization and Impinging Jets. The very powerful effect of high-pressure air as an atomizing agent has been demonstrated by Joyce (*5B*). Lewis and associates

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(*7B*) have found excellent correlation between the measured sizes of drops atomized by high-velocity gas streams with the equations developed by Nukiyama and Tanasawa (*6L*), so long as conditions are held within certain limits. The behavior of sprays of *n*-heptane, benzene, toluene, and other fuels has been studied by Garner and Henny (*3B*) by use of a small air-blast atomizer under reduced pressures. A marked increase in the Sauter mean diameter was obtained for benzene and toluene as compared with *n*-heptane, which parallels their poor performance in gas turbines. Duffie and Marshall (*2B*) give a theoretical analysis of the breakup characteristics of a viscous-jet atomizer and show high-speed photographs of the process.

The use of high-velocity vaporizers has been studied by Comings, Adams, and Shippee (*1B*). The liquid to be vaporized is introduced into a high-velocity, high-temperature air stream at the throat of a Venturi section. The liquid is vaporized in a divergent cone. The vapor condenses to form a smoke composed of very fine particles when this air-vapor stream mixes with the cool ambient air. The shatter of liquid drops in streams of air is discussed by Lane (*6B*).

Heidmann and Humphrey (*4B*) have investigated two impinging jets of water. Their results show that the liquid sheet formed on impingement disintegrates intermittently, forming groups of drops, which appear as waves propagating from the point of impingement. Photographs of spray patterns are presented.

Production of Aerosols. Until now the techniques discussed for producing small particles have been atomization processes. It is possible to condense vapors on nuclei to build droplets of the desired size. Certain of these techniques produce remarkably uniform suspensions of these droplets. The production of particles in this fashion is known as aerosol formation.

A major contribution in this field has been made by La Mer and Sinclair. La Mer and associates (*9D–11D*) discuss the preparation, deposition, and nucleation of aerosols. Particles as large as 40 microns can be obtained by using a slight variation of the standard type of aerosol generator. Nuclei are supplied by the heating of salt to just below red heat and are carried through the generator, where they are intimately mixed with heated vapor and air. The mixture passes downward through a chimney and is allowed to cool. Droplets form around the nuclei. Careful temperature control gives the desired particle size and uniformity.

Sinclair (*13D*) gives a detailed drawing of the aerosol generator. The size of the resulting droplets is a function of the mass of condensable vapor and the number of nuclei. A development of analytical expressions describing the growth of sea salt particles by condensation of atmospheric moisture is presented by Keith and Arons (*8D*). To test the theory, sea water was atomized to give salt particles which were held on a spider web. A steady stream of moist air was allowed to flow over the particle. Growth was measured with a microscope. Ranz and Wong (*9S*) describe their apparatus.

Burgoyne and Cohen (*5D*), using a variation of the La Mer–Sinclair generator, obtain droplets as large as 55 microns. Results show that droplets under 10 microns burn in a fashion similar to a gaseous fuel. Larger drops produce individual diffusion-type flames. Berly, First, and Silverman (*3D*) produce droplets between 0.5 and 3.0 microns by vaporizing a liquid on a heated plate. Browning and Krall (*4D*) use a similar technique. The hot vapor is mixed with cool air to form a uniform suspension which is passed through a Bunsen tube for flame study. Submicron particles give lean limits of flammability similar to those of a gaseous counterpart. Rich limits of the droplet suspensions are higher. Salter (*12D*) describes an apparatus which transforms up to 3 cubic inches per minute of liquid fuels into fog.

Johnstone, Feild, and Tassler (*7D*) have developed a Venturi atomizer to produce dense fogs of liquid drops. This equipment is similar to that used by Comings, Adams, and Shippee (*1B*). Durbin (*6D*) has studied the formation of condensation particles in supercooled hypersonic air flow.

Two excellent publications (*1D*, *2D*) present collections of papers dealing with aerosol generation and measurement.

Solid Suspensions. The category of solid suspensions is split into two sections. The first deals with the preparation and combustion of coal and carbon particles, while the second includes particles and powders of other materials.

The combustion of coal and carbon particles has been extensively studied by Hottel and associates (*5G, 10G, 14G*). Individual particles of coal experience three periods in their combustion—ignition, distillation and combustion of volatile matter, and combustion of the fixed carbon. A discussion of the laws of particle distributions is included (*5G*).

Sherman has studied the burning characteristics of pulverized coal and the radiation from their flames (*11G–13G*). For uniform mixtures of air and coal, the fineness of the coal becomes of more importance as the combustion space is reduced. The type of coal influences the rate of combustion, and high furnace temperatures are conducive to rapid burning.

Solid particles above about 40 microns are easily graded into size fractions by screening. To obtain a uniform suspension of these particles is difficult. Ghosh and Orning (*2G*) have studied the influence of physical factors in igniting pulverized coal by the use of specialized apparatus. A circulatory system in which a fan is fully enclosed assures a uniform mixture. A portion of this mixture is introduced into a heated furnace for measurement of ignition delay. Sonic energy is imposed on the circulating material to keep it from settling to the walls of the enclosing tube. Coal concentration, particle size, and other factors play important roles in determining ignition delay periods. Omori and Orning (*8G*) have found that a pressure increase affects adversely the completeness of combustion.

In coal pulverizers it is desirable to supply heated air to vaporize the water in the coal. However, the temperature of this heated air should not be so high that ignition could occur. Craig (*1G*) in studying this problem discusses the effect of coal concentration of flame velocity. Maximum flame velocity occurs at an air-fuel ratio of about 5 to 1. Godbert and Greenwald (*3G*) report the effect of fineness on the flammability of coal dusts.

The combustion of pulverized coal at both atmospheric and higher pressure has been studied by Hazard and Buckley (*4G*), using three sizes of burners. The coal is pulverized to 93% through a 200-mesh screen. Experiments on burning pulverized coal under pressure have also been described (*7G*).

Hartmann and associates (*24G–28G*) have conducted a great deal of experimental work on the combustion of dust dispersions. Explosions can be caused by particles as large as 700 microns. Many different dusts, including rosins, metal powders, and coal, have been investigated. Zirconium powder is the most explosive. Coal dust explosibility is closely associated with its volatile combustible content. Representative pressure rises as high as 75 pounds per square inch in an enclosed volume are reported. In all cases this maximum pressure is attained at mixture strengths well beyond stoichiometric.

The limits of flammability of dusts have been investigated (*30G, 34G, 35G*). Using various metal powders, Boyle and Llewellyn (*15G*) have found the minimum ignition energy to be proportional to particle size. Browning, Tyler, and Krall (*10*) report a variation of the lean limit as a function of particle size; particles of about 60-micron diameter give the leanest combustible mixtures.

Cassel, Das Gupta, and Guruswamy (*18G*) have found that maximum flame velocity is obtained for the finest suspensions. This would seem to be in agreement with Meek and Dallavalle (*32G*), who report maximum pressure rises for the smallest particle sizes. Griffen, Adams, and Smith (*23G*) treat the burning of individual particles of solid fuel, while Mason and Taylor (*31G*) investigate the explosion of aluminum powders.

Powdered metal flames have been extensively studied at Temple University. Conway and Grosse (*20G*) report the development of a torch using powdered metal as a fuel. A history of past work in this field is included. For successful results powders less than 200-mesh must be used. Branstetter, Lord, and Gerstein (*16G*) have used metal fuels, both powders and wire, in a 2-inch-diameter ram-jet-type combustor.

An apparatus for providing a uniform flow of a mixture of dust and air is shown by Clark and Line (*19G*) in connection with their work on the combustion of boron.

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Burgoyne and Thomas (*17G*) have passed mixture air through an iron-electrode arc prior to passing into a Bunsen tube. The effect of the minute iron oxide particles contained in the stream is to lower the lean limit of flammability of hydrogen. Sanger (*33G*) deals with such topics as the dependency of combustion on pressure, temperature, and the moisture content of powders, and gives a series of equations in support of his hypothesis.

Powders can be prepared from coarser pieces of material by grinding. Work (*20A*) gives an excellent list of references in relation to particle size measurement, grinding, classification, and collection. Schweyer (*36G*) discusses the effect of viscosity of the medium on the rate of grinding in pebble mills.

Measurement

To use particles in combustion experiments, it is often necessary to know their size and distribution. Single drops suspended from silica filaments may easily be measured by photographic means. However, when the drops are small and moving at high velocity, the problem becomes much more difficult.

A general approach to the problem of size determination is given in several papers (*1T–4T, 6T–8T*). Sinclair (*13D*) reviews possible methods of size measurement. He lists microscopic examination (light and electron types), centrifugal separation, thermal precipitation, gravity settling, mass concentration, and various optical methods. Four major headings are suggested by Manson, Ferrié, and Kling (*5T*) under which all measuring equipment may be included: mechanical, physicochemical, optical, and electrical methods. The headings of Manson are followed in this paper as a convenient method of grouping the many different techniques.

Mechanical. ABSOLUTE SLIDE METHOD. It is possible in some cases to collect droplets on slides coated with suitable material. Fuchs and Petrjanoff (*1H*) coat slides with a mixture of Vaseline and light mineral oil. The immersion fluid employed by Herring and Marshall (*3E*) is Stoddard solvent. Water droplets, dyed black with 3% nigrosine dye, can be collected for later investigation. This method is not suitable for collection of drops larger than about 500 microns, because of breaking of the drops upon impact with the liquid surface. Lee (*2H*) first used trays containing glycerol for catching droplets in a settling chamber, but later found a smoked plate to be better. Burgoyne and Cohen (*5D*) used magnesium oxide coatings. A system is described in which spray particles are caught on Plexigum thread for examination (*4T*).

JET IMPACTION. A rapidly moving particle, striking a suitably coated surface, will leave an impression whose size is a function of the original drop diameter. Pilcher (*7S*) illustrates the operation of the jet impactor. The higher the jet velocity, the smaller the particle size which will impinge. An instrument called the cascade impactor consists of a series of these slides. The jet velocity is increased from slide to slide; thus, the cascade is useful in determining droplet size distributions.

May (*5S*) uses a cascade impactor consisting of four slides coated with magnesium oxide. He describes new methods of dealing with volatile drops and analyzing the samples. May (*6S*) has determined that the ratio of true drop size to impression size equals 0.86 for liquid drops larger than 20 microns. The ratio decreases for smaller sizes. The layer of magnesium oxide should be at least as thick as the diameter of the droplets striking the surface. The system is calibrated by means of known size drops thrown from a spinning disk. The magnesium oxide is deposited by moving a burning magnesium ribbon under the glass slide. Reliable results down to particle diameters of 0.25 micron are reported for the cascade impactor (*7S*).

Ranz and Wong (*8S–10S*) have made a detailed investigation of the impaction of dust and smoke particles on surface and body collectors, and have developed a mathematical statement of the problem. They include an outline of the history of jet impaction work.

Pilcher (*7S*) describes the cascade impactor and makes a study of the dynamics of droplets. Stoker (*12S*) uses a surface coating of soot instead of magnesium oxide. He has found the impression diameter to be a function of the Weber number. Gillespie (*2S*) has used a cascade impactor for determining the particle size distribution of hygroscopic aerosols in the micron and submicron range. Brown, Fisher, and Boyer (*1S*) compare the size of the smallest particles revealed by light and dark field illumination with samples obtained from impactors and electric precipitators. Landahl and Herrmann (*3S*) discuss the use of wires, cylinders, and slides as impaction surfaces, while Rubin (*11S*) compares impaction with other techniques.

SEDIMENTATION. "Settling offers a method which is an absolute determination of particle size and concentration which is not dependent on other apparatus or techniques" (*4W*). Kemle, LaJoy, and Kemler (*4T*) outline the theory of settling of particles. Stokes' law holds for particles larger than 1-micron diameter, while Cunningham's factor should be applied for smaller particles. Two major methods of size determination by settling techniques are available. The incremental method begins with a uniform dispersion. Samples at a particular point in the suspension may be withdrawn periodically for weighing. Also, the pressure change at a point is a measure of the distribution curve. The second method relies on cumulative collection on a pan placed in the suspension. Kemle, La Joy, and Kemler (*4T*) give a very complete bibliography on this subject as well as on other methods of size determination.

Bishop (*2W*), investigating the settling of particles in a liquid, reports two types of particles which settle onto the bottom of the container. The first group includes all those particles of sufficient size to settle the entire height of the suspension. Small particles which have settled only from lower portions of the suspension are also collected. A simple relationship enables the separation of these two categories, once the amount collected–time curve is known.

The Central Aerosol Laboratories, Columbia University, have used differential settling techniques to calibrate their more elaborate instrumentation (*1W*, *4W*).

A sensitive balance which records the weight of particles accumulating in an 88-inch fall at various intervals is used to determine the particle-size distribution (*7W*). This apparatus allows one to obtain the final result in an hour using samples of the order of 0.1 gram. A patent (*3W*) describes an apparatus which introduces the particles into a high-velocity air stream at the throat of a Venturi tube. The suspension then passes into a horizontal expanding collecting zone with vertical collecting funnels arranged along its length. The distance which the particles travel into the collecting zone before falling into one or another of the funnels depends on the particle size and the velocity of the air stream. Additional references treat the subject of settling for size determination (*5W*, *6W*, *8W*).

ELUTRIATION. A process in which a column of air is moved vertically upward through a suspension to remove all particles below a certain size is called elutriation. When a sufficient amount of the smallest size range is removed from the suspension, the air velocity is increased to make the next larger separation. Roller (*40*) gives a detailed analysis of this process and has developed practical apparatus to make such separations routine. The use of a tapping hammer and electrical grounding of the apparatus is recommended to keep the particles from clinging to the walls of the vertical tube. Browning, Tyler, and Krall (*10*) describe a similar technique.

Pollard (*30*) found elutriation to be very successful for particles below 40 microns. The air is allowed to run for 30-minute intervals. When the sample remaining in the tube is less than 10% by weight of the previous one, the air flow is increased to remove the next size range. Excessive humidity and rough tube surfaces cause trouble. Tapping loosens the particles which might otherwise adhere to surfaces. Corcoran (*20*) gives a theoretical discussion of the determination of particle size, followed by a brief account of the elutriation process.

CENTRIFUGAL SEPARATION. Theoretical as well as experimental studies have been made on the separation of powder in a cyclone by Nishihara, Kori, and Yoshizumi (*1G*). The inner distributions of velocity are measured, and a method of calculating the separable size of powder is presented.

MOMENTUM MEASUREMENT. Hagerty (*8C*) discusses work conducted at the University of Michigan on determining nozzle spray uniformity by means of mo-

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mentum comparisons at different points within the spray. All equal-sized portions of a perfect spray pattern have the same momentum at an equal distance from the orifice. This assumes that all the particles have the same velocity. Within an inch of the nozzle the assumption of uniform velocity holds.

MASS FLOW MEASUREMENT. The use of collectors for the determination of aerosol mass flow rates is reported. La Mer and Hochberg (*10D*) pass the mixture through a glass wool filter. Burgoyne and Cohen (*5D*) use a similar technique. A discussion of the efficiency of collector screens is given by Berly, First, and Silverman (*3D*).

Physicochemical. FREEZING OF DROPLETS. Taylor and Harmon (*2Q*) have sprayed drops of water into a bath of hexane cooled by dry ice. The drops are frozen and subsequently settle onto shutters, which are later opened. Differential settling theory is used to give drop sizes. Choudhury and Stevens (*1Q*) capture and instantaneously freeze an entire spray in a bath of liquid nitrogen, and later determine size distributions by screening techniques.

DROPLET EVAPORATION. Hardy (*1M*) has deduced the concentration of free water from measurements of humidity of the air after the water had been vaporized.

WAX METHOD. Joyce (*1Z*, *2Z*) has simulated a spray by using molten wax. The solid particles formed on cooling of the spray can be sieved for size-concentration analysis.

THERMAL PRECIPITATION. Sinclair (*13D*, Chap. 8) describes an apparatus developed to test the theory of thermal precipitation. An aerosol particle will move in a temperature gradient from a hot body toward a colder body with a velocity proportional to the temperature gradient.

GAS ADSORPTION. The unimolecular layer of a gas adsorbed on each particle at low temperature may be used for surface area measurements (*4T*).

Optical. PHOTOGRAPHIC. Until the advent of high-speed methods it was impossible to photograph rapidly moving spray particles. Excellent photomicrographs of the breakup of liquid jets, obtained by Lee and Spencer (*10V*), clearly show the formation of ligaments. York and Stubbs (*12V*) have been able to determine both the size distribution and velocity of spray particles. Velocities are determined by taking two exposures on the same film and measuring the displacement of the drops in the interval between exposures. The technique is applicable to sprays in which the drops range between 15 and 500 microns. Additional photographs showing the breakup of sheets of liquid, presented by York, Stubbs, and Tek (*27C*), show that in many cases a hole first appears in the sheet with subsequent rapid breakup.

Graves and Gerstein (*4V*) show a sketch of Ingebo's photographic equipment used for spray analysis. The speed of the drops across the field of view is cancelled by rotating a mirror in the opposite direction. Drop velocities can be calculated knowing the correct speed of the mirror to produce clear images. Kling (*7V*) shows the breakup of liquid injected into a high-velocity air stream. Tate and Marshall (*24C*) have included several photographs of the breakup of spray sheets.

Bolt, Boyle, and Mirsky (*2E*) have reported that for the photography of burning droplets a high-contrast Ortho film is most satisfactory. A circuit to produce two flashes of light with a controlled time interval between flashes of 0.000155 to 0.00138 second is described.

One of the major problems in the photography of a volume of air containing droplets is the lack of an adequate depth of focus. Only those particles contained within a shallow depth present true images. It is difficult to make measurements when the majority of droplets are out of focus. La Mer and Lee (*8V*) have developed a method which places all the drops within a very shallow band. An aerosol stream is forced to pass through an extremely fine slot, so that stream thicknesses of only 0.02 mm. can be formed.

Oil mists traveling at high velocity have been successfully photographed by Deryogen and Vlasenko (*2V*), who have provided a let-up zone in the direction of vision. Engel (*3V*) describes the photography of gas turbine sprays and suggests that a new nozzle should always be tested in the atmosphere prior to installation.

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If two spherical particles are made to touch by moving them with a micromanipulator, the microscopic image shows a distinct overlap. Helml and Schedling (*6V*) have found that the amount of overlap varies from 5% for spheres of 5-micron radius to 15% for 0.5-micron radius.

It is extremely difficult to examine microscopic images of the thousands of droplets required to give an accurate sample. The most common technique used in the automatic examination of particles shown in photographs is the use of a scanning beam of light. If repeated scannings are made, the size distribution may be obtained simply from the number of times the beam is obscured per unit lengths of the beam. Details of this system and variations are given (*1V*, *5V*, *9V*, *11V*).

DIFFRACTION TECHNIQUES. Instead of listing all the individual contributions of the many excellent references, a very cursory examination of diffraction theory and its applications is presented. The detailed theory is complex and cannot be adequately treated here. Similar references have been included under the same subject headings.

Two books (*1K*, *3K*) give an introductory treatment of the theory Meyer (*2K*) presents an extensive bibliography.

A small particle of the order of size of a wave length of light is forced to oscillate at the same frequency as the incident light which strikes it (*6K*, *8K*, *12K*, *14K*, *17K*, *24K*, *25K*). The angular distribution of the intensity and the degree of polarization of the resulting scattered light are a function of the particle size, the index of refraction of the particle, and the wave length of the incident light.

The solutions of Maxwell's equations which hold for this condition were first obtained by Mie in 1908. Particles such as those contained in colloidal suspensions are much smaller than the wave length of light, and Rayleigh scattering is found to hold. The theory reduces to Huygen's principle for particles considerably larger than the wave length of light. Such particles are contained in coarse suspensions and natural fogs. No simplifying assumptions appear for the particle size range about equal to that of the wave length of light. Solution of the resulting equations is simplified by the use of tables of scattering functions (*38K*–*44K*).

The ability of diffraction techniques to determine size is in most cases a direct function of the degree of monodispersity of the suspension being tested. Several alternative techniques are available, dependent on the size of the particles. Some suspensions exhibit higher order Tyndall spectra for incident white light. Size determination is then easily made.

Large droplets scatter light only through a small solid angle in the forward direction; thus adequate instrumentation is of great importance (*9K*, *10K*, *40K*, *41K*). The light transmitted directly through a suspension is an inverse measure of that scattered in all other directions. Beer's transmission equation may then be applicable. Corona effects have been used to advantage for coarse suspensions (*1K*, *15K*, *21K*). Special equipment is available for measuring the angular distribution and polarization of the scattered light (*27K*, *28K*, *30K*). Counting of particles by use of photoelectric equipment is described (*31K*).

For nonuniform suspensions it is sometimes possible to combine scattering theory with differential settling to obtain a size-distribution curve.

Electrical. It has been determined that electrical pulses created by drops touching a probe wire are proportional to the 1.6 power of the particle diameter (*3N*, *4N*). The analyzer described consists of a charged wire, inserted into a moving suspension, connected to electronic circuits which amplify, classify, and count the electrical pulse. The wire interceptor is maintained at a high positive potential.

A flight instrument that uses electric means for obtaining a measure of the droplet-size distribution in above freezing clouds has been devised and given preliminary evaluation in flight (*1N*). An electric charge is placed on the droplets and they are separated aerodynamically according to mass.

Another electrical method involves an analysis of the current voltage characteristics of a parallel plate condenser through which the aerosol is passed continuously (*2N*).

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Sproul and Nakada (*5N*) discuss the effect of moisture and temperature on the operation of Cottrell precipatators.

The change of resistance of a hot wire when struck by a liquid drop has been investigated (*24E*).

Distribution of Sizes. Although special techniques can in some cases produce nearly uniform suspensions, most spray combustion research must be conducted on systems composed of a wide range of droplet sizes. A knowledge of the distribution of particle size is of great importance.

Three widely used distribution equations, discussed by Bevans (*1L*), include the Rosin-Rammler (*7L*) and Nukiyama-Tanasawa (*6L*) equations as well as the log-probability equation. A fourth relationship, the upper-limit equation of Mugele and Evans (*5L*), is also discussed. Hawthorne and Stange also discuss the Rosin-Rammler relationship (*4L, 8L*). An excellent analysis of distributions is given by Dubrow (*3L*), who has studied atomized magnesium powders.

Often bimodal, or even multimodal, distributions are encounted. Dallavalle, Orr, and Blocker (*2L*) discuss procedures for analyzing such distributions.

Particle Shape. Guruswamy and Srinivasan (*1X*) have determined that a rectangular prism approximates the shape of coal particles. Coal particles produced by fracture are generally more angular, thicker, and more elongated than those obtained by crushing. Watson and Cruise (*2X*) suggest parameters for defining the shape of irregular particles.

Flow of Suspended Particles. Small particles suspended in the combustible stream have been used for the study of Bunsen flames. Andersen and Fein (*2P*) use stroboscopically illuminated particle tracks for the determination of normal burning velocities and flame temperatures. Flame studies using similar techniques are reported by Fristrom, Avery, Prescott, and Mattuck (*3P*). Wolfhard and Parker (*10P*) have made temperature measurements of flames containing incandescent particles. The acceleration of flow through a flame front causes particles greater than about 2 microns to lag. Thus, the particles may not follow the flow streamlines. Gilbert, Davis, and Altman (*4P*) discuss the corrections which must be applied to obtain accurate results.

The subject of the movement of particles in a stream of gas arises in connection with pulverized coal, catalytic "fluid cracking," etc. Khudyakov and Chukhanov (*5P*) derive equations and present an experiment using sand particles ranging between 70 and 845 microns. The particles are introduced into a stream of air flowing vertically down through glass tubes of varying diameter.

Miesse (*7P*) treats the velocity variation of a single drop injected into an air stream of increasing velocity. Colloids used in industry involve suspensions of particles with a wide range of size, shape, and surface state. Williams (*9P*) discusses the effect of particle size and shape on such suspensions. Alexander and Coldren (*1P*) have found that transfer coefficients much higher than those for gases must be used in calculating droplet transfer from the suspending air to the duct walls. They believe that this may be due to the higher mass of the particles, which helps them penetrate the boundary layer.

Spilhaus (*8P*) treats the shape of falling drops and the variation of the drag coefficient. Langmuir and Blodgett (*6P*) present a mathematical investigation of water droplet trajectories.

Aggregation of Particles. Sinclair (*9I*) discusses the coagulation in a homogeneous aerosol. For ordinary concentrations of aerosols the coagulation rate is low. Stirred settling of the aerosol produces faster rates. Equations applicable to these processes are given.

A history of various studies and theories of aerosol coagulation is given by Gucker (*4I*). Kivnick and Johnstone (*7I*) treat the subject of coalescence of droplets in a turbulent jet. Aerosol build-up techniques are presented by Fahnoe, Lindroos, and Abelson (*3I*).

The growth of cloud droplets is allied closely to that of aerosol build-up. Howell (*5I*) gives an equation for the growth of such a particle, and the size spectra of both the condensation nuclei and resulting drops formed in a natural cloud. Squires (*10I*) also discusses the growth of cloud drops.

Sound energy may be used as an aid to coagulation of particles. Kiddoo (*6I*) reports that at any given sound intensity there is an optimum frequency for each particle size, which gives the greatest relative motion for particles contained in an aerosol. Similar studies are presented by Danser and Neumann (*2I*) and St. Clair (*8I*). The effect of electrical charge on the aggregation of fine particles suspended in air is given by Dallavalle, Orr, and Hinkle (*1I*)

Metering of Powdered Solids. Powdered solids have been successfully metered by use of a simple converging nozzle. Farbar (*1V*), using a constant air flow for suspending and carrying the particles, has found that the pressure differential across such a nozzle varies linearly over a range of solids to gas flow ratios. Particles ranging between 12 and 208 microns were tested.

Static Electrification of Dust Particles. Kunkel (*1Y*) has made an extensive study of the charge and size distribution of particles ranging from 0.5- to 30-micron radius in dust clouds in air and has investigated both calm and turbulent conditions.

Droplet Internal Circulation. Savic (*2R*) shows that the ignition delay of droplets may be influenced by internal circulation of the fluid contained in the droplet. Very small drops experience no internal circulation. Larger drops have internal circulation build-up, and thus may have shorter ignition delays. McDonald (*1R*) discusses internal circulation as a possible cause of drop breakup and presents a good bibliography. Marshall (*15A*) has obtained excellent photographs showing droplet internal circulation. Such a circulation is set up by the relative motion between the drop and its surroundings.

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Drop-Size Distributions of Fuel Sprays

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Experimental methods for determining the drop-size distribution of fuel sprays are reviewed. The procedures described are of six general types: microscopic examination of drops collected on slides or in cells, freezing of drops in spray followed by sieving, direct photographic methods, optical methods based on the scattering or absorption of light, electronic and radioautographic techniques, and selective impaction. The advantages and disadvantages of each method are pointed out and special attention is given to the importance of representative sampling of the spray. Explicit mathematical expressions for basic drop-size distributions are included. Averages and moments of the length-, surface-, and volume-weighted forms of these distributions are summarized. Principal relations existing among the corresponding arithmetic, geometric, and harmonic means are tabulated.

The experimental determination of drop-size distributions of fuel sprays is important for all studies involving the atomization of liquid fuels. Investigations of the mechanism of atomization, influences of the many factors that determine fineness of the spray, and methods of atomization and nozzle design all require some means for determining the extent to which the liquid is broken up into droplets in preparation for combustion.

A formidable obstacle to research on the combustion of petroleum has been the lack of a simple, feasible, and accurate method for describing the spray in terms of drop size.

Experimental Methods for Determining Drop-Size Distributions

Much ingenious and painstaking work has been done by more than 40 investigators seeking methods for describing fuel sprays in terms of drop-size distribution. In many instances the methods are similar; consequently, the procedures have been divided into six general types, or classes of methods.

Collection of Drops on Slides or in Cells. The method most frequently used consists of collecting a sample of the spray on a glass slide or in a cell containing a special liquid. The droplets are then observed, or photographed, with the aid of a microscope. This general method, which has many variations, is relatively simple, and was used by Kühn (*32*), Sauter (*63*), Lee (*40*), DeJuhasz, Zahn, and Schweitzer (*10*), Woeltjen (*77*), Sass (*62*), Nukiyama and Tanasawa (*52*), Houghton and Radford (*28*), Burdette (*4*), Doble (*12*), Dimmock (*11*), Pigford and Pyle (*56*), Merrington and Richardson (*50*), Pierce (*55*), Limper (*43*), Maxwell (*47*), Lewis, Edwards, Goglia, Rice, and Smith (*42*), Conroy and Johnstone (*7*), Rupe (*61*), and Golitzine (*19*).

The measuring and counting of hundreds of droplets are obviously tedious and time-

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consuming. It is extremely difficult, if not impossible, to sample the spray without discrimination against the smaller sizes which tend to follow the air stream around the collecting device. Discrimination becomes a serious problem for particles smaller than 20 microns in diameter, and almost no drops smaller than 5 microns will deposit on a slide when ordinary sampling methods are used. No satisfactory correction can be made to compensate for this. However, the magnitude of error resulting from discrimination against small droplets during sampling can be minimized by using narrow slides.

Collection of the spray in a cell containing a confining liquid has two advantages over collection on a slide. The drops remain almost perfectly spherical, if the density of the confining liquid is only slightly less than that of the sprayed liquid, and evaporation is prevented. A minimum of about 500 to 1000 drops should be measured and counted, and only a small fraction (about 1%) of the area of the cell or slide should be covered with droplets to reduce the probability of coalescence. The duration of the sampling period is, therefore, extremely important for all methods requiring collection of drops on slides or in cells.

Frozen-Drop and Wax Methods. Holroyd (*26*) proposed that drops should be made to solidify before coming in contact with any solid surface. The rigid drops could then be studied at leisure. He tried atomizing melted beeswax with some success and suggested the use of alloys of low melting point. However, it was Longwell (*44*) who developed the frozen-drop method to a high degree.

Longwell's (*44*) procedure consisted of collecting the fuel spray in a stream of liquid in which the oil drops were immiscible. The stream was allowed to flow far enough so that the drops regained their spherical shape after being deformed by impact. The fluid carrying the droplets was fed into an alcohol bath kept at approximately the temperature of dry ice, which was cold enough to freeze the drops into solid spheres. The drops were sieved, while still cold, to separate them into different size groups. The relative amounts of the various size fractions were determined colorimetrically after the oil had been dissolved in benzene.

Figure 1 shows a cross section of Longwell's drop sampler. The drops fell through the opening of the sampler upon a glass plate over which a mixture of alcohol, water, and glycerol was flowing.

Taylor and Harmon (*72*) designed an instrument for measuring drop-size distribution of water sprays that combined the drop-freezing technique and Stokes' law of separation. The drops were frozen quickly in hexane, cooled to −20° C. with dry ice, and collected on a shutter. They were then allowed to fall, approximately according to Stokes' law, onto a scale pan. The weight on the pan *vs.* time relationship was then used to compute the drop-size distribution.

Choudhury and Stevens (*6*) recently developed a procedure that involved the

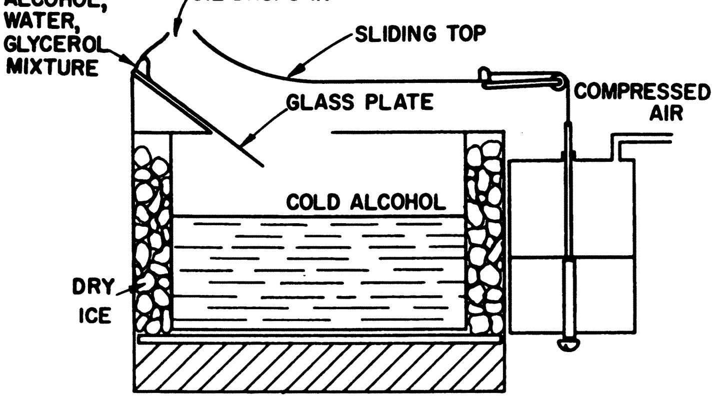

Figure 1. Drop sampler for frozen-drop method (Longwell)

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capture and instantaneous freezing of the entire spray in a bath of liquid nitrogen. The resulting solid spheres were screened on a set of standard test screens inside a walk-in cold room kept at −60° F. (−51.1° C.). The weight of each fraction after being allowed to melt was accurately determined on an analytical balance.

Joyce (*29*) developed the wax method of spray-particle-size measurement to a high degree of perfection during 1942 to 1946. His technique is based upon the observation that paraffin wax, when heated to a suitable temperature level above its melting point, corresponds closely, in the significant characteristics of viscosity and surface tension, with jet fuel.

In making droplet-size tests liquid paraffin wax was atomized to produce a spray that appeared exactly like that produced with jet fuel. The small liquid-wax droplets solidified rapidly in the air, and the entire wax spray was directed into a funnel-like bath of flowing water, from which a sample of the water-borne spray was collected in a suitable vessel.

Figure 2 shows Joyce's funnel for collecting the wax spray. Usually, between 5 and 10 grams of wax droplets were collected, and the sample was passed through a series of six or more graded gauze sieves with nominal size openings of 295, 245, 215, 180, 142, 122, 101, and 75 microns. The smallest particles that passed through all the gauzes were trapped on the surface of a filter paper and examined microscopically. The weight of

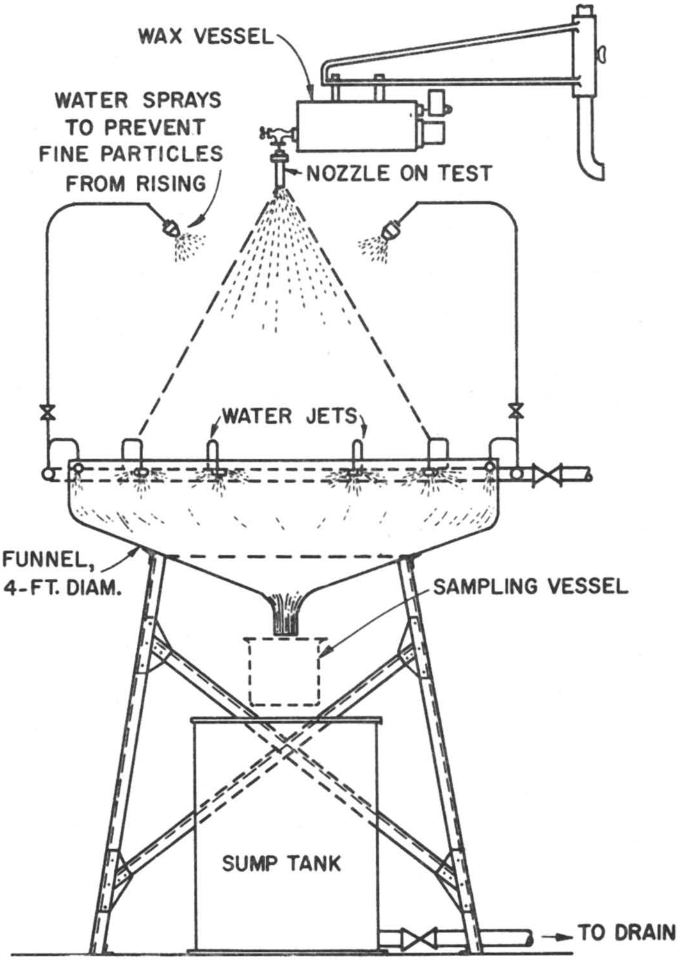

Figure 2. Collecting funnel for wax spray (Joyce)

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wax droplets collected on each gauze and on the filter paper was used to compute the spray distribution by weight in a set of known size groups.

Heath and Radcliffe (*25*), in studying the performance of an air-blast atomizer, used a molten-wax technique similar to that of Joyce. The burner nozzle was heated and the air blast was preheated to the same temperature as the wax, so that the liquid characteristics were not altered at the moment of atomization. Instead of sieving the solidified drops, they collected them on a microscope slide held vertically for a short time in a beaker in which the wax particles were being agitated while dispersed in liquid. The dry slides were photographed and drop-size counts were made microscopically. Difficulty was experienced in measuring small drops that were grouped around a larger neighbor.

Wetzel (*75*) atomized both molten wax and a molten alloy in a Venturi nozzle and established empirical equations for expressing the magnitudes of the effects of operating conditions on the particle-size distribution of the spray. An advantage of molten alloy is that a permanent record of the spray is obtained and large numbers of particles may be sized by physical methods.

The frozen-drop and the wax methods eliminate the tedious and time-consuming operations of microscopic counting of the larger droplets, and sampling errors are less likely because all of a large increment of spray can be collected and handled by employing screens and gravimetric methods of analysis. The chief limitation is that screens are not available to obtain data on particles smaller than 75 microns. Some form of microscopic count or air elutriation procedure is necessary for the smaller droplets.

Photographic Methods. With photographic methods no object is placed in the path of the spray, which might result in unrepresentative sampling of the droplets. Errors resulting from coalescence or evaporation of droplets after sampling are eliminated.

On the other hand, the photographic methods have two definite disadvantages. Droplets smaller than 20 microns cannot be photographed satisfactorily in a fast-moving spray, and the photograph records the spatial rather than the more important temporal distribution of drops. The latter objection can be overcome if drop velocities are known, but data on velocities are not easily obtained. Another serious problem is determination of whether a droplet is in or out of focus when it appears near the boundary of the field of focus.

Generally speaking, the photographic method is too laborious for routine spray analysis, and it is not ideally suited for extensive research on spray analysis. However, it may serve as a primary means of calibrating some more simple, indirect method.

Gilman (*18*), Stubbs and York (*71*), and McCullough and Perkins (*45*) employed the photographic method in various ways.

Figure 3 shows the arrangement of elements used by Stubbs and York (*71*) in photographing sprays. These investigators overcame the objection that the photographic method gives spatial distribution, rather than the more desired temporal distribution, by determining the velocity of each droplet. By taking double exposures of regions in the spray, the velocity was calculated from the distance between images and the time interval between exposures.

The open-shutter method was used and the photolight had a duration of useful illumination of about 1 microsecond. The water cell contained a solution of nigrosin

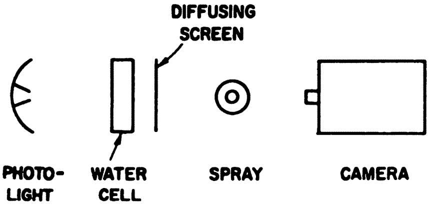

Figure 3. Arrangement of elements for photographing sprays (Stubbs and York)

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dye of the proper concentration to control the intensity of illumination. Drops ranging in size from 15 to 500 microns in diameter could be measured and counted by magnifying them 100 times and projecting them on a ground-glass screen.

This photographic method is laborious, especially if quantitative data for a large number of prints throughout a spray are desired. The effort may be more efficiently expended by obtaining semiquantitative information at a few points to indicate the trends and the general nature of the spray.

McCullough and Perkins (*45*) developed a camera to photograph cloud droplets in their natural suspension in the atmosphere. A magnification of 32× made it possible to distinguish all sizes of droplets greater than 5 microns in diameter. Flight tests conducted in cumulus clouds showed that droplet-size-distribution studies could be made with this camera, if a large number of photographs were taken.

Optical Methods. Optical methods, based on the scattering of light by dispersed droplets, provide a relatively simple and rapid measure of particle size. However, optical techniques give data concerning the average drop size or the predominant size only, and size-distribution data cannot be obtained. Optical methods are more suited to the size analysis of aerosols and extremely fine mists than to the analysis of typical fuel sprays.

The photometer method, based on a measure of the light absorbed by a spray, is recommended as a rapid means of comparing sprays produced under various injection conditions. The effects of variations of spray-nozzle design or of physical properties of the atomized liquid might be investigated by this indirect method of spray analysis.

The measurement of small particle sizes by observation of the scattering of light is based primarily on the electromagnetic theory developed by Gustav Mie in 1908. The complete theory is given in compact form by Stratton (*70*). The pertinent equations are outlined by Sinclair and LaMer (*68*), who employed four types of light-scattering methods based on light transmittance, intensity of scattered light, color of scattered light, and polorization of scattered light. The methods based on transmittance of light and on the color of scattered light appear most promising for studies of fuel sprays.

Optical methods have been devised by Durbin (*14*), Schmidt (*66, 67*), Sauter (*64*), and Mehlig (*49*).

Electronic and Radioautographic Methods. Electronic methods of determining drop-size distribution, based upon the electrostatic charge that may be carried by small particles, are extremely rapid and should be applicable to certain problems of spray analysis. However, additional development of electronic methods will be required to improve the stability of the equipment and the reproducibility of the tests. All electronic methods require calibration against some direct method of determining drop-size distribution. Work in this field has been reported by Guyton (*22*), Gucker and O'Konski (*21*), Geist (*16*), Geist, York, and Brown (*17*), Dodd (*13*), Kunkel and Hansen (*33*), and Daniel and Brackett (*9*).

The size distribution of radioactive compounds was studied by Leary and Fitzgibbon (*38, 39*), who used radioautographic techniques. The method is especially useful for solid particles in the size range of 0.1 to 10 microns and may have limited application, as a research tool only, in the study of fuel sprays.

Cascade-Impactor Method. The cascade-impactor method offers the most promising solution to the problem of determining drop-size distribution for fine sprays containing drops under 100 microns in diameter. This method is based upon the principle that a droplet moving at high velocity will, because of its momentum, impact upon a slide placed in its path. By increasing the velocity of the stream containing the droplets, smaller and smaller sizes will impact. By employing isokinetic sampling, the probability of discrimination against the smaller sizes can be practically eliminated. After calibration, the amount of drops in each size range, collected in each stage of the cascade impactor, can be obtained by gravimetric, chemical, or colorimetric methods, and the tremendous labor and time required for microscopic analysis can be avoided. The theory of impaction, as it occurs in the cascade impactor, provides the basis for designing an instrument to achieve impaction of particles of a specified size range in each stage.

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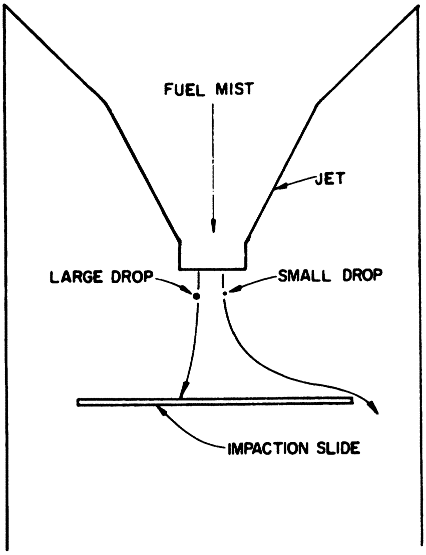

Figure 4. Schematic diagram showing principle of cascade impactor (Pilcher)

May (*48*) was the originator of the cascade impactor. Various designs of impactors are described by Sonkin (*69*), Cadle (*5*), Laskin and associates (*35–37*), Levine and Klineknecht (*41*), Ranz and Wong (*58*), Male (*46*), and Harp and Pilcher (*23*).

Figure 4 shows schematically what happens when a fine spray approaches a glass slide in one of the early stages of a cascade impactor. The large droplets impact on the slide, whereas the small droplets follow the air stream into the next jet, which is smaller in diameter and thereby imparts a higher velocity to the stream of mist. At the higher velocity, smaller sizes of droplets will impact on the slide. In this way the instrument accomplishes a size classification of droplets by increasing the speed and efficiency of impaction as the mist is drawn through the various stages.

Figure 5 is a photograph of the parts of Harp's (*23*) cascade impactor. A special feature of this instrument is that wall loss of droplets in the sampling port and on the jets for the second and third stages is greatly reduced by passing air through the walls of these three parts which are made of porous metal.

Drop-Size Distributions and Their Averages

In the mathematical description of size distribution of sprays, several fundamental types of distributions are discussed frequently in the literature. These distributions arise naturally in the course of investigations involving different experimental techniques. For example, microscopic examination usually leads to drop-size distributions based on the relative number of droplets found in a specified range of drop sizes. Distributions of this type are usually referred to as frequency, or unweighted, drop-size distributions. In the sizing of sprays by sedimentation and by impaction, the volume, or weight, of the droplets found in a specified size range is obtained. For data of this type the volume-weighted, or weight-weighted, size distributions yield convenient representations of the drop sizes. Similarly, experimental techniques involving the extinction of light yield drop-size distributions based on the surface areas of the droplets. Many useful mathematical relations have been developed among the parameters associated with the various types of drop-size distributions. These relations enable the investigator to make transformations from one type of distribution to another, and to compare experimental data.

In practice, the horizontal axis is generally scaled in terms of droplet diameter, so that, for example, a surface-weighted distribution can be transformed to a volume-

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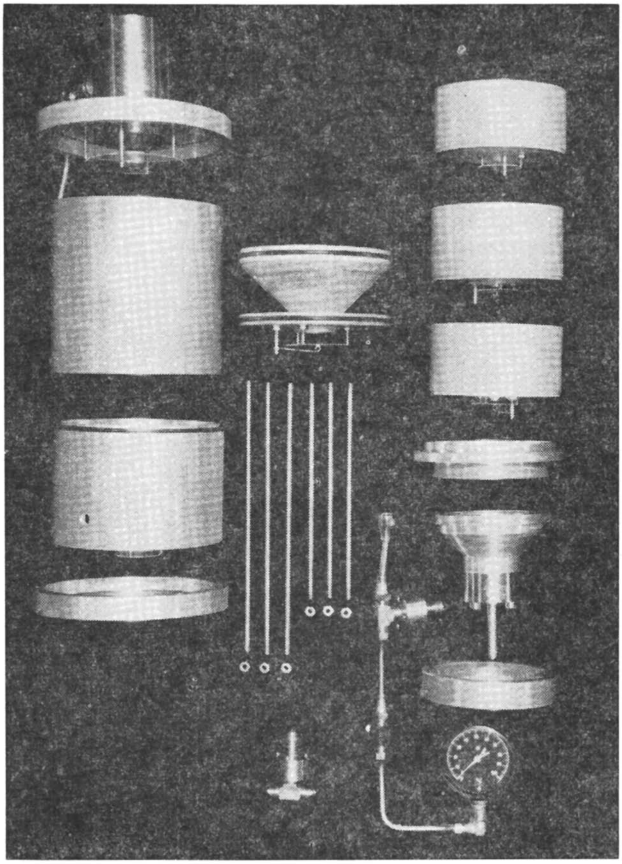

Figure 5. Battelle No. 7 cascade impactor (Harp and Pilcher)

weighted distribution without transforming the unit of measure along the horizontal axis. Thus, the surface-weighted size distribution is written in terms of the surface increments over each size range. Symbolically, if $f_n(t)\,dt$ denotes the number of droplets in the infinitesimal size range, t to $t + dt$, then the corresponding increment of surface is given by

$$dS(t) = \frac{t^2 f_n(t)\,dt}{\int_{-\infty}^{\infty} t^2 f_n(t)\,dt}$$

and the cumulative distribution function of the surface-weighted size distribution is given by

$$S(x) = \int_{-\infty}^{x} dS(t)$$

Similar expressions hold for the length-weighted and volume-weighted size distributions.

Many of the averages and mean droplet diameters in current use may be expressed in terms of the moments of the various weighted size distributions. For example, the first moment of the surface-weighted size distribution is given by the expression

$$\int_{-\infty}^{\infty} t[t^2 f_n(t)\,dt] \Big/ \int_{-\infty}^{\infty} t^2 f_n(t)\,dt$$

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In discrete terms the corresponding expression becomes

$$\sum_{i=1}^{\infty} x_i(x_i^2 f_n(x_i)\Delta x_i) \Big/ \sum_{i=1}^{\infty} x_i^2 f_n(x_i)\Delta x_i$$

where $f_n(x_i)\Delta x_i$ denotes the number of droplets in the finite size range, Δx_i. This moment is often called the Sauter, or volume surface mean diameter. As this example suggests, the moments of the weighted size distributions are expressible in terms of the moments of the unweighted, or frequency, distributions. Thus, the Sauter mean diameter may be regarded as the first moment of the surface-weighted size distribution, or as the ratio between the third and second moments of the unweighted size distribution.

As a consequence of Cauchy's inequality,

$$\left(\sum_i a_i b_i\right)^2 \le \left(\sum_i a_i^2\right)\left(\sum_i b_i^2\right)$$

it follows that the various moments of a drop-size distribution are nondecreasing as the order of the moment increases. Thus, the arithmetic mean of the unweighted size distribution is less than, or equal to, the arithmetic mean of the volume-weighted size distribution. The fact that the volume-surface mean diameter is greater than the arithmetic mean of the unweighted size distribution and is less than the arithmetic mean of the volume-weighted distribution accounts for much of the acceptance of the Sauter mean diameter in droplet statistics.

Because the inequalities among the various mean diameters are usually strengthened when the drop sizes are widely dispersed, the ratio of some higher-order moment to a lower-order moment is often useful as a measure of the dispersion of the drop sizes. For example, the coefficient of variation for the surface-weighted size distribution is a function of the ratio of the weight-weighted mean drop size to the volume-surface mean drop size. The variance of the drop-size distribution may also be expressed in terms of the moments of the unweighted size distribution.

Results of this type have proved of value in experimental investigations involving surface-volume relations. Of particular interest is the fact that specific surface is inversely proportional to the first moment of the surface-weighted size distribution, and this moment, in turn, is equal to the harmonic mean of the volume-weighted size distribution.

Another popular technique for obtaining an average diameter based on surface area consists of calculating the diameter of a hypothetical droplet whose surface area is equal to the total surface area of the spray divided by the total number of droplets in the spray. An average of this type may be expressed as a geometric mean of an appropriate set of distribution moments.

Table I lists some of the basic mathematical expressions of importance in droplet statistics. The expressions are given in terms of an arbitrary p^{th}-weighted size distribution. The specific forms are obtained for various integral values of p. For example, the substitution of $p = 2$ into the equations of Table I yields the cumulative distribution, arithmetic mean, variance, geometric mean, and harmonic mean of the surface-weighted size distribution. Analogous expressions valid for frequencies or mass distributions are obtained by setting p equal to 0 or 3, respectively.

In contrast to the large variety of averages and measures of dispersion prevalent in the literature, the number of basic distributions which have proved useful is relatively small. In droplet statistics, the best known distributions include the normal, log-normal, Rosin-Rammler, and Nukiyama-Tanasawa distributions. The normal distribution often gives a satisfactory representation where the droplets are produced by condensation, precipitation, or by chemical processes. The log-normal and Nukiyama-Tanasawa distributions often yield adequate descriptions of the drop-size distributions of sprays produced by atomization of liquids in air. The Rosin-Rammler distribution has been successfully applied to size distribution resulting from grinding, and may sometimes be fitted to data that are too skewed to be fitted with a log-normal distribution.

Table I. Mathematical Expressions of Importance in Droplet Statistics

Cumulated p^{th}-weighted size distribution

$$F_p(x_k) = \frac{\sum_{i=1}^{k} x_i^p f_n(x_i)\,\Delta x_i}{\sum_{i=1}^{\infty} x_i^p f_n(x_i)\,\Delta x_i}$$

Arithmetic mean of p^{th}-weighted size distribution

$$\bar{x}_p = \frac{\sum_{i=1}^{\infty} x_i(x_i^p f_n(x_i)\,\Delta x_i)}{\sum_{i=1}^{\infty} x_i^p f_n(x_i)\,\Delta x_i}$$

Variance of p^{th}-weighted size distribution

$$s_p^2 = \frac{\sum_{i=1}^{\infty} (x_i - \bar{x}_p)^2 x_i^p f_n(x_i)\,\Delta x_i}{\sum_{i=1}^{\infty} x_i^p f_n(x_i)\,\Delta x_i}$$

Geometric mean of p^{th}-weighted size distribution

$$\bar{x}'_p = \left[\prod_{i=1}^{\infty} x_i^{\alpha x_i^p f_n(x_i)\Delta x_i}\right]^{1/\sum_{i=1}^{\infty} \alpha x_i^p f_n(x_i)\Delta x_i}$$

Harmonic mean of p^{th}-weighted size distribution

$$\frac{\sum_{i=1}^{\infty} x_i^p f_n(x_i)\,\Delta x_i}{\sum_{i=1}^{\infty} x_i^{p-1} f_n(x_i)\,\Delta x_i}$$

Table II shows the mathematical forms of the normal, log-normal, Rosin-Rammler, and Nukiyama-Tanasawa distributions for an arbitrary p^{th}-weighted size distribution. As in Table I, the formulas yield the surface increment in the size interval, t to $t + dt$, for $p = 2$; number or volume increments are obtained by setting p equal to 0 or 3, respectively. In these expressions b and n are constants, and α denotes an appropriate shape factor.

Table II. Size Distributions of Importance in Droplet Statistics

I. p^{th}-weighted normal size distribution

$$f_p(t) = \frac{1}{\sqrt{2\pi}\,s_p} \exp\left[\frac{-(t - \bar{x}_p)^2}{2s_p^2}\right], \qquad -\infty < t < \infty$$

II. p^{th}-weighted log-normal size distribution

$$f_p(t) = \frac{1}{t\sqrt{2\pi}\,s_{\log t}} \exp\left[\frac{-(\log t - \log \bar{x}'_p)^2}{2(s_{\log t})^2}\right], \qquad t > 0$$

III. p^{th}-weighted Rosin-Rammler size distribution

$$f_p(t) = anbt^{n-1+p}e^{-bt^n}, \qquad t > 0$$

IV. p^{th}-weighted Nikiyama-Tanasawa size distribution

$$f_p(t) = \frac{ab^3}{2!}\,t^{p+2}e^{-bt}, \qquad t > 0$$

Any nonnegative function which has a finite integral over the range of drop sizes may serve as a size-distribution function. However, to form a valid basis for statistical inferences, the distribution of each parameter involved in the chosen distribution must be known. Because the distributions of the parameters often present overwhelming mathematical difficulties, considerable care must be exercised in using various curve-fitting techniques which introduce new parameters into the distribution.

The field of droplet statistics involves a strong mutual dependence between the experimental techniques which are used to obtain the drop-size data and the mathematical formalism required to interpret and summarize the data. Special experimental techniques may lead to drop-size distributions, averages, and measures of dispersion that are appropriate to no other technique. Any attempt to restrict all techniques to the use of certain prescribed distributions together with certain mean diameters appears doomed. At present, only general outlines of the mathematical criteria appropriate to all techniques are discernible. These criteria merely prescribe that the parameters appropriate to drop-size analysis should have known distributions, and that the various measures of dispersion and mean diameters should be expressible as functions of the moments of the parent drop-size distribution.

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Flame Propagation in Premixed Gases

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The study of combustion has, over the years, produced a great mass of information on the behavior of flames. These observations have been studied with the purpose of culling whatever generalizations are available. The following fundamental features of flame propagation are discussed: flame structure, burning velocity, flame stability, and quenching. Both laminar and turbulent flows are considered. Only the case of homogeneous fuel-air mixtures is treated. An attempt has been made to include enough descriptive material to give the reader less familiar with the field an up-to-date view of the significance of the data in the literature, without going into detail on theoretical questions.

The structure of a laminar flame must be discussed before other features of flame propagation can be appreciated. These flames are those that exist in laminar—i.e., streamline flow—in which adjacent layers of the flowing gas do not interfere with one another except on the molecular scale (viscosity). The flame itself is the zone of intense chemical reaction, generally luminous, that separates the cold fresh gas from the hot exhaust products.

The flame is not, however, a discontinuity. There are definite gradients of temperature and composition because of conduction of heat and diffusion of reaction products into the fresh gas. The temperature gradients have been studied by three techniques: direct measurement with very fine thermocouples (*24*, *25*, *43*); refraction of a narrow slit of light (*11*, *16*); and tracing the path of a stroboscopically lighted dust particle and computing temperature from its direction and velocity (*1*, *27*).

Figure 1 shows a typical temperature traverse for a lean propane-air flame burning at atmospheric pressure (*24*). From about 0.2 to 0.04 cm. upstream of the luminous zone, the fresh gas is heated mainly by conduction, as shown by the fact that the curve is convex toward the distance axis; this region is therefore the preheat zone. At about 0.04 cm. ahead of the luminous zone, the curve goes through an inflection and is thereafter concave to the distance axis up to the end of the luminous zone. Therefore, each element of gas is in this region a heat source, the temperature rising because of chemical reaction. This particular flame is about 0.23 cm. thick. The presence of a preheat and a reaction zone (which includes the luminous zone) is a general feature of laminar flames, but the actual flame thickness varies depending on the fuel and its concentration, the pressure, and the mixture temperature. Measurements of flame thickness in the literature refer almost without exception to the luminous zone, so these thicknesses are only lower bounds.

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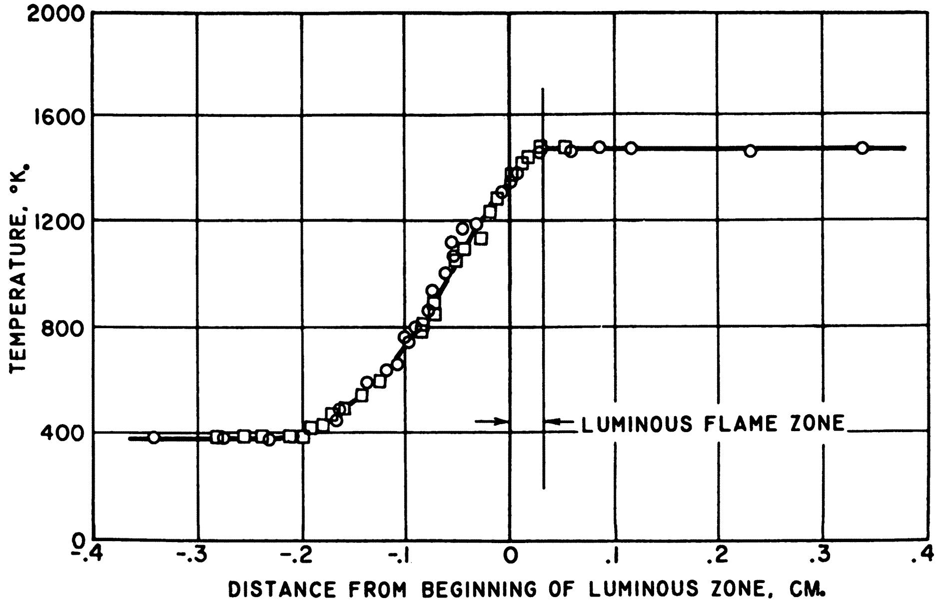

Figure 1. Temperature profile of a lean propane-air flame at atmospheric pressure (*24*)

Laminar Burning Velocity

Measurement of Laminar Burning Velocity. The structure of a flame in laminar flow shows that it is a rapid, self-sustaining chemical reaction, taking place in a discrete and rather narrow region. Thus it is a wave in the gas, the speed of which may be measured. The velocity at which fresh gas flows through a stationary combustion wave in a direction normal to its surface is defined as the laminar burning velocity. The normal direction is specified in order to make burning velocity independent of the actual shape of the flame.

The description of laminar flame structure shows that the burning velocity will be a complex function of both the rate of the initiation process in the preheat zone and the rate of the chemical process in the reaction zone. In the literature, burning velocity is sometimes discussed as if it were purely a chemical phenomenon, but this cannot be the case; to date, the only way to get information on the chemical process alone is with the aid of one of the flame-propagation theories that makes assumptions about events in the preheat zone.

The flame adopts a shape that depends on the flow field in which it finds itself (*3*, *29*, *31*, *33*). For example, a flame atop a Bunsen burner through which there is fully-developed laminar flow, with a parabolic velocity profile, has roughly the shape of a cone with a rounded tip. In view of the many flame shapes that appear in different experimental arrangements and the various photographic and visual means that have been used to locate the flame, it is not surprising that burning velocities do not always agree (*53*). There has been much debate on the best method of measurement. Ideally, one would like to stabilize a flame in a flow having a perfectly flat velocity profile, so that the flame is simply a disk; in that case, the burning velocity is

$$\text{Burning velocity} = \frac{\text{volume rate of flow}}{\text{area of flame}} \tag{1}$$

where the flame area comes from a simple measurement of flame diameter. This has been done in two relatively new methods (*2*, *9*, *20*, *21*). If the flame is not flat, Equation 1 still holds, but it is then necessary to use care in choosing the means of locating the flame; one must find a surface that has the shape of the flame, yet is in the unburned gas.

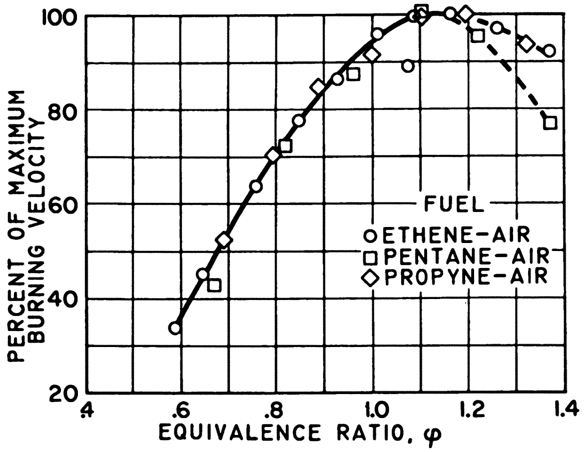

Figure 2. Change in relative burning velocity with equivalence ratio at 25° C. and 1 atmosphere (67)

Thus, the beginning of the luminous zone cannot be correct, because the mixture has undergone great changes before it reaches that point. Schlieren photography yields a flame surface with a temperature close to that of the unburned gas, so it is a desirable method of observation (*1*, *10*, *37*, *43*, *50*).

Effects of Variables on Laminar Burning Velocity. Burning velocity has not yet been made an absolute measurement, as various techniques give different results. However, any one method, carefully used, shows up trends, and it is the trends that are discussed.

CHEMICAL VARIABLES. As the fuel concentration is increased from the lean limit of flammability, burning velocity also increases. It reaches a maximum at an equivalence ratio φ (fuel-air ratio divided by stoichiometric fuel-air ratio) that generally lies between 1.0 and 1.3. That is, the maximum burning velocity $U_{L,\text{ max.}}$ most often

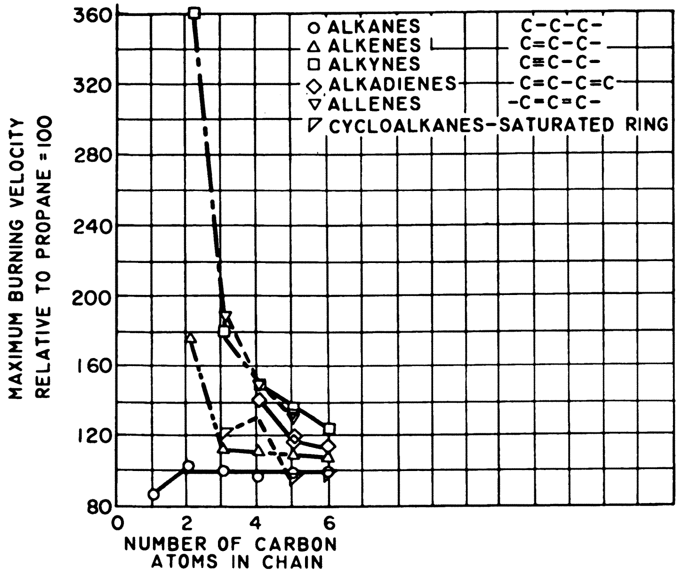

Figure 3. Effect of chain length and saturation on relative burning velocities of straight-chain (or nonsubstituted ring) hydrocarbons at 25° C. and 1 atmosphere (30, 32, 48)

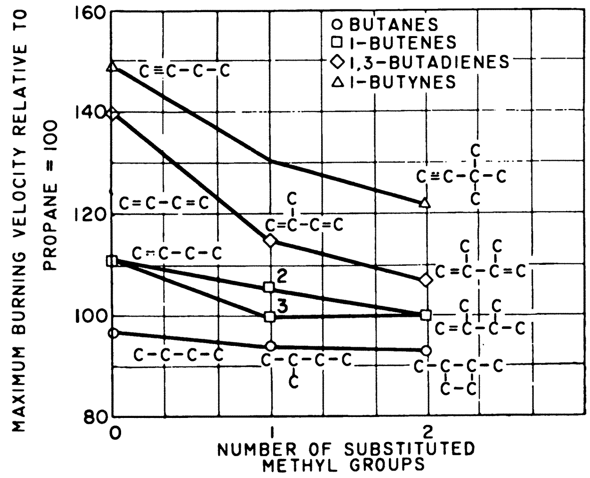

Figure 4. Effect of methyl substitution on relative burning velocities of four-carbon-atom, straight-chain hydrocarbons (30)

occurs for hydrocarbons in slightly rich mixtures. Figure 2 illustrates this behavior (*67*). The measurements do not extend very far to the rich side because the flame shapes become irregular (*28*, *67*). The burning velocity near the lean flammability limit (φ = 0.5 to 0.6 for most hydrocarbons) is one-fourth to one-third of $U_{L,\max}$ (*21*, *67*). Figure 2 shows that the percentage change in burning velocity with equivalence ratio is the same for all three fuels for $\varphi < 1$, even though different hydrocarbon types are represented.

Figures 3 to 5 show some effects of hydrocarbon structure on maximum burning velocity (*30*, *32*, *48*, *72*). Figure 3 deals with straight-chain alkanes, alkenes, alkynes, alkadienes, and allenes; Figure 4 shows the effects of methyl substitution in four-carbon-atom alkane, alkene, alkyne, and alkadiene molecules. In general, the burning velocity decreases with increased chain length or methyl substitution, except for the alkanes,

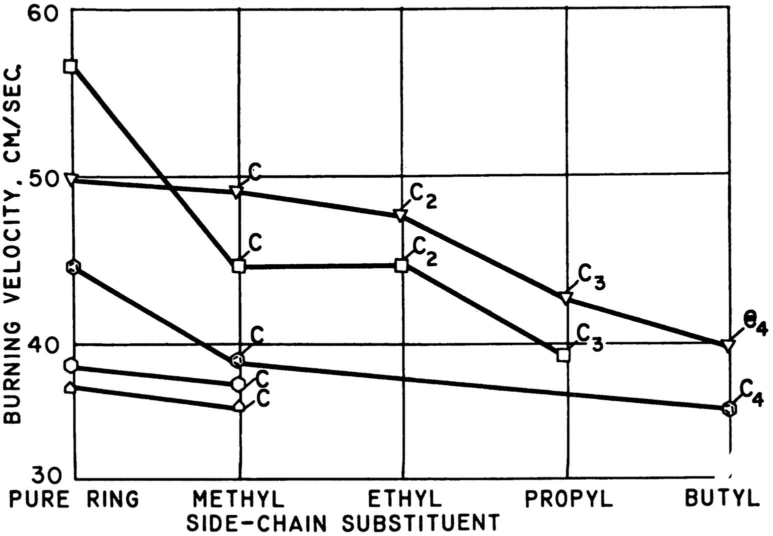

Figure 5. Effects of ring size and substitution on burning velocities of cyclic hydrocarbons (72)

which are insensitive to either. Unsaturation raises the burning velocity in the order alkanes < alkenes < alkadienes (isolated $\simeq$ conjugated < accumulated double bonds) < alkynes. Figure 5 shows the effects of the size and type of ring and of alkyl side chains on the burning velocities of cyclic hydrocarbons. The small saturated rings, cyclopropane and cyclobutane, have burning velocities considerably higher than the corresponding alkanes. Side chains decrease the burning velocity.

The effects of hydrocarbon structure on maximum burning velocity have been correlated empirically (*39*). Each type of C—H bond was considered to make a separate contribution, as shown by the following expression:

$$U_{L,\,\mathrm{max.}} = N_A K_A + N_B K_B + N_C K_C + \cdots \qquad (2)$$

where N_A, N_B, N_C, N_D, N_E, N_F, N_G, and N_H are the numbers of methane, primary, secondary, tertiary, alkene, alkyne, cyclohexyl, and aromatic C—H bonds, respectively, per unit volume of mixture: K_A, K_B, K_C, etc., are the burning velocity coefficients of these bonds. Empirical K values derived from the maximum burning velocities for 34 hydrocarbons predicted $U_{L,\,\mathrm{max.}}$ with an average deviation of 1.9%. These coefficients, modified to give an arbitrary reference burning velocity of 100 for propane, are given in Table I. $U_{L,\,\mathrm{max.}}$ for all hydrocarbons except acetylene, in air at 25° C. and 1 atmosphere, falls in the range 30 to 80 cm. per second; $U_{L,\,\mathrm{max.}}$ for acetylene is about 140 cm. per second.

Table I. Empirical Coefficients for Calculating $U_{L,\mathrm{max.}}$ from Hydrocarbon Structure (39)

Type of C—H Bond	Coefficient[a], Cm./(Sec.)(Bond/Cm.^{3})
Methane	$K_A = 90 \times 10^{-19}$
Primary	$K_B = 109$
Secondary	$K_C = 122$
Tertiary	$K_D = 116$
Cyclohexyl	$K_G = 129$
Alkene	$K_E = 207$
Aromatic	$K_H = 216$
Alkyne	$K_F = 574$

[a] Relative to propane = 100.

It has long been hoped that proper additives or fuel blends would exert synergistic effects on the burning velocity of the base fuel. However, no striking changes are observed with hydrocarbons, although small amounts of water or other hydrogen carriers greatly raise the burning velocity of dry carbon monoxide (*22, 50, 57*). Additives chosen on the basis of their easy oxidation changed the burning velocity of city gas-air mixtures in the same way as dilution with excess fuel would (*46*). Later work by Leason did show some binary mixtures in which the burning velocity was greater than that of either component, but the effects were small (*47*). Antiknock agents might be expected to retard the flame, but no such effect is found in constant-pressure combustion (*68*); on the contrary, at temperatures above 300° C. *n*-butane is partly oxidized and this lowers the burning velocity, while tetraethyllead suppresses the oxidation.

On the other hand, very large increases in burning velocity are obtained if the molar ratio $\psi = O_2/(O_2 + N_2)$ is raised. Figure 6 shows typical curves for propane (*19*).

PHYSICAL VARIABLES. Currently, the pressure dependence of burning velocity is in dispute. Most workers find that $U_L \propto p^{-n}$, where n is between 0.1 and 0.5. Recent work at the U. S. Bureau of Mines indicates that the exponent on the pressure is actually a function of the burning velocity (*49, 58*), an observation that may clarify the situation. Figure 7 is a plot of the exponent, n, in the empirical equation

$$\frac{U_a}{U_b} = \left(\frac{P_a}{P_b}\right)^n \qquad (3)$$

where U_a is the burning velocity at a reference pressure P_a, and U_b is that at a different pressure, P_b. Thus, in mixtures with a reference burning velocity U_a below 50 cm. per second, U_L increases with decreasing pressure; in those with U_a from 50 to 100 cm. per second, the pressure dependence is nearly zero; and in those with U_a from 100 cm. per second upward, U_L decreases with decreasing pressure.

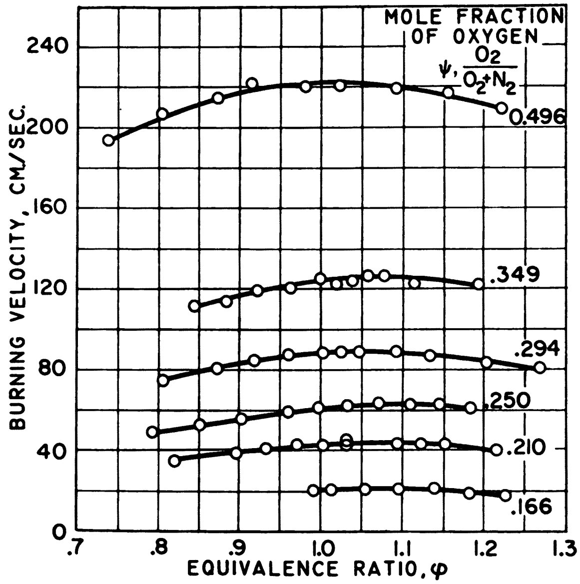

Figure 6. Burning velocity as function of equivalence ratio and oxygen concentration for propane-oxygen-nitrogen mixtures at 311° K., measured by schlieren total-area burner method (*19*)

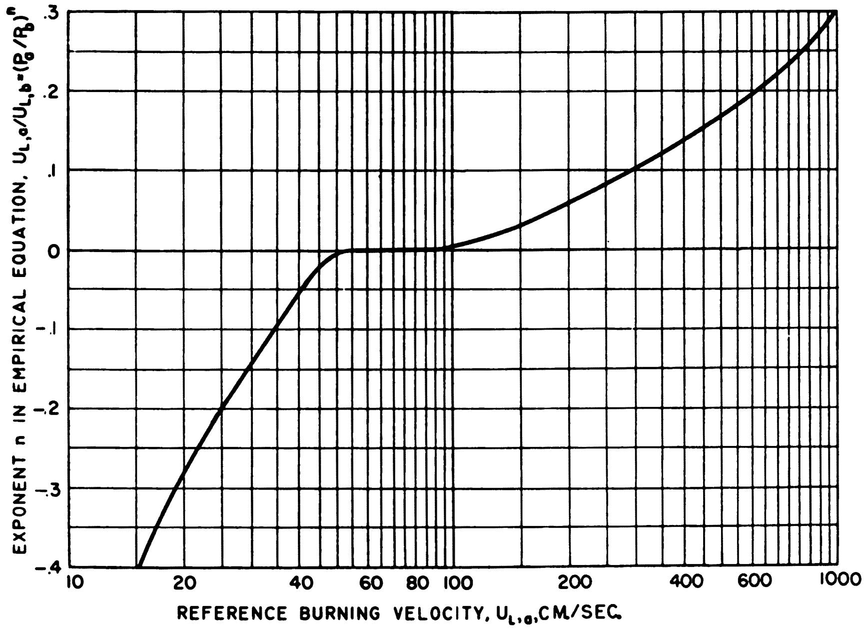

Figure 7. Relation of burning velocity to its pressure dependence (*56*)

The initial temperature of the fresh gas has a considerable effect on the burning velocity. Figure 8 shows the effects for methane-, propane-, and ethene-air mixtures, relative to an arbitrary value of 100 at 25° C. (*18*). It is generally possible to fit such data by an equation of the form

$$U_{L,\,\mathrm{rel.}} = B + CT_0^b \tag{4}$$

where $U_{L,\,\mathrm{rel.}}$ is the maximum burning velocity relative to 100 at 25° C., T_0 is the temperature in ° K., and B, C, and b are empirical constants. The value of b lies between 1.4 and 2.1 and depends on both the fuel and the temperature range covered. The following equation holds for propane-air from 200° to 615° K. (*18*):

$$U_{L,\,\mathrm{rel.}} = 25 + 0.00085T_0^2 \tag{5}$$

Propane is a typical hydrocarbon, so Equation 5 should hold reasonably well for most paraffinic fuels. Another type of correlation involves the computed adiabatic equilibrium partial pressure of hydrogen atoms p_{H}. The following relations hold for initial temperatures from 200° to 615° K. for methane-, propane-, and ethene-air mixtures, respectively (*18*):

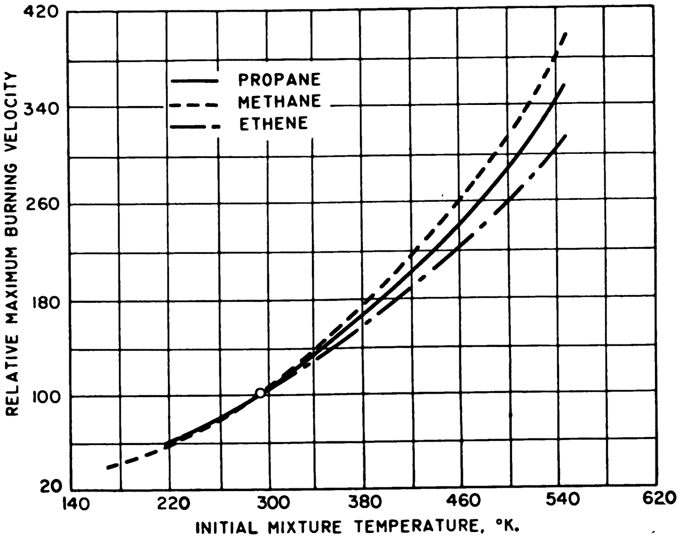

Figure 8. Percentage change in maximum burning velocity with initial mixture temperature, relative to 100% at 25° C. (*18*)

$$U_{L,\,\mathrm{rel.}} = 2.91 \times 10^5 p_{\mathrm{H}} - 50 \tag{6}$$

$$U_{L,\,\mathrm{rel.}} = 2.89 \times 10^5 p_{\mathrm{H}} - 75 \tag{7}$$

$$U_{L,\,\mathrm{rel.}} = 1.33 \times 10^5 p_{\mathrm{H}} - 97 \tag{8}$$

Turbulent Flames

Structure of Turbulent Flames. The great technical importance of turbulent burning lies in the fact that the turbulent flame can consume fuel-air mixture at a faster rate than the laminar flame.

If the unburned gas is in a condition of turbulent flow, the flame no longer appears as a well-defined stationary wave in the gas, as it does in laminar streams. A turbulent Bunsen flame, for instance, appears to the eye or in a time-exposed photograph as a brush-like region of indefinite extent, quite thin near the base and becoming wider toward the top (Figure 9). In short, a turbulent flame has a very complicated structure compared to a laminar flame and does not provide the observer with a ready frame of reference for the measurement of burning velocity. The reason is of course the turbulent fluctuations of velocity superimposed on the main flow.

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The basic problem in turbulent flames is thus to determine the structure of the flame. It is unfortunate, in view of the great technical importance of turbulent burning, that this has not yet been done. There are two schools of thought on the subject:

The classical view is that a turbulent flame is equivalent to a distorted and wrinkled laminar flame. The turbulent flame brush is thus supposed to be an integrated picture of a rapidly fluctuating surface, and instantaneous schlieren pictures seem to support this interpretation (*50*). Grumer, however, has shown that schlieren snapshots of turbulent hot gas issuing from a Bunsen burner look very much like the flame pictures (*34*); the implication is that one sees, not the instantaneous flame surface, but the boundary of the hot gas.

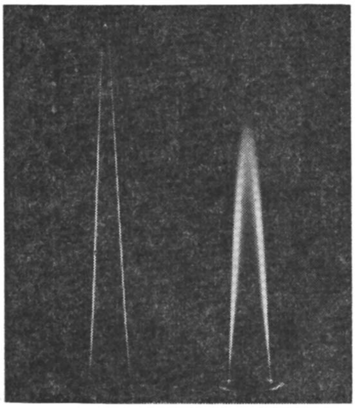

Figure 9. Comparison of direct photographs of a laminar and turbulent flame at the same flow rate, fuel-air ratio, and burner size

The more recent view, adopted by Summerfield and his coworkers, is that the turbulent flame brush is a thickened or extended reaction zone (*70*). The evidence for this idea, like that for the wrinkled flame, must still be considered inconclusive.

Of course, one might combine these two concepts and maintain that some flames are wrinkled and some thickened, depending on the nature of the flow, or that both features may be included.

The point is that no unambiguous turbulent burning velocity can be measured at present. However, it is perfectly possible to determine burning rates with reference to arbitrarily chosen surfaces in time-exposed photographs; these rates must serve at present to characterize turbulent flames.

Characterization of Turbulent Flames. TURBULENT BURNING VELOCITY. Most workers have followed the lines laid down by Bollinger and Williams (*8*) who assumed the fluctuating-flame model and measured "turbulent burning velocities," U_T, with respect to a flame surface midway between the inner and outer boundaries of the flame brush. A better defined and more reproducible surface is that of maximum light intensity, found by taking densitometer traces across the time-exposed image of a turbulent Bunsen flame (*42*). References to several other methods are given in the Bibliography. The maximum burning velocity of the laminar flames is 30 to 80 cm. per second for all hydrocarbons except acetylene. However, even though turbulent flames consume fuel-air mixture faster than laminar flames, not all methods of measurement yield a turbulent burning velocity such that $U_T/U_L > 1$. For the most part, measurements on turbulent Bunsen flames do give $U_T/U_L > 1$. The trends of U_T/U_L with chemical and physical variables are more important than the absolute magnitudes of the ratio.

CHEMICAL VARIABLES. In general, turbulent burning velocity rises to a maximum rich of stoichiometric, and then declines, in a manner similar to that of laminar flames. Figure 10 shows the typical behavior (*8*). The maximum does not shift with changing Reynolds' number; some data do show a slight shift to richer mixtures at higher turbulence levels (*78*).

Turbulent burning velocities of various mixtures, as measured from Bunsen flames, are directly proportional to the laminar burning velocities of the same mixtures. For example, the following equation applies to propane, ethene, and acetylene, over the Reynolds' number range 3000 to 40,000 (*8*):

$$U_T = U_L(0.18 d^{0.26} \mathrm{Re}^{0.24}) \tag{9}$$

where d is the burner tube diameter and Re the Reynolds' number. Thus, one may expect U_T to change with molecular structure in the same way as U_L.

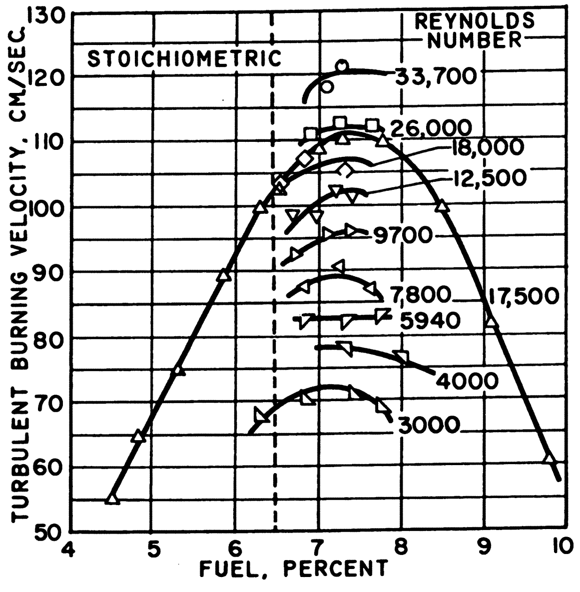

Figure 10. Effect of fuel concentration on turbulent burning velocity of ethene-air mixtures at various Reynolds' numbers. Constant density and viscosity; 3/8-inch burner (8)

PHYSICAL VARIABLES. There has not yet been any adequate study of the effects of pressure, so only changes in temperature and in the nature of the turbulent flow can be considered. The small amount of data available shows that turbulent burning velocity changes with temperature in very nearly the same way as laminar burning velocity. For instance, the values of Heiligenstaedt (*12*) for coke oven gas-air mixtures, over the range 10° to 400° C., can be correlated within 10% by the Reynolds number of the flow when plotted as U_T/U_L. Similarly, Delbourg (*12*) found for town gas-air flames

$$\frac{U_T}{U_L} \propto \frac{T_0^{1.65}}{T^{1.74}} = T_0^{-0.09} \tag{10}$$

which indicates a very low order of dependence on initial mixture temperature.

Inasmuch as the trends in turbulent burning velocity with fuel concentration and type and with initial temperature parallel those shown by laminar flames, it is clear that the differences between turbulent and laminar flames originate in the nature of turbulent flow. It is, therefore, not surprising that the Reynolds' number, which is a hydrodynamic similarity parameter, has proved useful in correlating turbulent flame data.

However, it is not yet proved that Reynolds' number is of general value. Several workers have studied the effects of flow velocity and burner diameter on U_T and have plotted their data against Reynolds' number. Figure 11 shows typical results (*8*); these particular plots were the ones that led to Equation 9. Reported dependencies of U_T/U_L on Reynolds' number range from $\mathrm{Re}^{0.24}$ to $\mathrm{Re}^{1.0}$ (*8*, *12*, *13*, *14*). The recent work of Wagner, in which viscosity and density were changed by using argon and helium as inerts, supported the value of Reynolds' number in correlating U_T/U_L (*71*). More studies of this kind are needed.

If Reynolds' number is useful, it is because flow velocity and Reynolds' number are related to the intensity and scale of turbulence in pipe flow. All the measurements cited so far were on flames in pipe-turbulent flow. However, such turbulence is not isotropic, so the scale and intensity are not usually known. Several workers have used screens of known characteristics to induce isotropic turbulence in the fresh gas and have found correlations between U_T/U_L and turbulence intensity. U_T/U_L data from rectangular-nozzle Bunsen burners are shown in Figure 12 plotted against $v'(U_0/U_L)$, where v' is the intensity of turbulence in the narrow dimension of the burner and U_0 is the mean flow velocity (*80*). A definite relation is noted. Table II summarizes some correlations of this kind; note that v' refers to intensity in a transverse direction and u' to that in an axial direction.

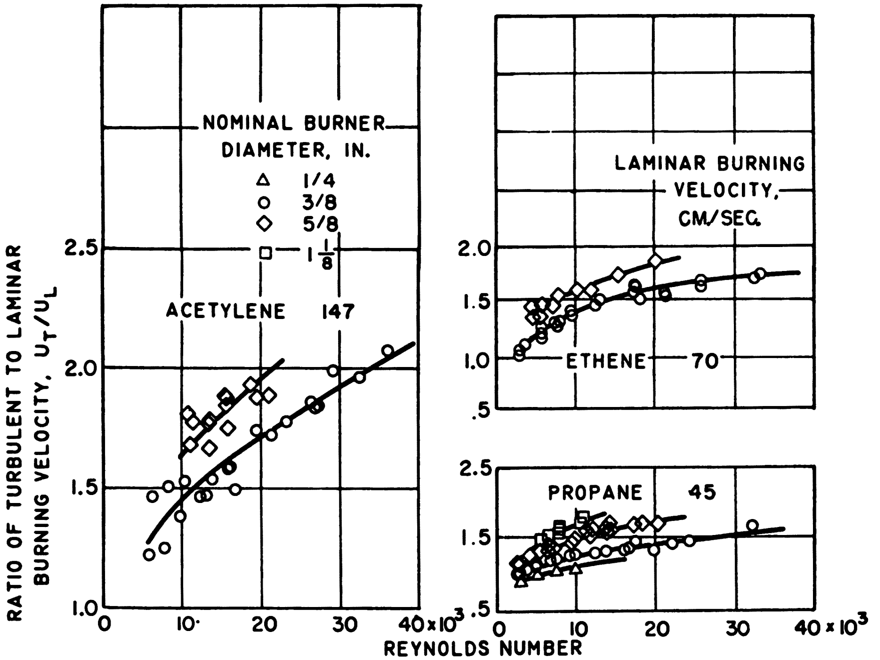

Figure 11. Effect of Reynolds' number on ratio of turbulent to laminar burning velocity for hydrocarbon-air flames. Constant density and viscosity (8)

Two other points about the present state of experimental work should be mentioned. One is that measurements of turbulence scale and intensity are necessarily made in the cold flow; the flame may upset the flow field, even generating added turbulence as suggested by Karlovitz (*42*). The second point is that the flame can never be thought of as burning in a region with constant scale and intensity throughout, not only because of the ordinary decay of turbulent fluctuations, but also because there may be (as in Bunsen

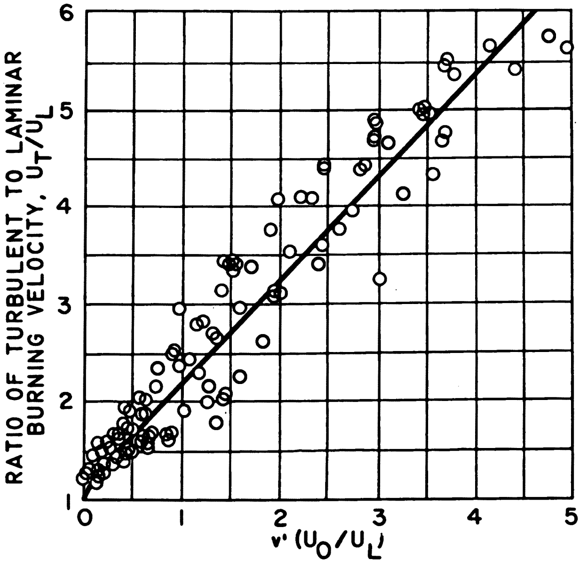

Figure 12. Correlation of U_T/U_L with turbulence intensities, v'. Propane-air flames on rectangular nozzles at various fuel-air ratios and average velocities (*80*)

flames) strong shear between the burning gas and the ambient atmosphere. A discussion of these points has been given in a recent article by Wong (*79*).

TURBULENT FLAME SPACE RATES AND SPACE HEATING RATES. Recognizing that turbulent flames cannot be uniquely characterized in terms of burning velocity, Simon and Wagner have recently described a new approach (*66*). The method has two advantages: It requires no a priori assumption about the nature of the flame—whether it is folded or thickened, and it gives the space needed for burning and the rate of heat release in that space—both important in practical applications.

Table II. Empirical Relations between Turbulent Burning Velocity and Turbulence Intensity

Mixture	Relation	Reference
Propane-air	$U_T \propto v'(U_0)$	(*80*)
Butane-air		
Stoichiometric	$U_T = U_L\left[1 + 0.02U_0\left(\frac{u'}{U_0} + 0.04\right)\right]$	(*76*)
1.25 stoich.	$U_T = U_L\left[1 + (24 + 0.0147U_0)\left(\frac{u'}{U_0} + 0.01\right)\right]$	
1.50 stoich.	$U_T = U_L\left[1 + (77 + 0.046U_0)\left(\frac{u'}{U_0} + 0.01\right)\right]$	
Propane-air stoichiometric	$U_T = U_L\left[1 + 26.2\left(\frac{u'}{U_0}\right) + 1.40\left(\frac{U_0}{24}\right)\right]^{1.12}$	(*78*)

Simon and Wagner define the flame space rate Z as

$$Z = \frac{V_0}{V_f} \tag{11}$$

where V_0 is the volumetric flow rate and V_f the volume of the flame. The space rate Z measures the quantity of fresh gas that will burn in a unit flame volume per unit time. The space heating rate ΔH_s immediately follows as:

$$\Delta H_s = Z\Delta H_f \tag{12}$$

where ΔH_f is the heat release per unit volume of unburned gas on passage through the flame zone. ΔH_f cannot be assumed equal to the heat release on complete burning; it must be measured to account for the possibility of incomplete combustion.

These parameters have so far been applied to turbulent Bunsen flames over a rather limited range of conditions. V_f was measured from time-exposed photographs of the flame brush. It was found that the space rate Z is independent of flow velocity, directly proportional to laminar burning velocity, and inversely proportional to burner diameter. Figure 13 is a plot of Z *vs.* U_L/d, showing the linear relation between these quantities. As the scale of pipe turbulence is proportional to the pipe diameter, Simon and Wagner point out that this relation suggests a chance for improved burner performance if the scale is reduced. Values of space heating rates ΔH_s from 5×10^7 to 11×10^7 B.t.u. per hour per cubic foot were found for Bunsen flames. These values are an order of magnitude above those obtained from aircraft combustors, but are an order below the rates shown by laminar flames.

This method of characterizing turbulent flames shows promise of being quite valuable; however, its validity should be tested over a wider range of variables.

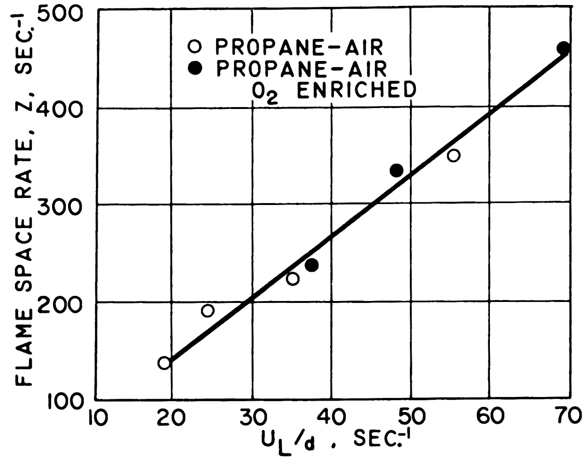

Figure 13. Flame space rate (66)

Flame Stability and Quenching

Although it is probably true that flames per se are inherently unstable as pointed up by the work of Markstein (*59*, *60*), nevertheless perfectly stable flames on burners or in ducts can be obtained. The stability arises from interactions among the flame, the flow, and the nearby solid surfaces. But given a stable flame, a condition may be changed —e.g., flow velocity—and the flame caused to flash back or blow off. This section considers flash-back and blow-off of open flames on cylindrical burners or nozzles, and of confined flames stabilized on simple flameholders in small ducts.

Stability Diagrams: Velocity-Concentration Limits. OPEN FLAMES WITH SECONDARY AIR. Figure 14 shows schematically the stability phenomena of an open flame with ambient air, such as an ordinary Bunsen flame. When the approach flow velocity becomes less than the burning velocity over some portion of the burner port, the flame flashes back into the burner. This always occurs at conditions in the unshaded area under the curve in Figure 14. On the other hand, when the approach velocity exceeds the burning velocity at every point, the flame will be extinguished completely for conditions in the unshaded region to the left of the blow-off curve; or, for rich mixtures, it will be lifted above the port until it reaches a new stable position, as a result of turbulent mixing with and dilution by secondary air. The lift curve is an extension of the blow-off curve beyond a critical fuel concentration, *A*. The blow-out curve gives the

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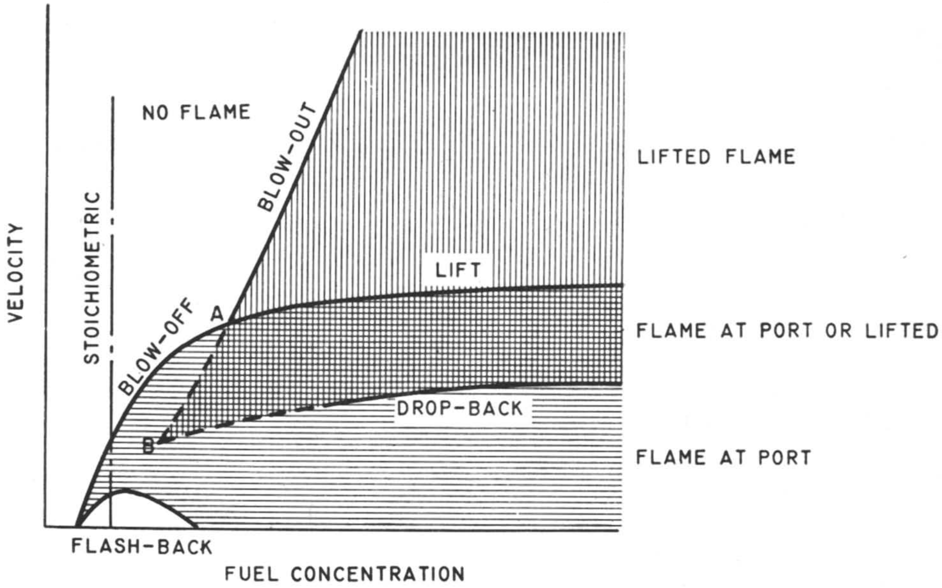


Figure 14. Characteristic stability diagram for open flames (77)

approach velocity needed to extinguish a lifted flame. A lifted flame will not drop back until the velocity is reduced well below that required to lift a seated flame. Between fuel concentrations *A* and *B*, the lifted flame blows out at a lower velocity than that required for blow-off; consequently, such a lifted flame can be produced in a mixture of constant composition only by ignition from above the port.

FLAMES WITHOUT SECONDARY AIR. Open flames isolated from ambient air by an annular flow of inert gas or in a Smithells burner have simpler stability diagrams. There is of course no lift or drop-back curve. The blow-off curve has a maximum at about the mixture for maximum burning velocity, as shown in Figure 15 (*44*). Flash-back is not affected by the presence or absence of secondary air, as it depends on the mixture inside the burner tube. As should be expected, the blow-off behavior of flames stabilized in ducts on flameholders is similar to that of open flames without secondary air.

Mechanisms of Flame Stabilization. CRITICAL BOUNDARY VELOCITY GRADIENT. A flame stabilized at the port of a Bunsen burner does not actually touch the rim. There is a dark region, called the dead space, between the rim and the flame. Heat is removed and free radicals are destroyed by the solid surface; the burning velocity is reduced to zero and the flame is quenched. Even beyond the dead space, where the flame is able to exist as a luminous reaction zone, the burning velocity only gradually rises to the value achieved at a distance from solid surfaces.

The quenching action and the lowered burning velocity in the fringe of the combustion wave are the features that permit flames to be stabilized on burners. Otherwise, the flame would always flash back, because the velocity at the wall is of course zero. Lewis and von Elbe have given a detailed discussion of the interactions of the nearby solid surfaces with the flame and with the flow of fresh gas (*50, 51, 52*), in the course of which they developed the concept of the critical boundary velocity gradient. It is a powerful means of correlating stability data. Figure 16 shows the fringe of a flame at low flow velocity on the verge of flashing back and at high velocity, about to blow off. The main effect of increased flow is to lengthen the flame; dead space remains the same (*23*). In Figure 16, *c*, the burning velocity is plotted as a function of radial distance from the burner rim for the two cases. The straight lines give the profile of flow velocity near the wall; it may safely be assumed linear in reasonably large tubes.

There is a critical boundary velocity gradient for each flame, g_f (for flash-back) and

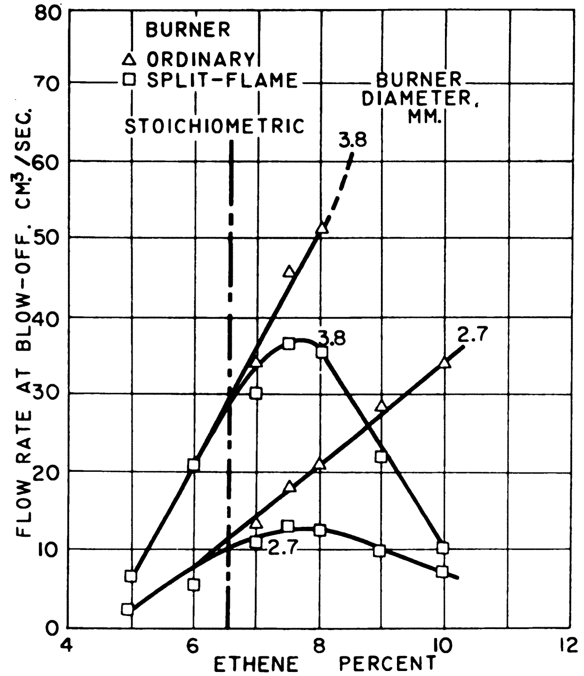
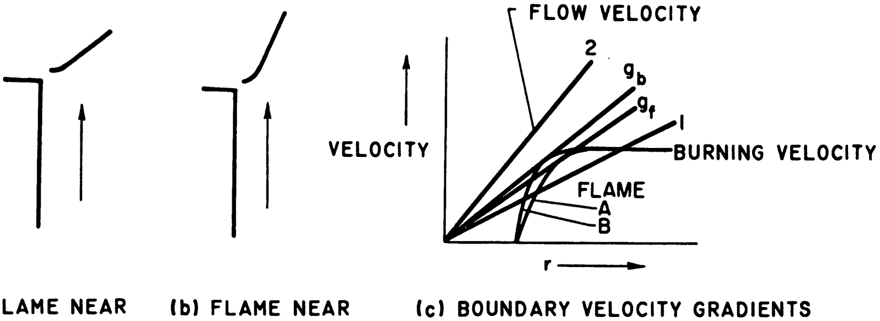


Figure 15. Comparison of blow-off curves obtained with split-flame (Smithells) burners with those obtained on ordinary single-tube burners. Ethene-air mixtures saturated with water vapor at 20° C. (*44*)

g_b (for blow-off). For gradients less than g_f, for example, line 1, the burning velocity is somewhere greater than the flow velocity, so the flame will flash back; for gradients greater than g_b, for example, line 2, the flow velocity is everywhere greater than the burning velocity, so the flame must blow off. Stability data for both laminar and turbulent flow may be correlated by g_f and g_b; this is reasonable because in either case there is a laminar sublayer at the burner wall (*23*).

The boundary velocity gradients may be computed from the following expression:

$$g_{f,b} = \frac{FU_0\mathrm{Re}}{2d} \tag{13}$$



(a) FLAME NEAR FLASH-BACK (b) FLAME NEAR BLOW-OFF (c) BOUNDARY VELOCITY GRADIENTS

Figure 16. Basis of critical boundary velocity gradients for flash-back and blow-off

where F is the friction factor from the empirical Fanning equation (*35*), U_0 the average flow velocity at flash-back or blow-off, and d the width of the tube. Table III gives expressions for F in various cases. In all of the expressions in Table III, the diameter used to compute Reynolds' number is the hydraulic diameter, that is, twice the cross-sectional area divided by the perimeter.

Table III. Expressions for Fanning Friction Factor

Type of Flow	Type of Burner	Friction Factor, F	Reference
Laminar	Long cylindrical	16/Re	(*50*)
	Orifice	$8.5/\mathrm{Re}^{0.85}$	(*36*)
	Long square channel	$18.9/\mathrm{Re}^{1.11}$	(*36*)
	Long rectangular channel	$40.2/\mathrm{Re}^{1.27}$	(*36*)
	Long triangular channel	$29.8/\mathrm{Re}^{1.29}$	(*36*)
Turbulent			
$3000 < \mathrm{Re} < 100{,}000$	Long, smooth, cylindrical	$0.080/\mathrm{Re}^{0.25}$	(*35*)
$5000 < \mathrm{Re} < 200{,}000$	Long, smooth, cylindrical	$0.046/\mathrm{Re}^{0.2}$	(*56*)

STABILIZATION BY EDDIES. The stabilization mechanism of Lewis and von Elbe has also been applied to flames supported on flameholders (*50*). However, it does not correlate the data on supported flames as completely as that for burner flames. A different mechanism, which seems preferable, is based on the existence of eddies in the flow just behind the flameholder. This region is a recirculation zone that acts as a source of heat and free radicals, and is thus a constant ignition source. One may then postulate that blow-off from a flameholder occurs when the eddy region regains less heat from the ignited gas than is required for ignition (*74*). The eddy size is important in such a model, and this depends on the size and shape of the flameholder and on the flow velocity.

The fuel-concentration limits for blow-off from flameholders are correlated by a parameter of the form U_0/d^n, where U_0 is the average flow velocity at blow-off, d is the projected width of the flameholder, and n is an empirical exponent. Recent work suggests that some dimension of the actual recirculation zone should replace the term d^n (to which the size of the zone is related) (*4, 81*). Table IV summarizes the reported correlating parameters for the concentration limits of blow-off from flameholders.

Table IV. Correlating Parameters for Concentration Limits of Blow-Off From Flameholders

Flameholder Mounted in Chamber	Correlating Parameter	Flameholder	Fuel	Reference
Transverse in 1 x 3 in.	$U_0/d^{0.45}$	Uncooled rods or gutters	City gas; propane	(*64*)
Transverse in 1 x 4 in.	$U_0/d^{0.5}$ $U_0/T_0^{1.2}$	Cooled cylinders	Hydrocarbon blend (C_6-C_8)	(*38*)
Axial, in 6-in. pipe	U_0/d	Uncooled rods, cones, annuli, or gutters	Naphtha (C_5-C_8)	(*55*)
Axial, in 4-in. pipe	$U_0/d^{0.85}p^{0.95}$	Disks	Propane	(*15*)
			Naphtha	(*54*)
			Hydrogen	(*54*)
Axial	$U_0/d^{0.5}$	Disks		(*75*)
	U_0/d	Spheres		(*75*)
Axial, above ⅜ in. in 1.25-in. nozzle	U_0/p (d constant)	Spheres	Propane	(*73*)

Effects of Variables on Flame Stability. CHEMICAL VARIABLES. As might be expected, the critical boundary velocity gradients for flash-back and blow-off of open burner flames are greater for fuels with higher burning velocity (*77*). Similarly, rod- or gutter-stabilized flames in ducts become more stable as burning velocity is increased (*64*). The stability of flames of mixtures of hydrocarbons is not notably different from that of the separate hydrocarbons, and blow-off velocities follow a simple mixing relation (*45*):

$$\sum_j \frac{X_j}{X^*_j} = 1 \qquad (14)$$

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where X_j is the mole fraction of the j^{th} fuel in the total mixture having a certain blow-off velocity, and X_j^* is the mole fraction of the j^{th} fuel in its binary mixture with air that has the same blow-off velocity.

PHYSICAL VARIABLES. At constant temperature and pressure, flame stability is related to a characteristic dimension of the burner or flameholder, and to the flow velocity, in the manner already discussed. Typical correlations for burner and supported flames are shown in Figures 17 and 18, respectively.

Approach-flow turbulence does not change the correlation of burner blow-off data by means of g_b. With supported flames, contradictory results have been reported. Scurlock found that as the intensity of turbulence was increased, the blow-off velocity decreased (*64*), while other work indicated the opposite effect (*75*). Turbulent flash-back is of interest, but it is not ordinarily encountered.

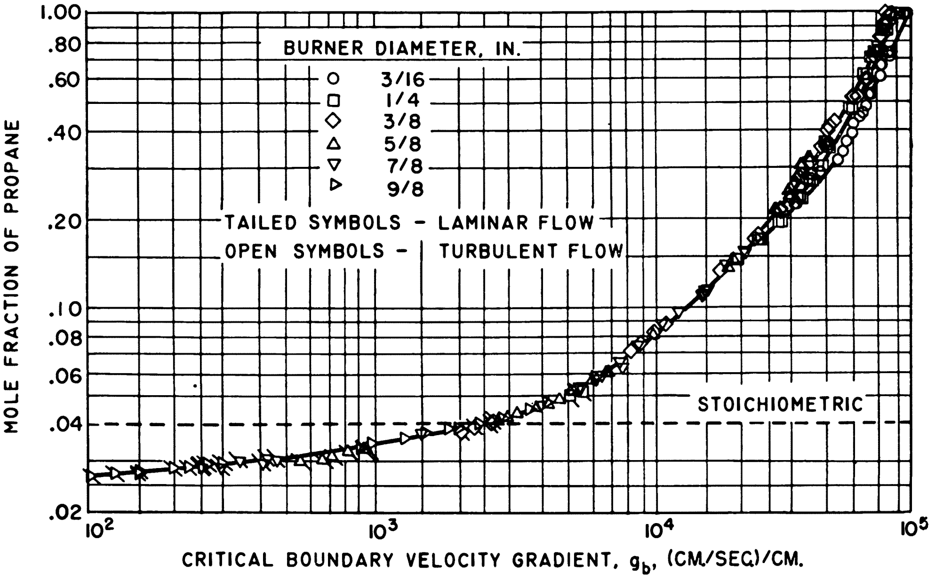

Figure 17. Variation of fuel-air ratio with velocity gradient at tube wall for blow-off of seated propane-air flames (*7*)

The effect of pressure on burner flames is related to the burner diameter; the parameter U_0/p_d correlates blow-off data for various fuel concentrations (*40*). In other words, for a given burner and mixture, the blow-off velocity is proportional to the pressure. Quite similar parameters serve for supported flames as well (Table IV).

Changing the initial mixture temperature affects stability. U_0 for blow-off from burners increases with approximately the square of the absolute temperature, whether the flow is laminar or turbulent (*17*). The exact dependence on temperature is a function of fuel type and concentration, and may also be affected by wall temperature. The flash-back velocity is even more sensitive to temperature (*17*), so that raising the temperature may actually decrease the relative range of flow velocities that will permit stable flames on burners. As to supported flames, the correlations in Table IV show that blow-off in such systems is less dependent on initial temperature than is blow-off from burners (*38*); the exponent on T_0 is only 1.2, as compared with 2.0.

Flame Quenching. Quenching at the fringe of a burner flame, with the consequent appearance of a dead space, has already been mentioned. However, there are also cases in which wall quenching puts the flame out completely. This is generally most notable at reduced pressure. As the pressure is lowered, flame can propagate without difficulty in a channel of given width, until some critical pressure is reached. At lower pressures,

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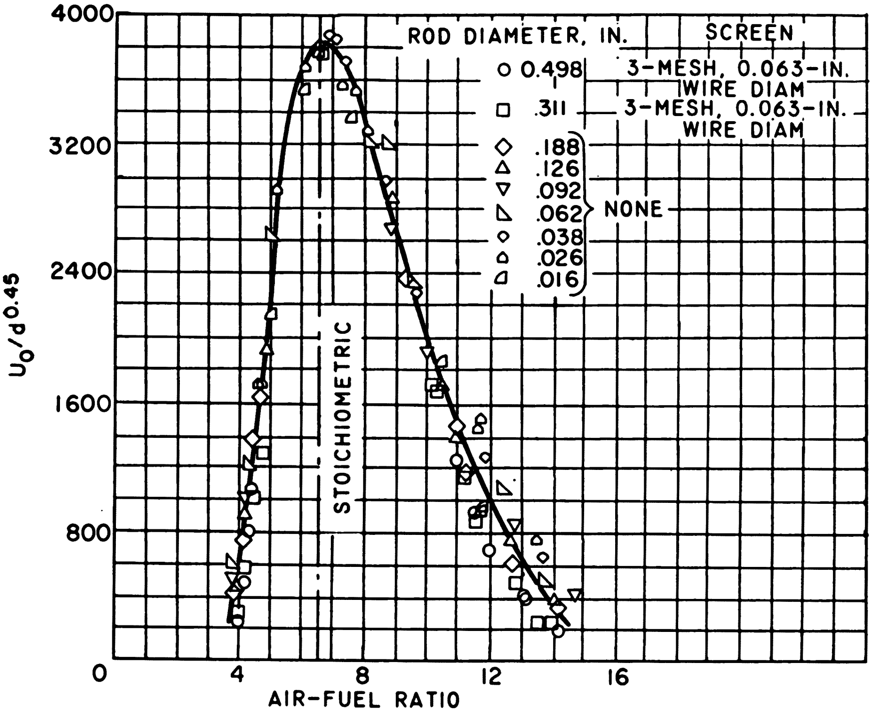

Figure 18. Correlation of rod stabilizer blow-out limit data. Fuel, city gas; stabilizers 9 inches from chamber entrance (64)

flame cannot even enter the channel. The width of the channel is then called the quenching distance d_q for that particular pressure and mixture. It is found that $d_q \propto p^{-n}$, where n is close to 1 for stoichiometric mixtures of most hydrocarbons, but is a function of concentration. At a fixed pressure, d_q is least for the mixture having the highest burning velocity, usually just rich of stoichiometric, and is decreased if the initial mixture temperature is raised (*5, 6, 26, 65*). In general, with various fuel types, the higher the burning velocity the smaller the quenching distance; for hydrocarbon-air flames, the product d_qU_L is fairly constant (*63, 65*), having a value of about 13.

There is good experimental evidence (*41, 61, 62, 69*) that another type of quenching sometimes occurs, entirely in the gas phase and without the influence of walls. If the level of turbulence is too high, or if there are very strong velocity gradients in the flow, it is possible that the flames may be overwhelmed. This may come about by dilution with cold gas more rapidly than it can be consumed, or the flame may be torn apart so that it cannot travel throughout the mixture.

Conclusions

The relatively simple structure of laminar flames has made it possible to characterize this class of flames rather completely. Except for the pressure-dependence of burning velocity, the effects of most variables on laminar burning velocity and on wall-quenching have been established. Turbulent flames, on the other hand, have a complex structure which has not yet been elucidated. Therefore, turbulent burning velocities can only be measured with reference to arbitrarily chosen flame surfaces. Another phenomenon connected with turbulent flames is gas-phase quenching; study of this problem has hardly begun.

The stability of burner flames is well accounted for in terms of critical boundary velocity gradients. The way in which flameholders stabilize supported flames in ducts is not fully understood; it seems that events in the recirculation zone held the key to this problem.

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Structural Factors Determining Knocking Characteristics of Pure Hydrocarbons

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During the past three decades, rules have been developed for correlating the knocking characteristics of pure hydrocarbons with their molecular structures. For the most part qualitative empirical relations have been proposed. To understand the theoretical significance of these relationships, knock must be viewed as an oxidation process which occurs following a branching-chain, free radical reaction. Molecular structure, therefore, influences the chain process by determining the amount and availability of internal energy required for bond fission and relative ease of attack at the C—H bonds. It also influences the stabilities and oxidizabilities of the radical fragments formed after fission and of the molecules formed from these radicals. Many workers have evaluated oxidation and knock in terms of one or more of these structural factors. Ideas that are relevant to the problem of knocking of pure hydrocarbons are evaluated here.

Knocking characteristics of pure hydrocarbons and observed correlations between structure and knock have been summarized by Lovell (*117*). Work of American Petroleum Institute Project 45 (*2*, *3*) represents a large fraction of this information. The reasons for these relationships have not been as adequately reviewed.

Observed Relationships between Structure and Knock

The fact that different hydrocarbons differ in their tendency to knock in an internal combustion engine was first noted by Ricardo (*58*, *175*) and Kettering (*100*), Midgley and Boyd (*139*, *140*) in the period 1919 to 1922. Most of the earlier studies with pure hydrocarbons were made with blends, because of the large amounts of pure hydrocarbons required, unblended, for engine study. For this reason blending effects were noted early (*30*, *67*, *140*, *176*, *211*). In fact, many early generalizations as to antiknock behavior of particular hydrocarbon types were actually generalizations as to their behavior in blends. It was left for subsequent work with pure materials to separate effects due to the hydrocarbon alone from those due to its blending behavior. Studies with unblended, pure hydrocarbons may be divided into those prior to 1935 (*1*, *30*, *50*, *58*, *67*, *123*, *149*, *175*, *176*, *211*) and those after 1935 (*2*, *3*, *14*, *32*, *65*, *97*, *117*, *163*, *164*, *172*, *184*, *190*, *201*).

Variations in response to tetraethyllead were noted early (*32*, *66*, *68*, *96*, *176*) and have since been a feature of antiknock studies (*234*).

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Several programs have been devoted principally to studies of hydrocarbons of a given type. Generalizations within the group were developed. Thus paraffins (*26, 50, 120, 176*), olefins (*11, 15, 16, 68, 79, 81, 121, 146, 147*), aromatics (*7, 29, 47, 66, 83, 124, 140*), naphthenes (*66, 122*), and diolefins and acetylenes (*97, 121, 163, 164*) have been centers of attention. Several papers describe the antiknock behavior of gaseous hydrocarbons (*1, 65, 149, 172, 184*).

Through the years a number of review papers relating knock with structure have been issued (*6, 7, 10, 44, 49, 51, 67, 88, 99, 114–19, 136, 138, 148, 211*). Many papers present generalizations and rules (*6, 7, 15, 23, 26, 56, 66, 80, 81, 83, 88, 114, 117–24, 136, 155, 161, 171, 176, 180, 201*), some of which are characteristic of blends.

The General Motors–Ethyl Corp. Laboratories have been active from the beginning in observing antiknock values and in making correlations (*11, 26, 30, 32, 50, 65, 98, 100, 114–24, 139, 140, 167, 168, 169*). Since 1938 the American Petroleum Institute has been very active in the field. It has obtained by far the largest body of precise data in existence on knocking characteristics of pure hydrocarbons under different engine conditions (*2, 3, 22, 115*). The National Advisory Committee for Aeronautics has done extensive work with pure hydrocarbons in blends, much of it in aircraft engines (*6, 7*). Other papers do not fit in any particular category (*27, 55, 58, 79, 162, 165, 166, 191, 192, 205, 206, 222*).

Rules and Generalizations. Rules for the relationships between structure and knocking behavior are not rigid and exceptions appear. Although the general tendencies apply under all engine conditions, the smaller or more detailed differences depend on the method of evaluation.

A fuel manifesting a wide range of knock ratings under different engine conditions is regarded as sensitive. Engine conditions that give poor ratings for sensitive fuels are considered severe. Increases in speed and in temperature work in this direction (*98, 117*). Reversals of order in resistance to knock are noted in certain instances as engine severity is changed.

Ratings of fuels depend also upon the fuel-air ratio used. A fuel knocks less as the fuel-air ratio is increased above stoichiometric—rich mixture appreciation. Within a given type of hydrocarbon there may be some direct proportionality between rich mixture appreciation and sensitivity (*117*). The correlation is very crude.

Data used to develop generalizations have been summarized (*2, 3, 117, 137*).

PARAFFINS. In a homologous series the knock rating decreases as carbon atoms are added to the longest straight chain. The effect is large, covering nearly the full range of known ratings.

Among isomers the knock rating increases as the number of side chains increases. This effect, too, is very large, more than spanning the full octane number scale. Adding chains in such a way as to increase compactness or centralization raises the rating most. Neopentane is an exception. It is worse than isopentane under all test conditions.

If a methyl group is added to a given paraffin and it introduces an added branch, it usually raises knock rating. The effect is larger if the methyl is added nearer the center of the chain. The paraffins are the hydrocarbons least sensitive to engine conditions.

ALIPHATIC OLEFINS. The effects of chain length and chain branching described for paraffins apply for olefins.

Among straight-chain olefins, the effects of chain length are less than with paraffins. Ethylene is exceptionally poor. Ethylene and propylene rate below the corresponding paraffins, while C_5 and higher olefins rate above the corresponding paraffins.

Among straight-chain olefins, knock rating increases as the double bond is moved toward the center of the molecule.

Introduction of a double bond in a branched paraffin raises the knock rating for slightly branched paraffins but lowers the rating for highly branched hydrocarbons.

Centralization of the double bond in branched olefins tends to raise knock ratings.

Introduction of a double bond in a paraffin has more tendency to raise knock rating if it is added next to the methyl in a monomethyl paraffin or near the quaternary carbon in a dimethyl paraffin.

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Cis-trans isomers rate alike.

Aliphatic olefins are much more sensitive to engine conditions than the corresponding paraffins except at low knock ratings.

CYCLOPENTANES AND CYCLOHEXANES. These naphthenes cover generally the same knock rating range as the paraffins. Naphthenes rate better than corresponding *n*-paraffins, although none are as good as the best branched paraffins.

Adding a straight side chain lowers knock rating. The effect increases with chain length.

Branching in a side chain of given length raises knock rating.

Change from one straight side chain to two at given molecular weight raises rating.

Among two-branched cyclohexane isomers, the order of decreasing knock rating tends to be: 1,1 > 1,2 > 1,3 > 1,4, and cis > trans.

The cycloparaffins are more sensitive than the paraffins. Sensitivity is greater at high knock ratings.

AROMATICS. The aromatics have high knock ratings, usually above 100 octane number.

Adding a straight side chain to benzene lowers knock rating. The effect increases with chain length. As an exception, ethylbenzene falls below *n*-propylbenzene by most methods.

Branching in a side chain of given length raises the knock rating—e.g., 3° Bu > iso-Bu > 2° Bu > 1° Bu.

Change from one straight side chain to an isomer with two chains meta or para to each other raises knock rating.

Di- or polysubstituted benzenes with groups in the ortho or 1,2 position have unusually low ratings.

Most aromatics are highly sensitive to engine conditions. They vary markedly in sensitivity.

MISCELLANEOUS. Diolefins are superior to the corresponding paraffins (with exceptions). Conjugation of double bonds raises the rating.

Acetylenes vary widely in knock rating relative to the corresponding paraffins. Acetylene is very bad. Centralization of the triple bond raises the rating.

Monocyclic olefins and diolefins rate below the corresponding saturates.

Double bonds in side chains of aromatics may raise or lower ratings.

Knocking Characteristics and Molecular Dimensions

Compactness or centralization in a molecule results in increased knock rating. Kobayashi and Mibashan have used this observation to develop empirical quantitative correlations between structure and knock.

Kobayashi used molecular dimensions directly (*101–4*). For paraffins he defined an unstability factor which was a measure of approach to a sphere. A fair correlation was obtained between his factor and blending octane number. The calculated factors indicated the observed rise in knock rating with centralization of the double bond in a straight-chain olefin. Gaylor (*69*) applied Kobayashi's method to aromatics and compared calculations with both clear and blending octane numbers. It is difficult to select molecular dimensions of a flexible molecule representative of its configuration during reaction.

Mibashan's (*61, 138*) relationship was entirely arbitrary. For paraffins, carbon atoms in the longest chain were numbered from the end to the center. A centralization index was developed by adding these position numbers. Corrections were made for various functional groups. Centralization index and octane number were then related by an empirical equation which could be used as a rough prediction guide.

Dependence of Knock on Physical and Chemical Properties

Gas Phase Oxidation Phenomena. SPONTANEOUS IGNITION. Knock occurs when the unburned charge in front of the flame front spontaneously ignites. Under knocking conditions the flame velocity towards the end of complete combustion is far greater than in nonknocking combustion (*195*). Moreover, when the residence time becomes vanishingly small, knock becomes independent of octane number (*5*). Photographs of engine combustion confirm that spontaneous ignition of the end gas causes knock (*233*). Several review articles are available on this topic (*45, 54, 110, 145*).

Specifically, spontaneous ignition in any equipment is a function of three interdependent variables—temperature, pressure, and ignition delay—each of which has been proposed as a criterion for knock by different authors.

Ignition temperature was used with partial success (*52, 57, 74, 135, 189*). Results depended critically on the method used—e.g., adiabatic compression, ignition limits in tubes, or crucible method. Jackson (*70, 86, 87*) determined ignition temperatures for a large number of hydrocarbons by the crucible method and developed correlations with structure.

Ignition pressures, determined at one temperature for a series of fuels, increase as the knock ratings of the fuels increase (*125, 159*).

Ignition delays, investigated in adiabatic compression machines (*89, 91, 92, 106, 182, 209, 212, 213*), have been correlated with knock (*90, 93-5, 111, 158, 160, 194, 203*). Ignition occurs in two stages. Levedahl (*106*) examined the effects of temperature, density, and fuel type on the induction periods, τ_1 and τ_2, corresponding to each ignition stage. A close correlation existed between total delay, τ, and knock resistance. Sensitivity was explained in terms of the relative partial contributions of τ_1 and τ_2 to τ.

PREFLAME REACTIONS. During the past 30 years, many workers have associated knock with the preflame reactions occurring prior to rapid combustion. Peroxides and aldehydes are important preflame products. It has become customary to consider these compounds, particularly the former, as important in the knock process (*28, 48, 142, 143, 170, 181, 235*). Motored engine experiments have tended to confirm this view (*42, 46, 154, 156, 157, 174, 193, 225*), although Ross (*183*) has obtained severe knock with *n*-heptane with no evidence of formation of prereaction products.

Knock resistance has also been correlated with other preflame reaction properties such as the rate of pressure development during adiabatic compression (*17*), the temperature coefficient of preflame reactions (*202*), and the pressure developed prior to firing (*34*). Estradère (*59*) made a correlation between the temperature of initial exothermic oxidation in a tube and knock. No quantitative connection exists between apparent activation energy (*160*) or the total heat (*179*) of the precombustion reactions and knock.

The preflame reactions include slow oxidation and cool flame reactions (*110*). Slow oxidation threshold temperatures and reaction rates have been considered important factors in controlling knock resistance (*43, 75, 133*). Knock ratings have been related to cool flame intensities and temperature limits (*36, 43, 153*). Recently, Barusch and Payne (*9*) have found striking correlations between octane number and the position of the cool flame in a tube (a parameter which should be a function of τ_1). The heat evolved during cool flame reaction may also be a vital factor in determining the occurrence of knock (*106, 156, 179*).

Other Properties. THERMAL STABILITY. Several attempts have been made to correlate knock resistance with thermal stability. Petrov (*162*) attempted to account for the knock characteristics of various gasoline fractions in terms of their cracking products. Rice (*177*) showed that a parallelism existed between yields of cracking products and knock tendency. Estradère (*60*) did not find a direct relation between temperature for initial cracking and detonation characteristics.

Free energy (*85*) and heat of formation (*216*) both correlate with knock rating but neither in itself is sufficient to account for the differences in reactivity found (*216*).

MISCELLANEOUS. Some workers have made empirical correlations to which, at present, no physicochemical significance can be attributed. In this category are the correlations of Howes and Nash (*84*) (with permanganate oxidation rate), Francis (*62*) (with functions of density–boiling point; boiling point–aniline point), Bonino (*18*), Glocker (*71*), and Ubbelohde (*219*) (with Raman spectrum), and Petrov (*161*) (with pour point).

Conclusion. Knock appears to be determined by spontaneous ignition, which in turn depends on the extent of preflame reaction. In general, both cool flame and precool flame reactions will be important.

Knock as a Free Radical Reaction

Knock will occur if the ignition lag in the end gas is less than the time required for the spark-ignited flame to cross the cylinder. Therefore, in attempting to correlate structure with knock, the factors possibly contributing to ignition lag are resolved. Next, each is discussed with particular attention to its importance and the effect of structure. Because a multitude of factors contribute to the ignition lag, knock cannot be expected to be a unique function of any one.

Ignition lag may be affected by:

Kinetic and thermodynamic properties of the hydrocarbon. Internal energy available. Collision frequency.

Rate of Initiation. Rate and mode of formation of the first few radicals. Rate of initial attack of the hydrocarbon molecule by free radicals (hydrogen abstraction).

Rate of chain propagation reactions.

Rate of chain branching reactions giving multiple free radicals (ending the τ_1 induction period).

Competition by stabilizing or terminating reactions.

Stability of molecular intermediates—reinitiation.

Reactions leading to second stage ignition—τ_2 regime.

Kinetic and Thermodynamic Properties of the Hydrocarbon

Internal Energy Available. Ubbelohde and coworkers (*215–18*) have suggested that as $> CH_2$ groups are added to methane, coupled oscillators are formed. This vibration coupling increases the internal energy content. The effect is larger the longer the chain. Branching or introduction of a double bond interrupts the vibrational coupling and breaks the molecule into systems of coupled vibrators. Thus *n*-octane has a higher heat content than tetramethylbutane. Double bonds lower heat content, and more so, if nearer the center of the molecule. These effects all parallel the observed trends in knock rating.

Irisov (*85*) related octane number with free energy of formation for alkanes, alkenes, and alkynes. Correlations were said to be better than those by Kobayashi and Mibashan.

$$RH \rightarrow RH^* \qquad \text{Molecular excitation} \qquad (1)$$

The rate of reaction between a hydrocarbon molecule and a radical depends on the amount of excitation energy available for surmounting the reaction energy barrier (activation energy). In the case of polyatomic molecules the energy is almost entirely vibrational. Ubbelohde and coworkers (*41*, *105*, *127–9*, *215*, *221*) have indicated that the efficiency of conversion of translational to internal energy is a function of hydrocarbon structure. Transfer is particularly efficient in the case of flexible molecules such as the long straight-chain paraffins. It is less efficient with the stiffer cyclopentanes.

$$RH^* \rightarrow R\overset{*}{-}H \quad \text{Internal transfer of energy} \qquad (2)$$

If a bond is to be ruptured, it is necessary that energy be concentrated in that bond. Vibrational coupling renders internal energy more accessible if the bond concerned has approximately the frequency of a C—C bond. Vibrational coupling is pronounced in the carbon skeletons of long straight-chain hydrocarbons. Branching or introduction of double bonds interrupts coupling. The amount of coupling between C—H bonds and parts of the carbon skeleton tends to be limited. Ubbelohde (*215*, *216*) attaches more importance to the effect of vibrational coupling on transfer of energy to a particular bond than to its effect on the heat content of the molecule as a whole. Among the hydrocarbon groups mentioned, increased vibrational coupling accompanies lower knock ratings.

Collision Frequency. Collision frequency is affected by concentrations, molecular

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weights, and collision diameters of reactant species (*78*). Decreasing molecular weight and increasing collision diameter increases collision frequency and the probability of reaction. Ubbelohde and coworkers (*39*, *40*, *126*, *215*, *216*) have shown that long-chain paraffins and 1-olefins exhibit extensive crumpling in the gas phase. Greater reactivity of long-chain molecules cannot then be accounted for solely on the basis of an increased number of collisions—cf., Kobayashi's relation.

Rate of Initiation

Rate and Mode of Formation of the First Free Radicals. Because the free radical reactions must be initiated during each knocking cycle, factors affecting formation of the first free radicals could be significant. In tube experiments initiation has been attributed to surface reactions (*109*, *217*, *224*). Boord (*20*, *25*) speaks of the formation of free radicals by absorption of a quantum of energy. Reaction of hydrocarbon with an excited oxygen molecule has been suggested (*21*, *25*, *38*). The effect of hydrocarbon structure on this step has not been discussed; however, if the reaction is oxygen-initiated and oxygen is regarded as a biradical, the considerations discussed in the following section may apply.

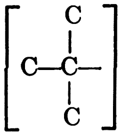
Rate of Initial Attack of Hydrocarbon Molecule by Free Radicals (Hydrogen Abstraction). BOND STRENGTHS AND STERIC EFFECTS AS FACTORS DETERMINING REACTION RATE. Attack of a hydrocarbon by the radical R′ will occur by Reaction 3

$$R'\cdot + RH \rightarrow R'H + R\cdot \quad (3)$$

For this reaction, the relative rates for different R's are often assumed to be directly related to the bond strengths of the R—H bonds. Many workers (*20*, *217*, *220*, *229*) have postulated that, during oxidation, hydrogen abstraction from hydrocarbon molecules by radicals should occur at rates determined by the numbers and strengths of C—H bonds present. According to Rice (*178*), the relative rates at 300° C. should be primary: secondary:tertiary = 1:3:33.

The actual bond strengths of particular C—H bonds in complex molecules are not known accurately. The configuration of substituent groups probably affects bond strengths. Study of even a few data, however, such as Boord's (*24*), indicates either that the rate of the hydrogen abstraction step 3 is not controlling or that hydrogen abstraction rate is not always directly related to normal bond strength. If Reaction 3 is controlling, steric effects may modify the effects of bond strengths.

In particular cases bond strengths may be controlling—for example, the extreme resistance of benzene to oxidative attack may be explained by the very high C—H bond strength (*12*, *208*). The anomalous low knock rating of neopentane may be correlated with the low strength of the neopentyl C—H bond. C—H bond strengths for methane, ethane, and neopentane are, respectively, 102, 98, and 96 kcal. per mole (*82*, *204*).

Reaction at a carbon atom may be inhibited by the proximity of neighboring groups. Steric effects of hydrogen atoms on carbon atoms, five atoms removed from the site of attack, are important. This principle, called by Newman (*150*) the rule of six, has been used (*63*) to explain yield distribution in hydrocarbon oxidation. Steric effects are probably important in the high resistance of some tertiary C—H bonds to attack (*63*, *196*) and in the retarding effect of *tert*-alkyl groups  $\left[\mathrm{C{-}\overset{\displaystyle C}{\underset{\displaystyle C}{C}}{-}}\right]$ noted by Livingston (*113*). Molecular crumpling tends to produce shielding and autosolvent effects even in long-chain molecules (*215*, *218*).

EMPIRICAL CORRELATIONS SUGGESTING IMPORTANCE OF INITIAL ATTACK. A number of empirical correlations have been developed between structure of complex molecules and knock. The effects of particular structural features which have been observed may be indicative of the bond strengths or steric effects in these molecules.

Hinshelwood (*77*) calculated methyl retardation factors which characterized the oxidation rates of paraffins. The extent of retarding effect on reaction rate was dependent on the distance of each methyl group in the molecule from the site of attack.

Livingston (*113*) made a comprehensive correlation of knock with structure. A number of functional groups were believed to exhibit retarding effects. By a method similar to that of Hinshelwood, Livingston calculated structural retardation factors which were found to vary progressively as the standard compression ratios for knock changed.

Hinshelwood (*77*) suggested that retardation reflected a difference in peroxide stability. Livingston gave no unequivocal interpretation in terms of mechanism. Taken at face value, however, both correlations indicate the knocking phenomenon is connected with the site of initial attack.

Panyutin (*155*) and Boord (*19*) have reported that knock rating falls as the number of methylene groups in a paraffin increases. Similarly Levedahl (*106*) found autoignition resistance falls as the number of 2° hydrogen atoms increases in paraffins, olefins, and oxygenated compounds. Cramer and Campbell (*35*) showed the aniline equivalent of a hydrocarbon decreased as the number of 2° and 3° C—H bonds in paraffins and olefins rose. Do these results suggest that rate of reaction is greatest for reaction at secondary hydrogens?

Boord and coworkers have made a number of empirical correlations. One paper (*20*) related high knock rating with high activity of C—H bonds, allyl activation, high activity of ring hydrogens, and ring activation of hydrogens on α carbons in aromatic hydrocarbons. It was believed that hydrogen stripping was in the order $3° > 2° > 1°$. Another paper related knock rating with 1°, 2° and 3° C—H bonds in alkyl aromatics (*24*). It indicated decreasing ratings in the order $3° > 2° > 1°$. Sensitivity was indicated to decrease in the order $3° > 2° > 1°$ C—H bonds (*20, 24*). These effects are in the opposite direction from those which would be expected if 3° hydrogen atoms were most active and if their reaction were controlling in causing knock.

Naphthenes also show this anomalous behavior. Although more susceptible to radical attack (*214*), naphthenes are relatively resistant to knock compared with normal paraffins (*2*).

In summary, the relationships between structure and either low temperature oxidation or knock are anomalous and opposite to the relationships found for most other reactions (*199, 216*)—either Reaction 3 is not controlling or steric effects are modifying the effects of bond strength.

POINT OF INITIAL ATTACK. As the point of initial attack appears to be significant, the hydrogen abstraction step is probably rate-controlling in certain cases.

It is of interest to review ideas as to the point of hydrogen abstraction. Through 1939 most investigators believed that attack of paraffins was at the primary C—H bonds at the end of a chain (*75, 109, 167, 168, 217, 220, 224*). Attack at the α-carbon atom of substituted benzenes (*217*) and at the end methyl of olefins (*109*) was proposed. Preferential attack at 1° C—H bonds fitted in with the comparative ease of oxidation of *n*-paraffins and their low knock ratings.

Walsh proposed ease of reaction in the hydrogen abstraction step was in the order $3° \gg 2° > 1°$ (*229, 230*). Boord has applied this idea (*20, 21, 24, 25*). If this order were to be accepted, it would have to be assumed that the rate of the hydrogen abstraction step is not controlling but something else, such as stability of peroxides (*228*) formed, determines knock.

The work of Panyutin (*155*), Levedahl (*106*), Boord (*19*), and Cramer and Campbell (*35*) suggested a high reactivity at the 2° C—H bonds. On the basis of his work Levedahl believed these bonds were the principal points of initial attack. Livingston (*113*) arrived at an order $2° \gg 3° > 1°$ without directly associating this with the initial attack. Cullis (*38*) and Malherbe and Walsh (*130*) have reported evidence for attack at 2° C—H bonds. Malmberg and coworkers (*132*) decided, on the basis of analysis of products, that 2°

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C—H bonds were attacked preferentially. Such preferential attack can be explained if the normal order produced by bond strengths is upset by a large steric retarding effect with 3° C—H bonds.

Hydroperoxide Chain

The various theories of combustion mechanisms are not elaborated here. Reference may be made to standard textbooks (*88*, *110*). The discussion that follows is intended to bring out particularly the explanations of effects of structure which are based on combustion mechanisms.

For aliphatic hydrocarbons a close relationship exists between knock and low-temperature, two-stage ignition (*110*). In both cases two induction periods are observed. One, τ_1, extends up to cool flame formation. The other, τ_2, follows τ_1 and lasts up to autoignition.

It is experimentally observed (*106*, *108*, *110*) in both engines and test equipment that initial reactions are nearly thermoneutral. Further reaction results in exothermic cool flames. These flames may die out after release of only a small fraction of the heat content of the reacting mixture. Then further reaction occurs with a slower heat release and culminates in autoignition. These steps may be the reflection of free radical peroxide formation, branched-chain peroxide reactions giving cool flame, some quenching effect on these branching reactions, and a further chain reaction terminating in ignition (*106*, *108*, *110*).

Differences of structure among aliphatics are believed to exert their effects on knock by their effects before or during cool flames (*9*, *106*). If this is the case, we should expect differences in rates among the reactions before and during cool flames and perhaps among those which quench cool flames. Levedahl (*106*) has noted that the threshold temperatures for the peroxidation stage and for cool flames are lower and the exothermicities of the cool flames are all higher for fuels of lower knock rating. On the other hand, the temperature for autoignition was essentially independent of structure. Stating that the effect of structure is on cool flames is not stating that the effect is all on τ_1. Levedahl (*106*) measured both τ_1 and τ_2 in the rapid compression machine and found significant variations in each with structure.

Certain compounds do not show two-stage ignition. These include methane, acetylene, benzene, hydrogen, methanol, formaldehyde, and glyoxal (*106*, *108*). Higher aromatics show the effects of their aliphatic side chains and act like aliphatics.

Chain Propagation.

$$R\cdot + O_2 \rightarrow R\overset{*}{—}O_2\cdot \rightarrow RO_2{}^{*}\cdot \qquad \text{Peroxy radical formation} \qquad (4)$$

$$RO_2{}^{*}\cdot + RH \rightarrow ROOH + R\cdot \qquad \text{Hydroperoxide formation} \qquad (3')$$

Reactions 4 and 3′ define an unbranched chain. Reaction 4 will have little or no activation energy (*72*, *134*, *173*, *199*). However, a low steric factor has been observed by Satterfield and Reid (*187*). Because the reaction is highly exothermic, instantaneous dissociation will occur unless the energy-rich $RO_2{}^{*}\cdot$ radical is stabilized (*199*, *200*, *226*). Ubbelohde (*218*) has suggested that vibrational coupling of the O—O bond with C—C bonds will aid in stabilizing the excess energy throughout the radical. This coupling will contribute most to stabilization in long, straight-chain alkylperoxy radicals. Reaction 4 is probably never rate controlling.

The excess energy in excited $RO_2\cdot$ radicals will depend on the R—O bond strengths (the approximate exothermicity of Reaction 4). Only limited data are available (*73*). However, by analogy with their C—H analogs, the R—O bond strengths should increase in the order benzyl, allyl < *tert*- < iso- < *n*-. If an energy chain is assumed, therefore, the excess energy in radicals entering Reaction 3′ should increase in the same order.

Formation of hydroperoxide by Reaction 3′ is known to occur (*13*, *72*). It may be rate-controlling. Two opposing factors contribute to determine the rate of this reaction. As Reaction 3′ is the same as Reaction 3, structural features affecting rate of hydrogen abstraction apply. However, as in many cases the R group is the same in RH and $RO_2{}^{*}\cdot$, when the hydrogen is most difficult to abstract, the excitation energy in $RO_2{*}\cdot$ is also highest. The relative contributions of bond strength, in one direction, and of excitation energy, in the other, may vary from case to case. The differential effect may explain the apparent greater activity of 2° C—H bonds and the low reactivity (high knock rating) of compounds with 3° C—H bonds or allylic hydrogens.

Evidence exists that Reaction 3′ may occur as an intramolecular reaction (*8, 131*). This provides a possible explanation of the extremely low knock rating of *o*-xylene compared with those of the meta and para isomers.

Branching.

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{HO}\cdot \qquad (5)$$

$$\mathrm{RCHO} + \mathrm{ROOH} \rightarrow \mathrm{R\cdot CH(OH)\cdot OOR} \rightarrow \text{new chain centers} \qquad (6)$$

$$\mathrm{ROOH} \rightarrow \text{stable products} \qquad (7)$$

$$\mathrm{RO}\cdot \rightarrow \text{carbonyl compound} + \mathrm{R}\cdot'' \qquad (8)$$

Various reactions have been proposed for the branching step. Norrish (*151, 152*) has favored branching via aldehydes; however, several objections to this hypothesis have been made (*229*). Many workers have believed Reaction 5 was the rate-determining branching reaction (*37, 75–7, 144, 217, 228, 229*). Objection has been raised in view of the high activation energy of Reaction 5, although there is little doubt that the reaction does occur (*53, 141, 198, 210*). Walsh (*232*) has indicated that the lower activation energy Reaction 6, similar to a reaction first proposed by Lewis and von Elbe (*110, 224*), would be consistent with a Frank-Kamenetsky (*64*) mechanism for cool flame formation. The effect of structure on Reaction 6 is hard to estimate, though it may be analogous to the effect on Reaction 5. In view of Thomas' discovery (*210*) that structure has little effect on the peroxide decomposition step (Reaction 5), contrary to previous suppositions, it appears probable that neither Reaction 5 nor 6 is rate-determining.

Semenov has proposed that degenerate branching reactions may be operative in oxidation reactions (*197*). According to this view, a nonbranching reaction would compete with Reactions 5 and 6, thus preventing explosive combustion. One possibility is decomposition by Reaction 7 to aldehyde or ketone and alcohol or water (*21, 109, 217*). Although Walsh (*229*) has suggested that Reaction 7 may occur heterogeneously, there is no experimental evidence that a homogeneous reaction occurs. Lewis and von Elbe (*108–110, 224*) proposed decomposition of the peroxy- radical to an aldehyde and hydroxyl or alkoxy radical as a nonbranching competitive process. The following reactions are also possibilities (*46*):

$$\mathrm{R}\cdot \rightarrow \text{olefin} + \mathrm{R}\cdot''' \qquad (9)$$

$$\mathrm{R}\cdot \rightarrow \text{olefin} + \mathrm{H}\cdot \qquad (9')$$

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \text{olefin} + \mathrm{HO_2}\cdot \qquad (9'')$$

Satterfield, Reid, and Wilson (*186–8*) have suggested that Reaction 9″ is the main olefin producing reaction in the low temperature oxidation of propane. [$E_{9''} = 20$ kcal.; $E_9 \approx 25$ kcal.; $E_{9'} \approx 40$ kcal. per mole (*204*)]. As temperature increases Reaction 9′ will become relatively more important.

Reaction 9″ appears to be favored over Reaction 4 when $RO_2{*}\cdot$ cannot be stabilized effectively. Thus branched paraffins yield relatively more olefins (compared with oxygenated products) than *n*-paraffins (*63, 154*).

The decomposition of the alkoxy radical by Reaction 8 occurs by α-scission at the C—C bond attached to the largest hydrocarbon group (*185, 229*). Straight-chain paraffins produce aldehydes, while highly branched paraffins yield ketones (Reaction 11). The knock resistance of naphthenes may be caused by the stability of the naphthene ring to C—C scission (*25*).

Termination and Transfer.

$$\left.\begin{array}{l}\mathrm{R}\cdot \rightarrow \text{wall} \\ 2\mathrm{R}\cdot \rightarrow \mathrm{R_2}\end{array}\right\} \quad \text{Chain termination} \qquad \begin{array}{r}(10)\\(10')\end{array}$$

$$R\cdot + R^{IV}H \rightarrow RH + R\cdot^{IV} \qquad \text{Chain transfer} \qquad (3'')$$

$$R\cdot^{IV} \rightarrow \text{wall} \qquad (10'')$$

Of the several inhibitions probably occurring during cool flame formation (*64, 111, 223, 227, 232*), chain transfer reactions seem to be of great significance, particularly when olefins are primary products.

Mention has already been made of the relatively small reactivity of allyl peroxy radicals compared with other alkyl peroxy radicals. Jost (*88, 96*) has reasoned that paraffins react by a small number of long chains, whereas olefins oxidize by a large number of short chains. Olefins are thus attacked more readily than paraffins but form less reactive allyl radicals. In addition, during oxidation chain transfer occurs in which alkyl radicals are replaced by allyl radicals. Shorter chains would then be expected. Comparison of the precombustion products of iso-octane and diisobutylene (*154*) indicates that marked self-inhibition of reaction chains was occurring in the latter case.

Chain transfer may be important in determining the enhanced effect produced by centralizing a double bond. A larger proportion of allylic hydrogens would be produced corresponding to relatively more allyl radicals.

Stability of Molecular Intermediates

$$\left.\begin{array}{l}\text{Olefins}\\ \text{Aldehydes}\\ \text{Ketones}\end{array}\right\} + O_2 \rightarrow \text{new chain centers} \qquad \begin{array}{c}\text{Initiation of}\\ \text{new chains}\end{array} \qquad (11)$$

The importance of olefins in chain transfer has been referred to. Ketones and aldehydes formed by Reactions 7 and 8 may also modify the combustion process. The greater reactivity of aldehydes compared with ketones was used by Pope and coworkers (*168*) to explain the relative oxidation resistance of straight-chain and branched paraffins and has been repeatedly cited (*20, 24, 25, 224*). Several workers have discussed the parts played by formaldehyde and other aldehydes in knock (*25, 46, 111, 217, 231*).

Although the influence of products enters as a perturbating factor in precombustion reactions, marked differences have been found in initial rates of reaction among isomers (*63*). Neither chain length nor product effects can therefore explain all the facts.

Reactions Leading to Second Stage Ignition—τ_2 Regime

The τ_2 period includes the cool flame reaction, which may be followed by a period of decreased reaction velocity, and leads up to autoignition. Lewis and von Elbe (*108, 110*) believe that in the τ_2 region unbranched chains are initiated by reaction of formaldehyde and perhaps other aldehydes with oxygen. Second-stage ignition is not believed to be of the branched-chain type but occurs as a result of unbalancing of thermal equilibrium.

Levedahl (*106*) noted that aliphatics from acetylene to octane all gave hot flames at ~600° C. He suggested that some reaction, such as thermal decomposition, which was common to all aliphatics, became important. Benzene showed a very high, inconsistent hot flame limit, while cyclohexane was low and variable. Levedahl believed the cool flame and subsequent reaction, along with compression, served to raise the mixture temperature to the critical value. Acetylene was believed to play a major role in the ignition reaction.

Livengood and Wu (*112*) correlated rapid compression, motored and fired engine experiments on the assumption that a reaction entity was formed in all cases by the same kind of reaction, and that ignition occurred when the entity reached a critical concentration.

Recent theories of knock (*4, 33, 45, 207*) have emphasized the role played by the hydroperoxy radical ($HO_2\cdot$) under incipient knock conditions. HO_2 radicals would be formed by Reactions 9″, 11, and 9′-4. Reaction 9′, with an activation energy of ~40 kcal. (*204*), might be the reaction required to trigger ignition. The yields of both hydrogen peroxide (*207*) and hydrogen (*107*) have in fact been observed to increase rapidly near autoignition.

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Structure of aliphatic hydrocarbons is believed to have comparatively little effect on reactions occurring towards the end of the τ_2-regime. Simple molecules and radicals formed from all hydrocarbons are involved. Structure manifests its effect primarily in the τ_1 and early τ_2 regimes.

Summary

Differences in structure among hydrocarbons affect many of the process steps leading to knock. The relative contribution of the effect on each step probably varies from hydrocarbon to hydrocarbon and from class to class.

The following are believed to be important in determining knock ratings:

Thermodynamic properties such as heat content and vibrational coupling.

Bond strengths and steric effects which usually dictate a free radical attack in the order 2° > 3° > 1° and which determine relative rates of formation of hydrocarbon free radicals and of hydroperoxide molecules (Reactions 3 and 3′).

The competition between chain branching and the various nonbranching or terminating steps.

Ease of reinitiation of chains with different molecular intermediates.

Differences in stability among hydroperoxides are probably not controlling. Moreover, the reactions immediately preceding autoignition probably involve simple entities formed in the combustion of all hydrocarbons and are only indirectly affected by structure.

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Engine Studies of Preknock Reactions

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Considerable effort has been expended during the past 30 years toward understanding and overcoming knock in spark ignition engines. Of all the explanations advanced for engine knock, the generally accepted theory involves autoignition of the unburned fuel-air mixture ahead of the flame front. Much experimental evidence supports this view. Recent studies have been aimed at understanding the various chemical reactions taking place ahead of the flame front and elucidating the actual knock mechanism as a combination of physical and chemical effects. In such work, use of bombs and other special apparatus has given way to the research engine which can produce actual performance conditions.

Although knock in spark ignition engines was known as early as 1882 (*24*), the importance of this phenomenon in limiting the efficiency and power output of engines was not generally recognized until the early twenties. Since then considerable effort has been devoted to understanding and overcoming this problem. As a result, great strides have been made in improving the knock resistance of fuels and engines, making possible large gains in engine performance.

Early studies of knocking combustion were concerned primarily with the development of a physical concept of knock, and many theories were proposed to account for its origin (*7, 12, 19, 29, 34, 38, 50, 63, 68, 97, 127*). The more popular theories suggested that knock was due to vibratory motion of the flame (*41, 88, 98*), explosion of products of initial partial combustion (*32, 66, 79*), pressure increase caused by dissociation of combustion products (*75, 87*), acceleration of the flame to detonation velocities by activation or ionization of new molecules by species originating in the flame front (*1, 54, 60, 75, 130*), and autoignition of the unburned fuel-air mixture ahead of the flame front (*9, 18, 20, 28, 39, 40, 122*). The large amount of experimental evidence advanced in support of the autoignition theory of knock has resulted in general acceptance of this theory. The development of the autoignition theory was given impetus by the realization that autoignition or knock was preceded by a rapid series of chemical reactions occurring ahead of the flame front (*8, 110, 111, 119, 121*). Recent investigations have been directed towards gaining an understanding of these chemical reactions and their controlling factors. Determination of the effect of hydrocarbon structure, fuel additives, and engine variables on the occurrence of knock is one phase of these studies. Elucidation of the actual knock mechanism as characterized by series of physical and chemical events occurring in the end gas region is a second phase.

Bombs, tube apparatus, rapid compression machines, and engines have been used extensively in knock studies. In recent years refinement of the engine as a research instrument has made possible detailed and quantitative investigations of the knock

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process. Studies of hydrocarbon oxidation previously confined to bomb and tube apparatus are now performed in special engines under actual performance conditions.

Nature of Knock Process

Knock in spark ignition engines may be defined as an abnormally rapid combustion of the unburned fuel-air mixture ahead of the normal flame front. A severe pressure unbalance due to this rapid combustion process sets up shock waves which impinge on the cylinder walls and piston and produce the characteristic metallic knocking noise (*43*).

The preflame process occurring in the end gas and leading to knock consists of one or more individual stages (*69, 90*) which can be defined on the basis of chemical analyses of the reaction mixture and radiation measurements. The number of stages and the relative importance of each in the over-all knock process are highly dependent upon hydrocarbon structure and reaction environment. Paraffin hydrocarbons, for instance, can exhibit as many as four different stages in the reaction process including peroxide or precool flame, cool flame, blue flame, and autoignition or hot flame stages (*69, 124*). Each of these stages is characterized by certain types of chemical reactions which result in the observed radiation, pressure, and heat release effects. Altering engine conditions or changing hydrocarbon type may reduce the number of experimentally isolable stages to that of only autoignition (*26, 89*).

The exact nature of the final autoignition step is subject to considerable debate. Three main possibilities have been suggested: combustion of the presensitized end gas by a detonation wave, combustion of the presensitized end gas by a flame propagating at less than detonation velocity, and spontaneous ignition of the end gas as a continuation of the preflame reactions. High-speed photographs of knocking combustion in engines by Sokolik and Voinov (*123*), Miller (*93, 94*), and Male (*82*) suggest the existence of a detonation wave initiated either in the flame or in a region of high activity in the end gas. Beatty and Edgar (*14*), Czerlinsky (*30*), Laffitte (*67*), and Jost (*61*) reviewed available data and concluded that true detonation does not occur in internal combustion engines. Failure to produce detonation with engine fuels in tube experiments (*116, 117*) geometric limitations of combustion chamber for detonation wave propagation, and the relatively low speeds of engine knock as calculated from engine photographs are cited. Lewis and von Elbe (*74*), differentiating between detonation and knock, pointed out that the role of shock waves observed in knocking combustion is not comparable to the role of the shock wave in the detonation process. Downs, Walsh, and Wheeler (*36*) have indicated, however, that the occurrence of preknock reactions may invalidate many of the reasons advanced in the literature for distinguishing between knock and detonation. Several investigators (*48, 117, 118*) have postulated that presensitization of the end gas is necessary to support a detonation wave.

The third possibility, spontaneous ignition of the entire end gas region, has never been satisfactorily demonstrated in photographic studies of engine combustion. Most of the photographs which have been obtained show the passage of one or more high velocity flames through the end gas at the time of knock instead of ignition of all parts of the end gas at the same time. The existence of the flame fronts can be explained as resulting from the nonhomogeneous nature of the end gas which prevents development of the preflame reaction to ignition conditions at all points in the end gas at the same time. In a nonhomogeneous mixture, autoignition would occur first in isolated regions and then give the appearance of propagating through the rest of the mixture as adjacent regions reached incipient ignition conditions. The apparent rate of propagation would be dependent upon the degree of homogeneity, which could explain the various velocities reported for knocking combustion (*59*).

Experimental Techniques

A large number of experimental engine techniques have been developed in the course of investigating the knock phenomenon. Highly instrumented, precision knock-rating engines have been used in studying the knock characteristics of various hydrocarbon compounds (*4*, *80*), hydrogen (*5*, *6*, *36*, *65*), carbon monoxide (*6*), and formaldehyde (*36*) under a wide variety of conditions. These findings have provided a broad picture of the knock mechanism and, in addition, have defined the effect of various physical factors on this mechanism.

Various modifications of the normal spark-ignited engine have been made to increase the utility of the engine as a research tool. Using these modified engines, the chemical and physical phenomena accompanying the knock reactions have been studied in detail. A brief description of these experimental techniques is included in this review.

Motored Engine. The motored engine technique, first used by Peletier and associates (*109*) and Damkohler and Eggersglus (*31*) has been developed into a quantitative method by Retailiau, Richards, and Jones (*112*, *113*) and Pastell (*107*). In the motored engine the fuel-air charge is compressed without spark ignition to simulate conditions to which the end gas of a fired engine is subjected. The entire motored engine charge is considered as the end gas, thereby overcoming many experimental difficulties associated with the study of fired-engine end gas reactions. The reactions leading to autoignition in the motored engine are considered to be the same reactions leading to knock in the fired engine. Pastell (*107*) has demonstrated that autoignition in the motored engine and trace knock in the fired engine occur at essentially the same temperatures and pressures. Davis, Smith, Malmberg, and Bobbitt (*33*) have concluded that the same types and yields of intermediate oxidation products are formed in motored and fired engines when the preflame reaction mixture is compressed along the same pressure-temperature-time path in both engines. Careful selection of motored engine conditions to achieve the same pressure-temperature-time path as in the end gas of the fired engine is necessary (*118*, *120*).

A modified version of the motored engine technique was developed by Levedahl and Howard (*71*) to study the events occurring in a single autoigniting cycle. These investigators equipped the engine with a pressure-limiting device which prevented compression of the inducted fuel-air charge in the cycles preceding the test cycle. During the test cycle the engine proceeded through the normal compression process which resulted in autoignition at or near top dead center. This apparatus was used in one series of experiments to study the influence of residual gases from one cycle on the preflame reactions of the succeeding cycle. In a sequence of two autoigniting cycles the reaction products remaining in the combustion chamber from the first cycle were reported to have an accelerating effect on the reactions of the second cycle. Contrary to this conclusion, the acceleration effect probably was due to an over-all temperature increase of the second cycle charge as a result of increased heat transfer from the hot walls and residual gases.

Radiation and Ignition Studies. The existence of cool flame radiation prior to the occurrence of autoignition in a motored engine was discovered early by Peletier, van Hoogstraten, Smittenberg, and Kooiman (*109*). Since then there has been a constant effort to define the engine conditions limiting the occurrence and extent of cool flame radiation with various hydrocarbons (*25*, *26*, *37*, *71*, *72*, *77*, *107*).

Motored engine cool flames are discernible with the naked eye only with great difficulty, hence the reliance on detection apparatus for quantitative investigations. The essential features of radiation detection apparatus, such as shown in Figure 1, include a quartz window mounted in the combustion chamber, a photomultiplier radiation detector, and an amplifier-oscilloscope arrangement (*107*).

Investigations of preflame radiation have been confined primarily to motored engines because of the difficulty of isolating such radiation in firing engines (*11*, *36*). Wentworth and Daniel (*131*), and Getz (*53*) in recent investigations, however, have observed the appearance of cool flame radiation before the passage of the hot flame in a spark-ignited engine.

Sampling Studies. To obtain a better understanding of the chemistry of preknock reactions, a number of investigators have sampled and analyzed hydrocarbon-air mixtures undergoing preflame oxidation in engines. The types and concentrations of some of the more stable intermediates taking part in these reactions have been determined. While

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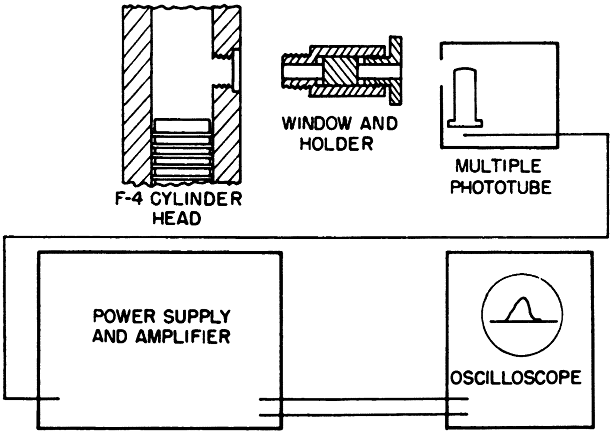

Figure 1. Block diagram of cool flame radiation detection equipment

many of the species formed in the reaction mixture are too short-lived to permit direct analysis, inferential evidence as to their existence and concentration was obtained.

One sampling technique involves the use of an electromagnetic sampling valve which removes a small amount of the mixture in the combustion chamber at a prescribed time in each cycle over the course of many cycles (*37*, *134*). The gas sample is led through a passage to a collection vessel, condensing system, or absorption column. By carrying out this sampling operation at a number of different points in the cycle, the preflame reactions can be followed from initiation to knock. This technique, applicable to both motored and fired engines is subject to certain limitations, the most serious of which is the relationship of the sample to the remainder of the reaction mixture. By nature of the sampling process, the sample has been in close contact with the wall, which is known to affect oxidation reactions. Turbulence, while lessening the effect of this factor, introduces another complicating factor—the same volume is not being sampled in successive experiments. The large surface-to-volume ratio of the sampling valve passages affects the composition of the sample as evidenced by the formation of polymer-type deposits in these passages. Cooling and shortening these passages have overcome this problem to some extent (*33*). A comprehensive study of sampling techniques by Williams, Johnson, and Carhart (*132*) points out the importance of the above-mentioned factors in oxidation studies.

In an effort to overcome some of the difficulties associated with the use of the sampling valve, a second procedure has been developed which involves sampling and analyzing the exhaust gases of a motored engine (*33*, *105*, *113*). A probe mounted in the exhaust passage directs a portion of the exhaust gases to a condensing train or an absorption column. One advantage of this technique is that the high temperature section of the probe can be kept to a minimum, which reduces the tendency of the probe surface to cause further reaction of the sample. A second advantage is that the gas sample is representative of the gas mixture which has been stressed in the engine. In a typical set of experiments, the amount of preflame reaction is varied from that of no reaction to that of incipient autoignition by varying the peak cycle temperature and pressure. Gas samples representative of various stages in the course of the knock reactions are obtained by sampling at different conditions of peak cycle temperature.

Many analytical techniques have been developed specifically for the analysis of engine exhaust gases with major emphasis having been placed on procedures for organic peroxides, hydrogen peroxide, formaldehyde, acetaldehyde, higher carbonyl compounds, acids, and various hydrocarbon compounds (*31*, *36*, *48*, *64*, *83*, *84*, *105*). The mass spectrometer also has been used successfully (*100*).

Photographic Studies. Beginning with the work of Withrow and Boyd (*133*), many

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photographic studies of knocking combustion have been conducted (*10, 82, 92-5, 104, 135, 137*). The rapidity of the knock process coupled with the difficulty of interpreting high speed two-dimensional photographs of a three-dimensional field are major obstacles to successful research along these lines.

The basic apparatus in these photographic studies of engine combustion consisted of an engine fitted with a large glass or quartz window, optics, and cameras. Various investigators have modified this basic arrangement to obtain higher time resolution (*82*) and combinations of direct, shadow, and schlieren photographs (*10, 82*).

Passage of cool flames and possibly blue flames through the end gas region before autoignition has created some confusion in the interpretation of photographs. In one case, a schlieren effect initially believed to be due to autoignition is now recognized as arising from cool flames (*73*). Other such instances probably exist, particularly involving a second cool flame or blue flame just prior to autoignition.

Spectrometric Studies. Spectrometric techniques have been used by a number of investigators for studying knock reactions, as these techniques identify reaction intermediates in situ without disturbing the course of the reaction. Emission spectra of cool-flame radiation in motored engines were obtained by Levedahl and Broida (*70*) and Downs, Street, and Wheeler (*35*) in the ultraviolet and visible regions by mounting a spectrograph on the engine. Agnew, Agnew, and Wark (*2*) obtained near-infrared emission spectra of cool flames in engines using a monochrometer equipped with a lead sulfide detector.

Thermal Relationships

Preflame reaction in an engine is accompanied by a pressure increase attributable to two factors: heat of reaction raising the temperature and hence pressure of the confined charge, and increase in the number of molecules of the system. The effect of the second factor is very slight, on the order of 2% or less of the total pressure increase (*69*). Pastell (*107*) and Rifkin, Walcutt, and Betker (*115*) have determined the pressure increase and the heat release due to preflame reaction for a number of hydrocarbons and have shown that heat release decreases as hydrocarbon knock resistance increases. Pastell found a straight-line correlation of heat release for various hydrocarbons in a motored engine with standard knock ratings of these hydrocarbons (*107*) (Figure 2). Several of the hydrocarbons, including cyclohexane and methylcyclohexane, did not

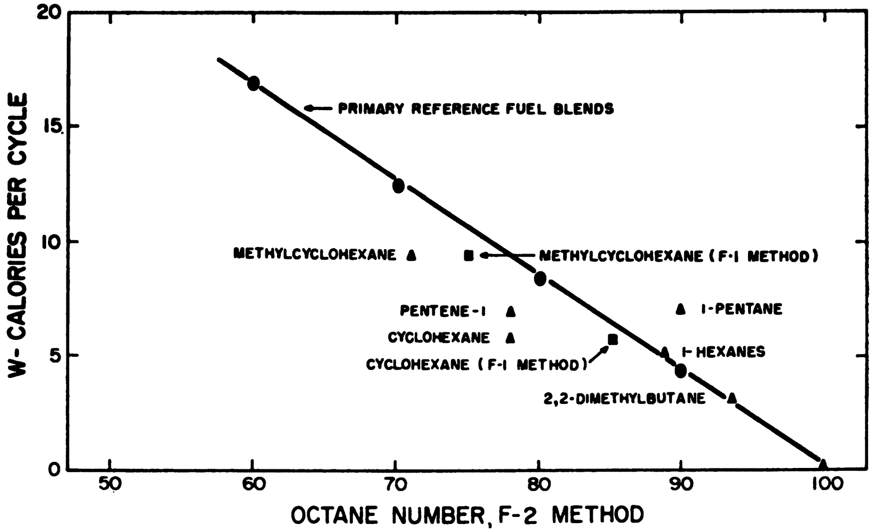

Figure 2. Relationship between fuel octane number and extent of precombustion reactions as measured by work equivalent of the reactions

appear to correlate as well as the other hydrocarbons. Cornelius and Caplan (*25*), in a later study of hydrocarbon blends, concluded that pressure development is not a unique function of the octane level but also is dependent upon hydrocarbon structure. They also demonstrated that engine physical variables affect the extent of preflame reaction in the same way as these variables affect the occurrence of knock. Heat released in preflame reactions of paraffin hydrocarbons can account for as much as 27% of the total energy available (*129*), although the more usual value is less than 10% (*25, 86, 108, 115*).

Rates of pressure development and heat release vary considerably throughout the course of the preflame reactions. In the case of paraffin hydrocarbons, an initial stage of very high heat liberation is followed by a period in which little or no heat is produced, as has been observed in delayed ignition engines (*25*), motored engines (*107, 113*), and rapid compression apparatus (*76, 77*). Cornelius and Caplan (*25*) found the maximum rate of pressure development due to preflame reactions occurred 11° before top dead center for a blend of *n*-heptane and iso-octane. As temperature continues to rise until top dead center, this result is somewhat surprising and suggests that reaction intermediates are being formed which inhibit the over-all mechanism. The existence of this negative temperature coefficient of reaction has been cited by others (*13, 62*).

Radiation

Emission of cool flame radiation is associated with an early stage in the preflame reactions of most hydrocarbons, as evidenced by the fact that the appearance of cool flames occurs at the same time as the initial pressure development. At a later time in the cycle a second radiation phenomena, described as a blue flame, has been observed under certain conditions (*36, 124*). A second cool flame also occurring late in the cycle may be the same phenomenon (*81, 103, 131*). While the importance of cool flame and blue flame phenomena in the over-all reaction mechanism is not fully understood, their occurrences can be used to mark certain stages in the course of the preflame reactions. This principle has been used extensively in studying the effect of hydrocarbon structure, physical variables, and additives on engine preknock reactions.

Downs, Walsh, and Wheeler (*36*) determined cool flame, blue flame, and hot flame limits for a wide variety of hydrocarbons in a motored engine as a function of fuel-air ratio. *n*-Heptane at half stoichiometric conditions formed cool flames (blue glow) at a compression ratio of 7.5, blue flames at 8.1, and white flames at 8.2. As the fuel-air ratio was increased, the blue flame and hot flame limits decreased while the cool flame limit increased. Pastell (*107*) found the cool flame region of *n*-heptane to be nonexistent at high manifold pressures, while at low pressures the cool flame region was very broad. Other factors such as mixture composition, oxygen concentration, and engine speed have been found to affect the extent of the *n*-heptane cool flame region (*26, 89*). These observations suggest that the autoignition process consists of several interrelated reaction mechanisms. The relative importance of each of these postulated mechanisms shifts not only with physical factors such as pressure, temperature, and time but also with chemical environment. This complicates the problem of understanding the over-all knock mechanism and gives rise to conflicting observations and conclusions.

Several hydrocarbons, including benzene, diisobutylene, and methane, do not form cool flames in engines (*26, 37, 105*). The absence of cool flame radiation does not indicate the absence of preflame reaction, as oxidation products have been isolated from a diisobutylene-air mixture in a motored engine (*105*). At lean air-fuel ratios, benzene, diisobutylene, and methane have been observed to form blue flames (*36*).

The nature of the radiation processes is not fully understood. Ball (*10, 11*), with the aid of a stroboscopic shutter, visually observed cool flames as actual flame fronts moving across the combustion chamber of a motored engine. This was later confirmed by Getz (*53*). The source of cool flame emission in tube experiments has been attributed to excited formaldehyde by Emeleus (*51*) and Gaydon (*52*). Cool flame spectra in engines obtained by Levedahl and Broida (*70*) and Downs, Street, and Wheeler (*35*) were reported to be due to excited formaldehyde. The nature of the blue flame spectra has not been fully explored, although some evidence points to carbon monoxide emission (*35*).

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Preflame Reaction Chemistry

Although preknock reactions are extremely rapid and involve highly reactive species, sampling studies of some of the more stable intermediates such as peroxides and carbonyl compounds have yielded inferential evidence about the course of these reactions. Wide differences in the knocking behavior of various fuel types are reflected in different oxidation patterns exhibited by representative pure hydrocarbons in engines.

n-Paraffins. The preflame reactions of *n*-heptane in a motored engine are characterized by the formation of large amounts of organic peroxides, hydrogen peroxide, higher aldehydes and ketones, formaldehyde, and unsaturates as shown in Figure 3 (*105*). The multistage character of the *n*-heptane oxidation can be seen from the composition curves. The first stage was initiated at 340° C. with the formation of organic peroxides, olefins, and higher carbonyl compounds. At a slightly higher temperature, but still in the precool flame region, hydrogen peroxide and formaldehyde were formed. Further thermal stressing resulted in the appearance of cool flames and the beginning of the second stage of reaction. Pronounced suppression of the reactions occurred in the second stage, as evidenced by the much slower build-up in the concentrations of the intermediate products. This suppression could be due to inhibition by some intermediate such as formaldehyde or an unsaturated compound, as these derivatives are known to inhibit hydrocarbon oxidation reactions (*27*, *28*).

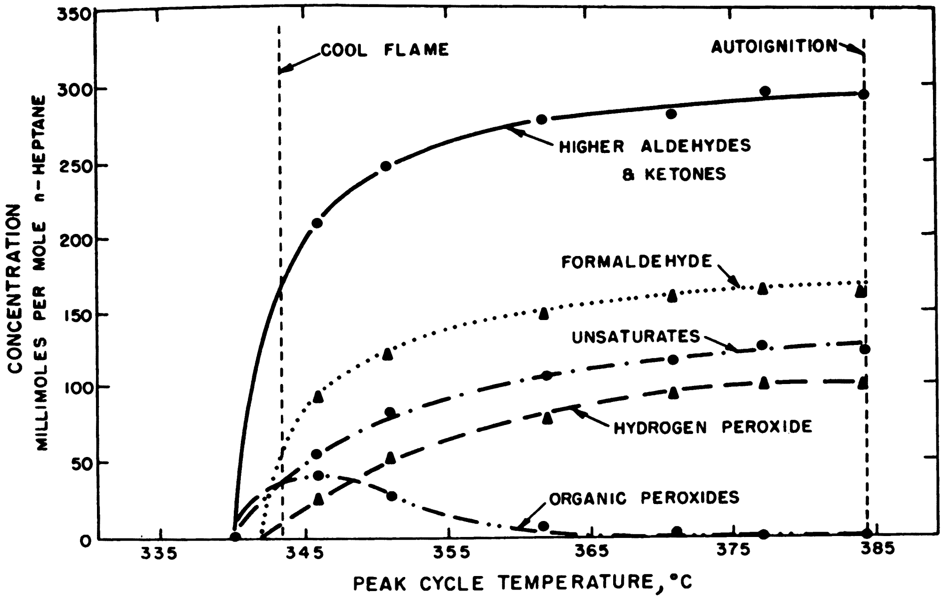

Figure 3. Exhaust gas composition for n-heptane

Organic peroxides, which have been singled out as important intermediates in preknock reactions, are formed in large quantities very early in the course of the preflame reactions (*69*, *100*, *105*, *106*). While the proknock character of peroxides as fuel additives is well known (*49*), Oberdorfer (*102*) has been able to establish further that precool flame products formed in a tube induce knock in engines. A study of the behavior of *tert*-butyl hydroperoxide in a motored engine has shown that cool flames can result from recombination of peroxide decomposition products (*105*). Oxygen appears to take part in the cool flame reactions, however, because peroxide decomposition in a nitrogen atmosphere did not produce cool flames (*124*).

Formaldehyde and acetaldehyde have been identified by Davis, Smith, Malmberg, and Bobbitt (*33*) as the major carbonyl compounds formed in the preflame reactions of

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n-pentane. The same investigations showed that propionaldehyde, acrolein, and crotonaldehyde were formed in appreciable amounts. The importance of carbonyl compounds in hydrocarbon preflame reactions is not very well understood. The formation of carbonyl compounds has been correlated with integrated cool flame intensity (*85*), which may be due to the previously cited role of formaldehyde in the cool flame reactions. Acetaldehyde and other higher aldehydes have little effect on the oxidation reactions and knock characteristics of paraffin hydrocarbons (*3*, *17*, *56*, *89*). Formaldehyde, which is considered to be an oxidation inhibitor, appears to knock by a high temperature mechanism when used as an engine fuel (*33*).

Conversion of the original hydrocarbon to other compounds appears to be extensive in the reactions preceding autoignition, as found in one investigation in which 70% or more of the inducted *n*-heptane was degraded to other products prior to autoignition (*105*). Hydrocarbon structure has an important bearing on the amount of conversion, as other studies have shown that *n*-hexane (*100*) and iso-octane (*105*) undergo less extensive oxidation. Although the course of the final autoignition reactions for *n*-heptane is dependent upon preceding reactions, certain characteristics distinguish the final process from the rest of the reaction. Under some engine conditions the final autoignition reactions occur so rapidly that it is impossible to follow them experimentally, as shown in Figure 3 (*105*). In later studies (*124*), however, under half stoichiometric conditions the autoignition step of *n*-heptane was slowed down sufficiently to enable the investigators to follow the intermediate concentrations in the autoignition or blue flame region (Figure 4). In this region hydrogen peroxide and formaldehyde concentrations rose rapidly, coupled with degradation of higher carbonyl compounds. Rapid formation of these simple products reflects formation of a large number of reactive radicals and liberation of considerable heat.

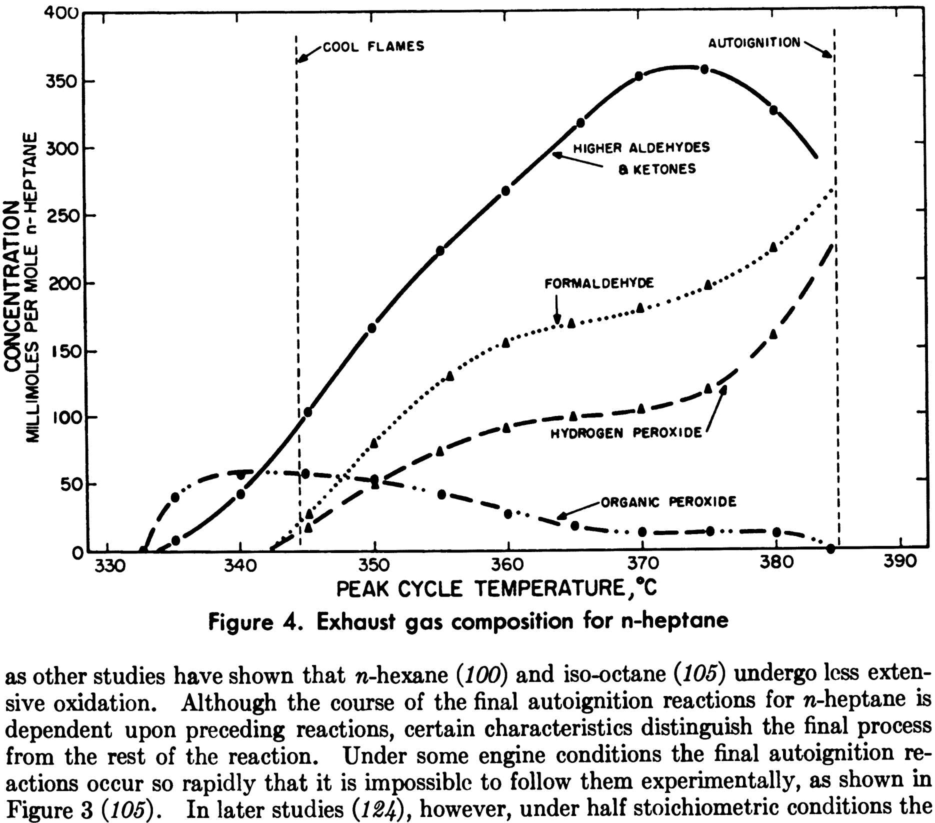

Figure 4. Exhaust gas composition for n-heptane

Motored engine sampling studies of iso-octane similar to those for *n*-heptane (Figure 3), shows this hydrocarbon behaves in general like *n*-heptane. The concentration of intermediates formed, however, were approximately one tenth those for *n*-heptane, even though the iso-octane–air mixture was stressed to higher temperatures. This attributed to the higher oxidation resistance of iso-octane as predicted by various investigators (*58*, *78*).

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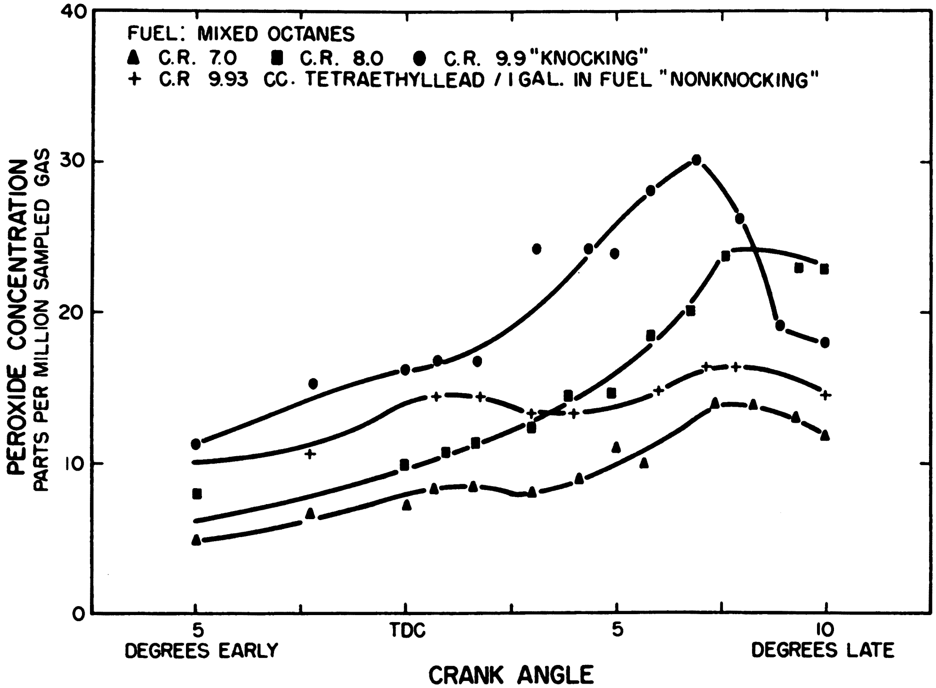

Figure 5. Peroxide concentrations in gases sampled from engine at various crank angles (36)

Downs and Wheeler (*37*) in sampling studies of mixed octanes using an electromagnetic sampling valve observed two peaks in the peroxide concentration, one occurring early in the cycle, the other later as shown in Figure 5. The peroxide concentrations, as determined by the authors, represent the summation of both the hydrogen peroxide and organic peroxide concentrations. One explanation for these data is that the first peak is primarily due to organic peroxides and the second to hydrogen peroxide, which is in agreement with the results of other investigators (*105*). The decay in the first peak corresponds to decomposition of organic peroxides which leads to the formation of hydrogen peroxide through recombination or further reaction of the peroxide decomposition products.

Olefins. The preflame reactions of diisobutylene are different in many respects from those of the paraffin hydrocarbons. Attempts to observe cool flame radiation with this hydrocarbon were unsuccessful (*36*, *105*). However, blue flame behavior has been reported (*36*). Sampling studies of diisobutylene have been carried out in a motored engine with intermediate concentrations being determined throughout the preflame reaction period as given in Figure 6 (*105*). These studies showed the initial stages of the diisobutylene preflame reactions to be inhibited by some mechanism, presumably by diisobutylene itself. This behavior was a direct contrast to the preflame reactions of iso-octane, which proceeded very rapidly in the early stages. The investigators postulated that the inhibiting mechanism deactivated free radicals leading to the formation of excited formaldehyde, thus accounting for the absence of cool flame radiation. The ability of diisobutylene to inhibit the oxidation reactions of hydrocarbon blends containing it as a component has been well established (*25*, *27*, *124*). Such properties, however, are not characteristic of all olefin hydrocarbons, because the long-chain olefins act more like the *n*-paraffins (*125*).

Aromatics. Investigators (*36*) in a sampling study of six different aromatic hydrocarbons did not find significant amounts of peroxidic compounds being formed prior to

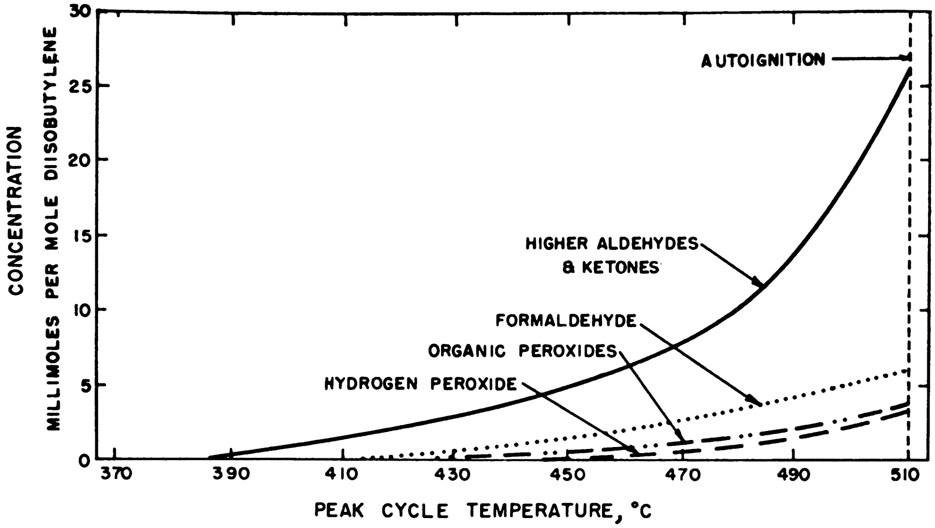

Figure 6. Exhaust gas composition for diisobutylene

autoignition, even for the hydrocarbon having the longest side chain. Other studies (*105*) demonstrated the absence of any oxidation intermediates prior to the final autoignition process of benzene. Limitations of sampling procedures undoubtedly prevent following the obviously rapid reaction mechanisms leading to autoignition of these hydrocarbons.

Hydrogen and Carbon Monoxide Combustion

The knock characteristics of hydrogen and carbon monoxide provide an insight into the nature of the knock process. Downs, Walsh, and Wheeler (*36*) and Anzilotti, Scott, Rogers, and Tomsic (*5*) demonstrated that hydrogen knocks in engines and has good tetraethyllead response. Over a wide range of fuel-air ratios, hydrogen acts much like the paraffin hydrocarbons and approaches iso-octane in knock resistance, as shown in Figure 7 (*5*). These similarities in the knock behavior of hydrogen and the paraffin hydrocarbons suggest that a simple hydrogen-oxygen reaction plays a major role in the reactions leading to hydrocarbon knock.

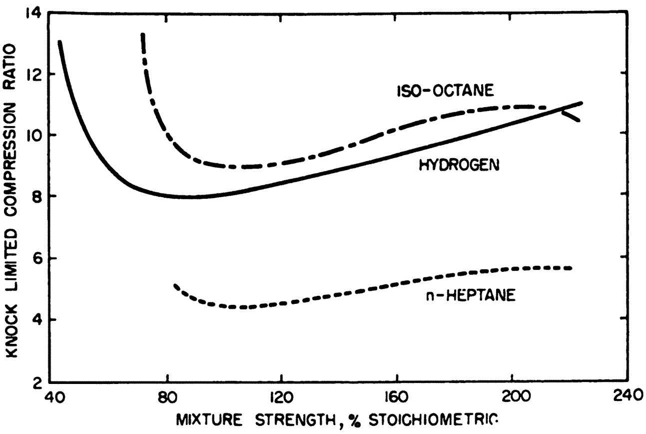

Figure 7. Knock characteristics of hydrogen, n-heptane, and iso-octane

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The importance of hydrogen-containing species in knock reactions is strikingly shown in knocking combustion studies of carbon monoxide by Anzilotti and Tomsic (*6*). The presence of 1.4 mole % of water markedly lowered the knock resistance of nearly anhydrous carbon monoxide. Other studies show that water enters into the combustion reactions of carbon monoxide and contributes hydrogen to the intermediate combustion products (*125*).

Downs, Walsh, and Wheeler (*36*) determined the effect of hydrogen on the knocking tendencies of benzene, methane, iso-octane, and cyclohexane. In benzene and methane, hydrogen had a proknock effect, and in cyclohexane and iso-octane it had an antiknock effect for initial hydrogen additions and then a proknock effect. As these authors have explained, this was due to the accelerating effect of hydrogen on flame velocity, which reduced the time available for knock to occur. Anzilotti and Tomsic (*6*) showed the burning rate of hydrogen in an engine to be three times as fast as that of iso-octane. The fuels in which hydrogen had a proknock effect at low concentrations, knock by a high-temperature mechanism, whereas cyclohexane and iso-octane knock by a mechanism involving considerable preflame activity. Time available for preflame reactions is expected to have a greater effect on the latter hydrocarbons. This finding stresses again the importance of the different stages in the knock process and points up the difficulty of interpreting a single set of results in terms of the over-all reaction.

Role of Antiknocks

Early theories of antiknock action have suggested that the antiknock absorbed electrons and slowed flames (*130*), absorbed hydrogen atoms and slowed flames (*126*), promoted slow oxidation which lowered fuel energy available to cause detonation (*23*), destroyed peroxides or other oxidation promoters (*127*), destroyed free radicals, thereby breaking reaction chains (*42*), and produced metal or metal oxide surfaces which acted as walls in breaking reaction chains (*55*). The chain-breaking theory, involving perhaps heterogeneous catalysis, has gained general acceptance as the mechanism by which tetraethyllead exerts its antiknock activity. Engine experiments involving pressure measurements, heat release determinations, and chemical analysis of preknock reaction mixtures support this theory.

Pressure development due to preflame reactions of paraffin hydrocarbons is affected little by the presence of tetraethyllead even though autoignition is suppressed (*25*, *115*). In one series of experiments (*25*), increasing fuel quality 10 octane numbers reduced the pressure development 10 pounds per square inch, while addition of tetraethyllead to achieve the same 10 octane number increase resulted in a decrease of only 2 pounds per square inch. These findings indicate that tetraethyllead is specific in its activity, inhibiting only certain types of reactions leading to the final autoignition step.

Tetraethyllead has little effect on the point of cool flame appearance but shifts the point of autoignition to more severe conditions (*89*, *107*). These findings and the ineffectiveness of tetraethyllead in reducing preflame pressure development indicate that this compound has little effect on the early oxidation reactions. Radiation occurring late in the engine cycle described as a blue flame (*124*), or second cool flame (*25*, *81*), was markedly reduced by the addition of tetraethyllead. Inhibition of the reactions giving rise to blue flame phenomena by tetraethyllead has been associated with inhibition of chain-branching reactions, occurring at the same time, which lead to the final ignition.

Sampling studies of *n*-heptane in engines have shown tetraethyllead to be ineffective in inhibiting the formation of organic peroxides, higher carbonyl compounds, and olefins (Figure 8) (*105*). This antiknock, however, markedly reduced the concentrations of hydrogen peroxide and formaldehyde. Tetraethyllead is visualized as deactivating free radicals, formed in part from organic peroxide decomposition, which could lead to hydrogen peroxide or formaldehyde formation. These same radicals are conceived to be critical species in the chain reactions leading to knock. In the case of the *n*-heptane experiments where the autoignition reactions were slowed down, the rapid formation of hydrogen peroxide was slowed and delayed (*124*).

The antiknock effectiveness of tetraethyllead when hydrogen is used as the fuel

(*5, 6, 36*) points to deactivation of one or more species containing hydrogen and oxygen as the antiknock mechanism. Chamberlain and Walsh (*22*) have obtained experimental evidence suggesting that the HO_2 radical is the critical specie which is deactivated. The much greater tetraethyllead response of carbon monoxide when water vapor is present lends further support to the theory that tetraethyllead functions by interfering with reactions involving the hydrogen and hydrogen-oxygen radicals.

Considerable controversy exists as to the identity of the active antiknock species when tetraethyllead is used in the fuel. Egerton and coworkers (*44-8*) concluded that antiknock substance must be oxidized, molecularly dispersed, and capable of existence in several stages of oxidation. Chamberlain, Hoare, and Walsh (*21*), in a series of detailed and comprehensive studies, concluded that tetraethyllead acts as an inhibitor by virtue of forming lead oxide (PbO). A large amount of additional evidence has been cited supporting the metal oxide theory (*57, 79, 99, 128, 138*).

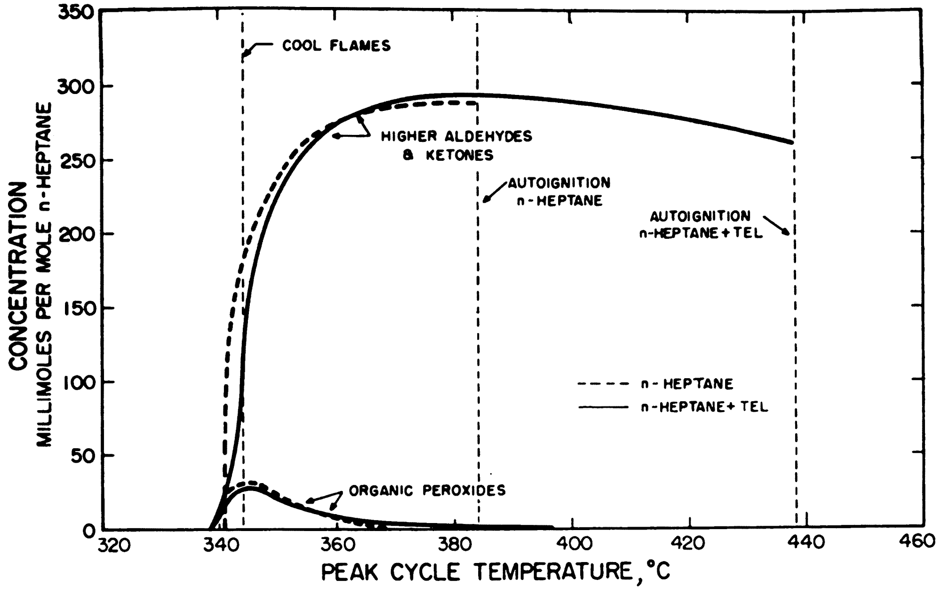

Figure 8. Effect of tetraethyllead on n-heptane oxidation

Early experiments of Berl and coworkers (*15, 16*), together with the findings of Withrow and Rassweiler (*136*), support the metallic theory of antiknock action. In Berl's work colloidal lead exhibited antiknock action, while colloidal lead oxide had no effect. Spectra of engine knocking combustion obtained by Withrow and Rassweiler showed the presence of metallic lead but not lead oxide or other lead oxides. The metallic theory is also supported by other investigators (*96, 101, 114*).

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Surface Ignition of Fuels in Engines

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Relative surface ignition resistance of fuels in engines could be predicted from data obtained in the laboratory: heat of combustion of the fuel, heat capacities of the fuel and its products, radiant energy of flames, ignition energies at the temperature and pressure existing in an engine at the time surface ignition occurs, extent and nature of preflame reactions at these temperatures and pressures, effect of fuel-air ratio on energy required for ignition at the temperature and pressure existing in an engine, and the relative activity of the igniting surface under the conditions existing in an engine. General experience has been that there are no short cuts. It is simpler and more satisfactory to measure surface-ignition resistance in an engine operating under the conditions of interest.

Internal combustion engines are designed to deliver the maximum amount of useful work when the fuel-air mixture is ignited solely by a timed spark and the flame moves completely across the combustion chamber in a uniform manner at a normal velocity.

Two generally recognized combustion phenomena considered undesirable in an engine are knock and uncontrolled ignition of the fuel-air mixture by hot surfaces within the combustion chamber. Knock differs from normal combustion in that the flame, initiated by the spark, advances at the normal rate through the charge, but before combustion is complete a portion of the charge begins to burn very rapidly. The sudden release of energy resulting from the rapid burning may be accompanied by a characteristic noise caused by vibration of the engine structure. Uncontrolled ignition is said to occur when the flame is initiated at some location in the combustion chamber different from the spark plug and at a different time in the cycle from the occurrence of the timed spark. The speed of a flame front initiated by a hot surface is identical with that following regular spark ignition (*10, 77, 79*). The actual event of ignition by hot surfaces is silent, but before the charge is entirely consumed knock may occur in the same manner as if the flame were initiated by the timed spark (*4, 38, 65, 66, 74, 92*). This ignition is commonly called either preignition or postignition, depending on the time of initiation relative to the firing of the spark (*73, 95*).

Much of the work reported in the literature does not distinguish between preignition and postignition, and preignition is often applied to the general phenomenon. The term surface ignition is used in this review in the sense given in a report issued recently by a Coordinative Research Council panel on nomenclature (*17*). The definitions recommended by this group are given in Table I.

The effect of preignition on engine efficiency can be illustrated by the pressure-volume diagram shown in Figure 1 (*52*). In the ideal engine process, *ABCD*, combustion

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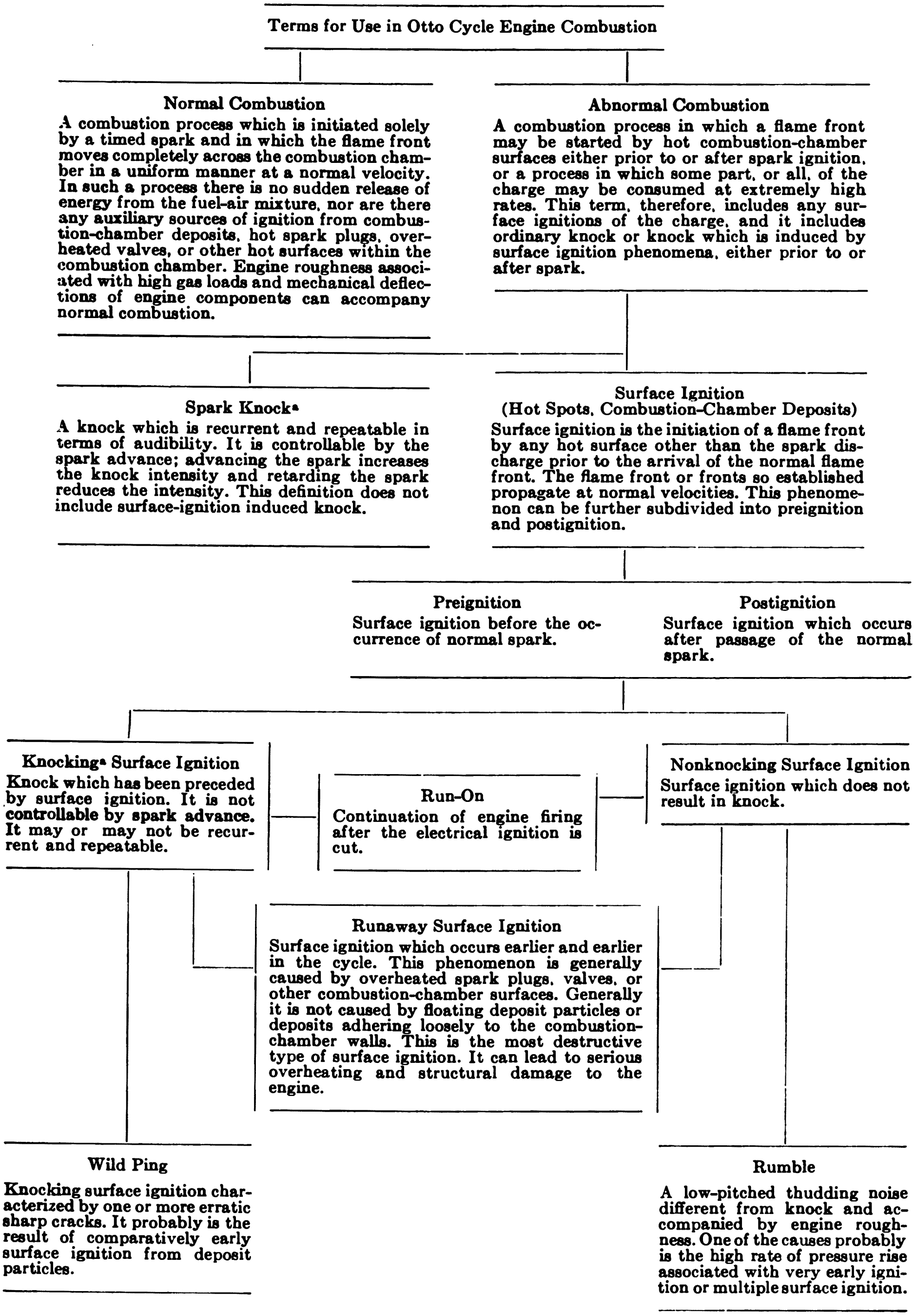
Table I. Terms for Use in Otto Cycle Engine Combustion



Terms for Use in Otto Cycle Engine Combustion

Normal Combustion
A combustion process which is initiated solely by a timed spark and in which the flame front moves completely across the combustion chamber in a uniform manner at a normal velocity. In such a process there is no sudden release of energy from the fuel-air mixture, nor are there any auxiliary sources of ignition from combustion-chamber deposits, hot spark plugs, overheated valves, or other hot surfaces within the combustion chamber. Engine roughness associated with high gas loads and mechanical deflections of engine components can accompany normal combustion.

Abnormal Combustion
A combustion process in which a flame front may be started by hot combustion-chamber surfaces either prior to or after spark ignition, or a process in which some part, or all, of the charge may be consumed at extremely high rates. This term, therefore, includes any surface ignitions of the charge, and it includes ordinary knock or knock which is induced by surface ignition phenomena, either prior to or after spark.

Spark Knock[a]
A knock which is recurrent and repeatable in terms of audibility. It is controllable by the spark advance; advancing the spark increases the knock intensity and retarding the spark reduces the intensity. This definition does not include surface-ignition induced knock.

Surface Ignition
(Hot Spots, Combustion-Chamber Deposits)
Surface ignition is the initiation of a flame front by any hot surface other than the spark discharge prior to the arrival of the normal flame front. The flame front or fronts so established propagate at normal velocities. This phenomenon can be further subdivided into preignition and postignition.

Preignition
Surface ignition before the occurrence of normal spark.

Postignition
Surface ignition which occurs after passage of the normal spark.

Knocking[a] **Surface Ignition**
Knock which has been preceded by surface ignition. It is not controllable by spark advance. It may or may not be recurrent and repeatable.

Run-On
Continuation of engine firing after the electrical ignition is cut.

Nonknocking Surface Ignition
Surface ignition which does not result in knock.

Runaway Surface Ignition
Surface ignition which occurs earlier and earlier in the cycle. This phenomenon is generally caused by overheated spark plugs, valves, or other combustion-chamber surfaces. Generally it is not caused by floating deposit particles or deposits adhering loosely to the combustion-chamber walls. This is the most destructive type of surface ignition. It can lead to serious overheating and structural damage to the engine.

Wild Ping
Knocking surface ignition characterized by one or more erratic sharp cracks. It probably is the result of comparatively early surface ignition from deposit particles.

Rumble
A low-pitched thudding noise different from knock and accompanied by engine roughness. One of the causes probably is the high rate of pressure rise associated with very early ignition or multiple surface ignition.

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[a] Knock. The noise associated with autoignition of a portion of the fuel-air mixture ahead of the advancing flame front. The flame front is presupposed to be moving at normal velocity. With this definition the source of the normal flame front is immaterial. It may be the result of surface ignition or spark ignition.

Autoignition. The spontaneous ignition and the resulting rapid reaction of a portion or all of the fuel-air mixture. The flame speed is many, many times greater than that which follows normal spark ignition. There is no time reference for autoignition.

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occurs from B to C at top dead center. In actual engine operation ignition occurs at B' and combustion ends beyond C' resulting in less work than is obtained from the ideal process. If preignition occurs at B'', the ideal process is given by the diagram $AB''C''D''$, which represents less work than is obtained from the spark-ignition process. The limiting case is preignition at A with combustion from A to E. Compression occurs along the path E to F, point F indicating the maximum possible pressure with preignition. The expansion process is from F to E, irreversible effects being neglected; the net indicated work is zero, and work has to be supplied to maintain operation of the engine.

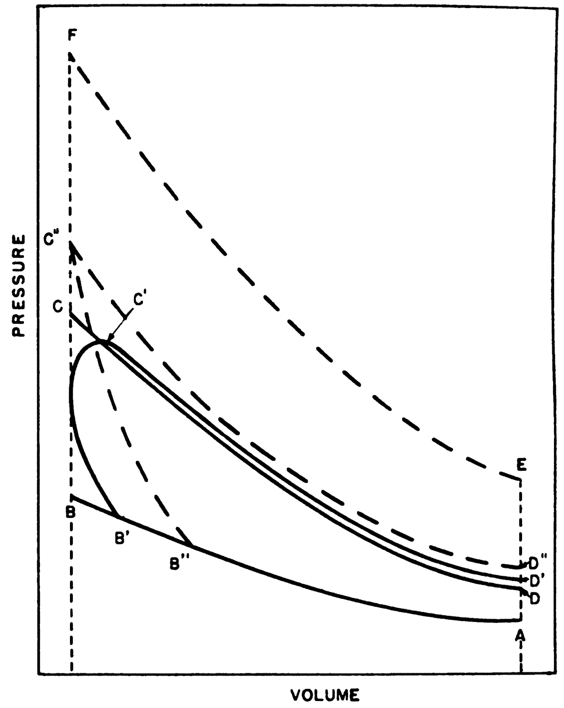

Figure 1. Pressure-volume diagram illustrating effect of preignition

The occurrence of preignition during one cycle sometimes results in further heating of the igniting surface, which causes ignition to occur earlier and earlier in subsequent cycles. This increasing temperature of the engine structure can be the source of spectacular harm, for unless this process is arrested promptly, temperatures rapidly reach the point where seizure of the piston in the cylinder occurs or part of the engine structure melts. Instances have been recorded in which cylinder head temperatures of aircraft engines have increased from 150° to over 350° C. within a few seconds after preignition was detected (*19*, *23*, *41*). Actual temperatures in the combustion chamber increased much more rapidly, because the aluminum piston actually reached the melting point. This "runaway" preignition is usually caused by hot spark plugs or hot exhaust valves and occurs much more frequently in aircraft engines than in automobile engines (*18*, *41*).

History

The uncontrolled ignition of the fuel-air charge in a spark ignition engine has long been recognized as a cause of engine malfunctioning. In 1904, the popular belief was that the performance of spark-ignition engines was limited by the onset of preignition (*71*). Ricardo assisted Hopkinson in a study of the phenomenon. They induced surface

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ignition in an engine by projecting into the combustion chamber a long steel bolt with a thermocouple embedded in the end. When the end of the bolt reached a certain temperature, ignition took place. There were no changes in the indicator diagram at first, but as the temperature rose, ignition took place earlier and earlier until the engine stopped. There was no trace of the knock, familiar in the gasoline or kerosine engine, which was popularly attributed to preignition from some hot spot, nor was the rate of pressure rise different from that when ignition was by timed spark (*71*). The probable reason why Hopkinson and Ricardo did not observe knock in these experiments was the very low compression ratio of their engine and the high octane quality of the illuminating gas which they were using as a fuel (*41*).

Heron (*36*) states that surface ignition was a matter of much interest to European builders of racing cars and motorcycles prior to 1914. This interest was evidenced by their efforts to secure suitable spark plugs, although it is not clear that the workers knew that their troubles were due to surface ignition. Moore (*62, 63*) in 1917 gave a very clear description of surface ignition, stating that it was caused by hot surfaces in the combustion chamber such as spark plugs and valve tops. In 1917 the Rolls-Royce water-cooled aircraft engine began to suffer from surface ignition caused by the mica spark plugs then in use. The bulletin discussing preignition in aircraft engines, issued by Rolls-Royce in 1918, has been reproduced recently by Heron (*36*).

The differences among normal combustion, knocking combustion, and combustion initiated by hot surfaces were recognized by Boyd in 1918 (*8, 9*). Indicator cards obtained at that time clearly showed the basic differences between knock and preignition (*45, 46*). Hallett (*35*) in 1920 attributed surface ignition to hot spots in the combustion chamber and discussed the role of flakes of combustion-chamber deposits in causing this ignition. Sparrow (*78*) in 1925 gave a complete description of knock and preignition.

The introduction of leaded aviation gasoline in 1928 was accompanied by increased occurrence of surface ignition in military aircraft (*36*). Leaded deposits in the combustion chambers may have been partially responsible, but the major cause of the difficulty was the considerable increase in engine output and, hence, increased cylinder temperature permitted by the increased octane number of the leaded fuel. The major sources of the hot surface ignition were exhaust valves and spark plugs. The primary cause of the exhaust valve difficulty was formation of an oxide coating on the head of the valve. This oxide coating had a rough surface, the points and edges of which were readily heated to the temperature which would ignite the fuel-air mixture. Improved valve materials of greater corrosion resistance and sodium cooling of valves introduced in the thirties gradually eliminated exhaust valves as a significant source of surface ignition in aircraft engines. Great improvements were also made in spark plugs during this period. Mica plugs were gradually replaced by ceramic plugs of more uniform heat rating. Breakage of the early ceramic plugs caused by excessive stresses in the cores was a frequent source of surface ignition, but this problem has been largely eliminated (*36*).

Surface ignition again became an urgent subject for investigation during World War II, and considerable progress was made in understanding the effect of engine conditions and of fuel composition on the occurrence of surface ignition (*2, 15*). Since then a great amount of effort has been devoted to study of the occurrence of surface ignition in automotive engines (*10, 27, 61, 89, 92*). The surface ignition problem in automobile engines has been greatly aggravated by the presence of combustion chamber deposits formed under low-duty driving conditions (*95*), and these deposits, rather than exhaust valves or spark plugs, have been recognized as the major sources of surface ignition (*95*).

Methods of Investigation

The earliest method of detecting surface ignition was based on the occurrence of abnormal noise. Ricardo mentions that in 1904 preignition was accompanied by a dull thud, but no trace of the ringing knock was found (*72*). Pressure-time records of combustion also have been used since the early days to detect the occurrence of surface ignition (*8*). A sudden increase in temperature of the cylinder head also has been taken as evidence of the occurrence of surface ignition, whether or not accompanied by noise, and a device has been proposed to detect the onset of surface ignition by monitoring the cylinder head temperatures of aircraft engines (*21*). Another scheme involves cutting off the spark ignition periodically and determining if ignition continues to occur (*75*).

Recently, electronic instrumentation has been developed to detect surface ignition. One method is based on the rate of pressure rise as measured by a time-rate-of-change-of-pressure pickup in the combustion chamber (*58*), and another involves the detection of flame fronts other than those originating at the normal firing spark plug. The latter method is based on the use of an ionization gap located at some distance from the spark plug to detect the presence of a flame.

Electronic circuits have been devised which can be used to establish whether or not a particular flame front is initiated by the normal firing of the spark plug or by hot surfaces in the combustion chamber (*34, 38, 39, 50*). Another scheme employs the spark plug as the ionization gap to detect flame fronts not initiated by the normal firing of the plug (*93*).

Factors Involved in Occurrence of Surface Ignition

There is now general agreement that surface ignition is caused by hot surfaces within the combustion chamber of an engine, either combustion chamber deposits, or overheated metal surfaces of the chamber. The temperature of these surfaces, composition, area, configuration, and location are important factors in initiating surface ignition in an operating engine. The design of the particular engine and the operating conditions are very important (*53*). The nature of the fuel and the lubricating oil also affects the occurrence of surface ignition.

Effect of Engine Conditions. The relative occurrence of surface ignition is dependent on engine design. Modern overhead-valve automotive engines are less susceptible to surface ignition than L-head engines (*38*). The actual factors involved are complex, but it is obvious that cooling of combustion chamber surfaces and scavenging of combustion chamber deposits are of great importance. The mechanical condition of an engine is also important because of the effect of such factors as large piston clearances, large ring gaps, improper alignment of rings, scuff marks on cylinder walls, and condition of exhaust valves in causing local areas to become overheated and promoting the occurrence of surface ignition (*15*).

Increasing the compression ratio of a given design of combustion chamber generally increases the occurrence of surface ignition because of increased peak-cycle temperatures (*58*). Male found that at stoichiometric fuel-air ratio in a supercharged [cooperative fuel research (CFR)] engine the effect of increase of compression ratio was to decrease the pre-ignition-limited [indicated mean effective pressure (IMEP)] by about 10 pounds per square inch per unit change of compression ratio (*55*). Serruys has stated that an increase in compression ratio of his engine from 5.54 to 1 to 6.52 to 1 reduced the hot-spot temperature required for ignition from 1832° to 1787° F. (*41, 75*).

Fuel-air ratio is an important factor in the occurrence of surface ignition because of its effect on the ignition of the charge and the temperatures reached by the combustion chamber surfaces. The actual distribution of the fuel within the combustion chamber also is very important, as local too-lean or too-rich mixtures will not be ignited by a hot surface which otherwise would cause ignition. This factor is difficult to study and is one reason for the difficulty in reproducing the occurrences of ignition in an engine by hot spots at different locations (*79*). In general, surface ignition is more likely to occur with a fuel-air ratio about 10% rich (*1*), probably because of the greater heat release which results in higher temperatures of the combustion chamber surfaces (*22*).

The effect of increasing the manifold pressure is to increase the occurrence of surface ignition. A greater amount of fuel is burned per unit time, and the hotter combustion chamber surfaces are more likely to cause ignition of the charge. The mixture is heated to higher temperatures, and precombustion reactions are likely to occur to a greater extent, thus increasing the ease of ignition of the charge (*58*). Serruys found that decreasing the intake-manifold pressure increased the critical hot-spot temperature required

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for surface ignition (*75*). Alquist and Male found with a supercharged CFR engine that the temperature of the hot spot required for surface ignition decreased about 70° F. when the intake-manifold pressure was increased from 30 to 45 inches of mercury absolute (*1*).

Increasing the inlet-air temperature will also increase the occurrence of surface ignition because of the increased cycle temperatures (*58*). This effect is less marked than might be expected because the increased mixture temperature also decreases charge density, which tends to reduce the occurrence of surface ignition (*58*).

The effect of engine speed on the occurrence of surface ignition is complicated by the fact that although increased speed tends to reduce the likelihood of surface ignition by reducing the time of contact between the mixture and hot surfaces, it also increases the occurrence of surface ignition, as more fuel is burned per unit time, and the combustion chamber surfaces reach higher temperatures. A supercharged CFR engine running with a stoichiometric mixture gave minimum values of preignition-limited IMEP at engine speeds between 1500 and 2100 r.p.m. (*55*).

Deposits

The prevalence of surface ignition often has been attributed to the use of leaded gasoline (*23*), but the fact that the phenomenon of surface ignition was recognized before the introduction of tetraethyllead as a fuel additive is evidence that lead compounds are not solely responsible (*95*). Waldeck in 1915 (*88*) and Hallett in 1920 (*35*) expressed the belief that carbon flakes and dust in the combustion chamber can serve as hot spots to cause surface ignition. King has suggested that surface ignition can be caused by finely divided carbon formed in the combustion chamber by the pyrolysis of fuel and lubricating oil (*49*). Campbell (*14*) in 1946 expressed the theory that combustion chamber deposits cause surface ignition because the carbonaceous material in the deposits is heated sufficiently to glow and hence to ignite the fuel-air mixture. Lead compounds deposited with the carbonaceous material, according to Campbell, catalytically lower the ignition temperature of the carbon and affect the ability of carbon to burn after the source of heat is removed. He presented data to show that lead compounds can lower the ignition temperature of carbon from over 1200° to as low as 680° F.

Withrow and Bowditch supported Campbell's theory by obtaining photographs of engine combustion which show that surface ignition can be caused by glowing particles of combustion chamber deposits (*95*). Glowing deposit particles caused ignition either when attached to the combustion chamber surfaces or when they floated as flaked particles in the cylinder for one or more cycles before passing out through the exhaust port.

In another approach to the study of the effect of deposits on surface ignition, deposit particles are injected into the intake system of an operating engine. Sturgis (*81*) and Melby, Diggs, and Sturgis (*58*) devised an engine test using a Waukesha cooperative oil test (COT) engine which readily showed the effect of inducted particles on surface ignition. The occurrence of surface ignition was proportional to the number of inducted particles, large particles were more effective than small particles, and the composition of the particles had a large effect on their efficiency in causing surface ignition. In general, when particles of engine deposits accumulated in other engines were injected into the COT engine, the deposits accumulated by operation on leaded fuel were significantly more harmful than deposits accumulated by operating on unleaded fuel. When particles of pure compounds were injected, pure carbon and pure lead chloride were only moderately harmful, but particles of an intimate mixture of carbon and lead chloride were very harmful, and mixtures of carbon and pure lead oxide were even more harmful. Data of Burk, Test, and Jackson are in agreement with this conclusion (*12*). These results are in agreement with the theory of Campbell that lead salts promote the surface ignition activity of carbonaceous material in combustion chamber deposits (*14*).

The particle injection studies also indicated that lead sulfate alone was more harmful than lead oxide or lead chloride, suggesting that in the absence of catalytic activity on carbon combustion, higher melting compounds are more harmful than materials of lower melting point. Flakes of iron oxide from a corroded exhaust valve and bits of ceramic material from a broken spark plug insulator are very potent sources of surface ignition

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(*36*). Particles of silicon dioxide accumulating in deposits from inducted air containing dust cause surface ignition (*41*). Apparently a material which does not melt readily can be heated on successive cycles to a sufficiently high temperature to cause surface ignition. King, however, has proposed that the reason inducted dust particles can cause uncontrolled ignition in an operating engine is the discharge of static electricity which can develop as the charge passes the restriction of the intake port (*48*).

A temperature of about 2000° F. (at least for metallic surfaces) is required to cause surface ignition (*41*). This means that the aluminum parts of the engine structure, which melt about 1200° F., are not probable sources of surface ignition. With the exception of lead sulfate, the lead compounds usually present in the combustion chamber melt below 2000° F. and could not cause ignition except for the short interval of time while they are being expelled from the combustion chamber in a molten state. Pure carbon will burn in air at about 1200° F. and in the presence of lead salts at temperatures as low as 680° F. (*14*). Hence, carbon should not cause surface ignition except while it is being burned away (*41*).

Analytical data on combustion chamber deposits accumulated from leaded fuel show the presence of both carbonaceous material and lead salts. An analysis of the extreme outer layer of deposits which have been causing surface ignition, however, shows that very little carbon is present and that nearly all the deposit is made up of lead salts (*24, 41*). This observation suggests that the carbonaceous portion of the deposit is consumed in the process of ignition, which is in agreement with the idea that glowing carbonaceous material is an important source of surface ignition (*14*).

Bench tests have been used to study the burning or glowing tendency of combustion chamber deposits and mixtures of carbon and lead salts (*73*). It seemed reasonable to postulate that the higher the temperature of ignition of a deposit particle the less should be its tendency to glow and cause surface ignition in an engine. A shorter duration of glow should also lessen the occurrence of surface ignition, as the probability of the glow enduring over a number of cycles would be diminished. Experimental results indicate that the presence of lead salts cause a substantial decrease of the temperature required to initiate glow and a very large increase in the duration of glow (*12, 73*). A synthetic lead-fuel deposit composed of a mixture of 10% carbonaceous material and 90% various lead salts exhibited the same glow characteristics as actual engine deposits.

Surface Ignition Resistance

Pure Hydrocarbons in Engines. Many workers have measured the relative ignition resistance of pure hydrocarbons in engines; the results, while in general agreement, vary in detail because a wide variety of test procedures have been employed (*22, 39, 55–57, 73, 79, 82*). Most workers have found that benzene and methanol are very prone to surface ignition, while iso-octane is much less so. Downs and Pigneguy have devised a preignition rating system in which iso-octane rates 100, and cumene rates zero. They proposed a comparison of the surface ignition resistance of fuels to blends of iso-octane and cumene in a way analogous to the octane scale based on blends of iso-octane and *n*-heptane (*22*). Downs and Pigneguy employed a Ricardo E.6 variable compression engine equipped with a hot spot and determined the occurrence of surface ignition by an ionization gap in the combustion chamber. Some of their data are presented in Table II.

Sturgis and coworkers (*82*) measured the relative surface ignition resistance of various pure hydrocarbons by a method based on deposit-induced ignition in a CFR

Table II. Preignition Rating of Fuels

Fuel	Preignition Rating
Iso-octane	100
Cumene	0
Benzene	31
Toluene	91
Diisobutylene	50
Xylenes (mixed)	>100
Mesitylene	>100
Methanol	<0

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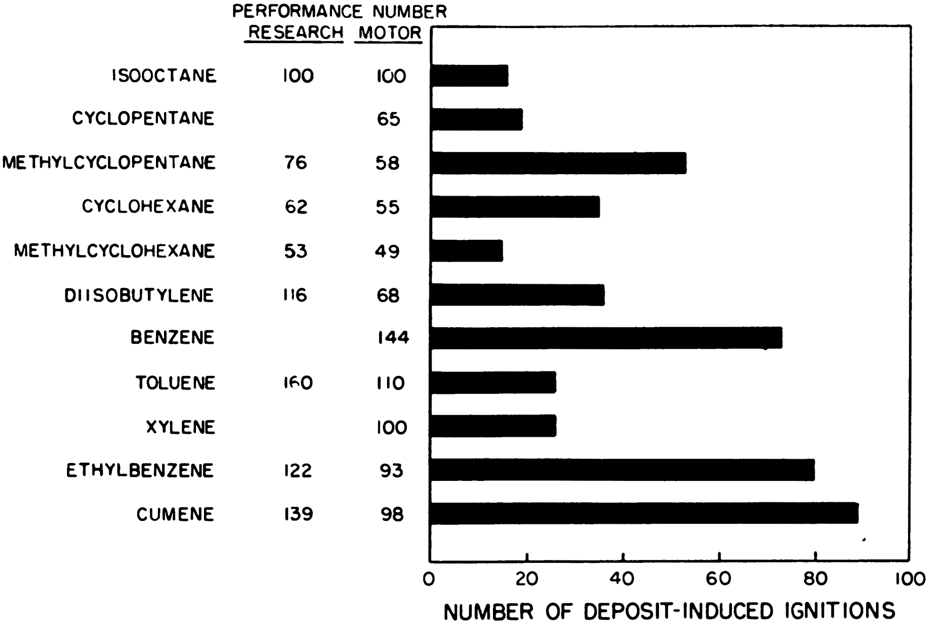

Figure 2. Relative ignition resistance of hydrocarbons

engine and found, as shown in Figure 2, that benzene, ethylbenzene, and cumene were much more prone to surface ignition than iso-octane, cyclopentane, and methylcyclohexane. Toluene and xylene, however, were almost as resistant to surface ignition as iso-octane. A considerable effort was made in these tests to maintain "standard" deposits in the engine, so that the fuels could be rated for intrinsic susceptibility to surface ignition independent of their tendency to contribute to combustion chamber deposits.

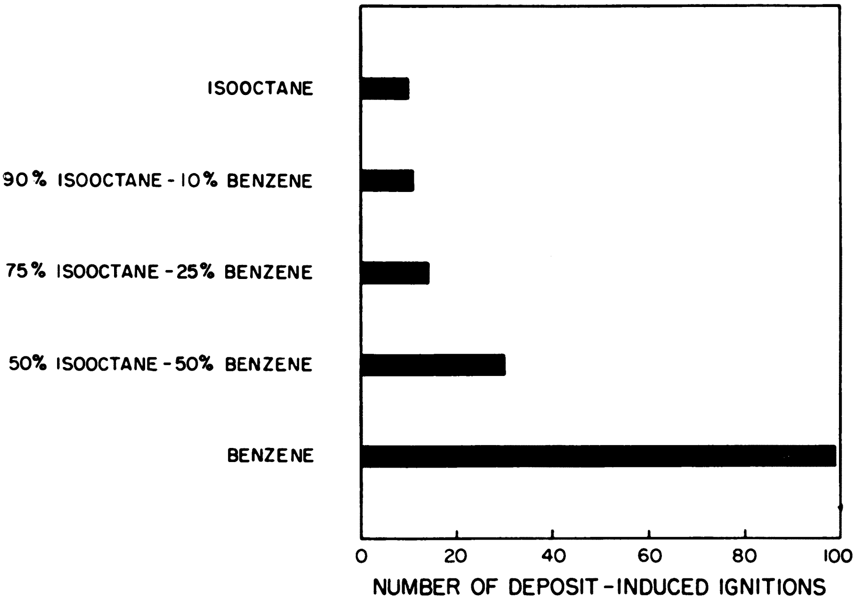

Figure 3. Ignition resistance of iso-octane–benzene blends

The same authors found, with another test procedure using high heat-range spark plugs as the ignition source, that while benzene, ethylbenzene, and cumene were less ignition resistant than iso-octane, toluene and xylene were more resistant. In determining the effect of speed on surface-ignition resistance, it was found that the relative ignition resistance of benzene and diisobutylene was anomalous in that at high engine speeds benzene was more prone to surface ignition than diisobutylene, while at low speeds the reverse was true.

The behavior of hydrocarbon blends with respect to surface ignition resistance is particularly important, since many blending stocks now available are highly aromatic in character. The results of tests made on blends of iso-octane and benzene with a deposit-induced ignition test in a CFR engine are shown in Figure 3 (*82*). Relatively large amounts of benzene can be tolerated in iso-octane-benzene blends without greatly increasing the occurrence of surface ignition.

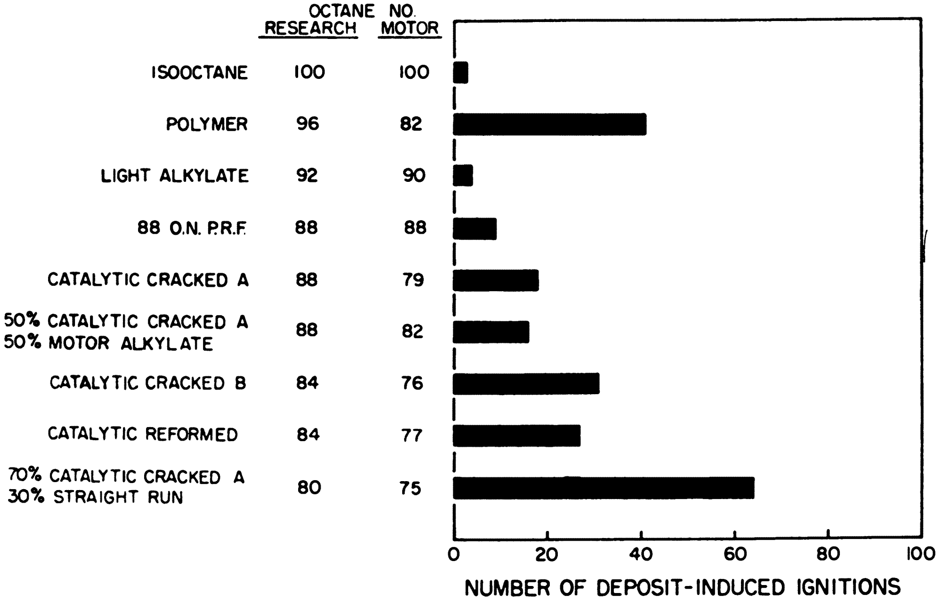

Figure 4. Ignition resistance of gasoline blending stocks

Figure 4 shows the relative surface ignition tendency of several unleaded commercial gasoline blending stocks together with their American Society for Testing Materials (ASTM) Research and Motor method octane numbers (*82*). These blending stocks vary considerably in their resistance to surface ignition by hot deposits in a CFR engine with no obvious relation between resistance to knock and surface ignition. The same result was found by a test method employing a hot spark plug as an ignition source.

Another approach to the problem of relative resistance to surface ignition of various hydrocarbons has been to compare the fuels being rated with the occurrence of ignition caused by the deposits they form (*39*). These experiments were run with leaded fuels in an effort to simulate practical conditions, and tests were made under conditions of both cyclic operation and constant speed and load. Without exception, less surface ignition occurred under the constant speed and load conditions, with very great reductions in the case of toluene and benzene. This result was not unexpected, as aromatic compounds are known to produce carbon deposits rapidly under conditions of idling and deceleration (*39*). Table III presents data for conditions of cycling and constant speed and load.

The effect of the addition of several aromatic amines on the surface-ignition resistance of an aviation gasoline has been determined by Male (*56*); 2% by weight of each of six

Table III. Cycling and Constant Speed Conditions[a]

Fuel + 3 Ml. TEL/Gal.	Deposit Ignition Rate, No. per Hour	
	Cycling	Constant speed and load
Cyclopentane	20	10
Benzene	430	20
Toluene	600	30
Triisobutylene	110	115
Iso-octane	15	5
Diisobutylene	15	5

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[a] Taken from a figure in (*39*).

aromatic amines were added to the fuel, and the ratios of the preignition-limited IMEP of the blends to the fuel were obtained in a CFR engine equipped with a hot spot. *N*-Methylaniline and *N*-methylxylidines had no detectable effect on the occurrence of surface ignition, while xylidines, *N*-methyltoluidines, cumidines, and *N*-methylcumidines lowered the preignition limit of the fuel from 2 to 10%, depending on the fuel-air ratio.

Commercial Gasolines. The surface ignition resistance of several commercial fuels, as determined by a deposit-induced ignition test in a CFR engine (*82*) is shown in Figure 5. Similar results were obtained by use of a General Motors research engine with hot spark plugs as the source of surface ignition. Gasolines with similar ASTM Research method octane numbers may differ widely in resistance to deposit-induced ignition.

Several authors have suggested that the aromatic components of gasolines may be responsible for the greater tendency of some fuel blends to cause surface ignition (*6*, *19*, *91*). It has been established, however, that within a hydrocarbon class there is a general tendency for the higher boiling materials to produce more surface ignition; this effect may be greater than that due to hydrocarbon type (*39*). The effect of volatility on surface ignition harm has been demonstrated by distilling a catalytically cracked naphtha into fractions of three different end points and measuring the deposit-ignition harm of the three fractions (*39*). These data are given in Table IV.

Another study has been conducted to determine whether differences in surface ignition susceptibility of gasolines of the same boiling range could be attributed to dif-

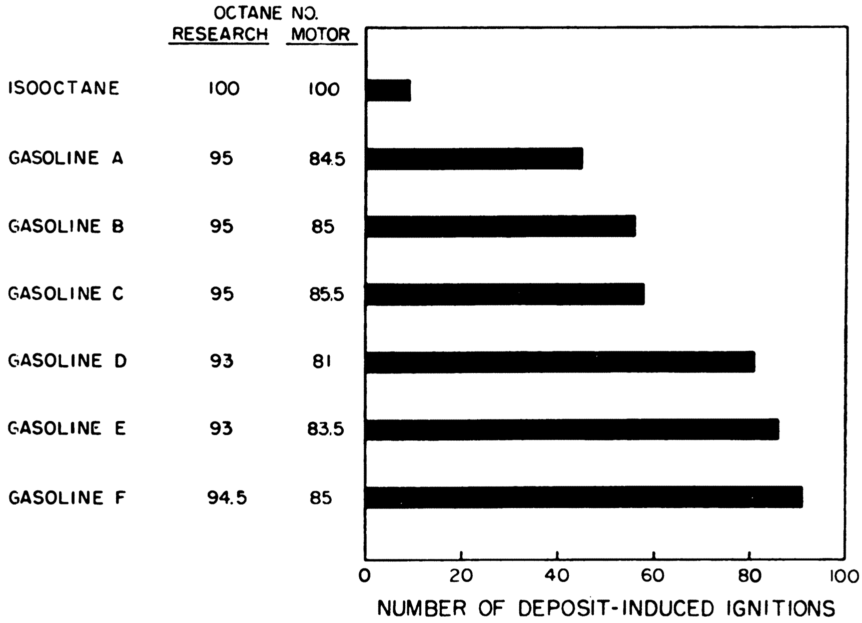

Figure 5. Ignition resistance of commercial premium gasolines

Table IV. Deposit-Ignition Rate Measurements

Fraction	90% Point, ° F.	End Point, ° F.	Deposit-Ignition Rate, No. per Hour
1	300	360	15
2	349	398	220
3	411	454	370

ferences in hydrocarbon composition (*39*). The results indicated that there was no simple relation between the hydrocarbon composition as determined by type analysis and the tendency to undergo surface ignition. The authors conclude that the deposit-ignition tendencies of complex-hydrocarbon mixtures as encountered in full-boiling gasolines cannot be predicted accurately by measuring their over-all hydrocarbon-type proportions by present standardized techniques. There is no doubt, however, that both fuel volatility and composition are highly important factors in the surface ignition problem (*28*).

Effect of Tetraethyllead. As tetraethyllead is almost universally used as an additive in commercial gasolines, much effort has been devoted to establishing the effect of this additive on the occurrence of surface ignition. Tetraethyllead can influence surface ignition of fuels by modifying the intrinsic ignition characteristics of fuel (*82*), by changing the activity of the igniting surface (*1*), and by its effect on the amount and nature of combustion chamber deposits as already discussed.

It is possible that tetraethyllead can reduce the incidence of surface ignition by deactivating hot metal surfaces which otherwise would cause surface ignition. There is abundant evidence that tetraethyllead does deactivate experimental hot spots, especially thermocouple junctions and coils of platinum wire (*1*). The same effect may be operative on spark plugs, exhaust valves, and other metal surfaces within the combustion chamber (*41*).

Many workers have stated that tetraethyllead is effective in increasing the intrinsic resistance of fuels to surface ignition. Part of the effectiveness is due undoubtedly to the activity of tetraethyllead in suppressing subsequent knock caused by the premature ignition of the charge (*91*). With proper allowance for this effect, tetraethyllead appears to increase the surface ignition resistance of those fuels to which it contributes knock

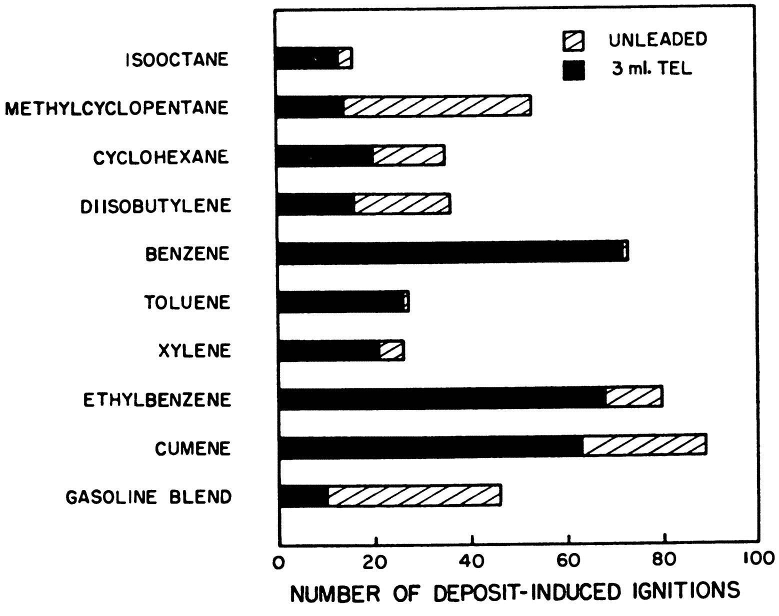

Figure 6. Effect of tetraethyllead on hydrocarbon ignition resistance

resistance and does not affect the ignition resistance of those fuels which have poor tetraethyllead susceptibility relative to knock (*82*). Tetraethyllead does not appear to increase surface-ignition resistance of a fuel to the same extent as it increases the knock resistance (*22*). The effect of tetraethyllead on the ignition resistance of nine hydrocarbons and one gasoline blend (*82*) is shown in Figure 6.

Tetraethyllead is believed to act as an antiknock by changing the course of the complex hydrocarbon oxidations which precede knock (*69*). It also may improve fuel-ignition resistance by its effects on these preflame reactions; it is most effective in fuels that undergo considerable preflame reaction and has little effect on fuels that do not. Some of the products formed in preflame reactions—aldehydes, for example—sensitize fuels to ignition (*47, 69, 86*).

Hirschler, McCullough, and Hall reported that the effect of tetraethyllead in promoting surface ignition was highly dependent on fuel type. They found tetraethyllead to have little effect on the occurrence of surface ignition with iso-octane, to increase greatly the occurrence with toluene, and to have an intermediate effect in commercial gasolines (*39*). These workers measured the surface ignition caused by the combustion chamber deposits formed by the fuels under investigation, while Sturgis and coworkers (*82*) measured the intrinsic resistance of fuels to surface ignition independent of deposit effects. The difference in the effect of tetraethyllead reported by the two groups probably can be attributed to the effect of lead in catalyzing the glowing of deposits formed by the aromatic fuels.

Effect of Lubricating Oil. The effect of lubricating oil on surface ignition is believed to be largely, if not entirely, due to the effect of the oil on the nature and amount of combustion chamber deposits. Data indicate that the occurrence of surface ignition is increased as the oil consumption of an engine increases, presumably because combustion chamber deposits accumulate more rapidly and give rise to surface ignition (*39*).

It has been established that an all-distillate lubricating oil will cause less surface ignition harm than a conventional straight mineral oil (*3, 5, 54, 70, 91*). As the boiling range of distilled neutral stocks is increased, the oil makes a greater contribution to the formation of combustion chamber deposits, which in turn result in greater surface ignition harm (*67*). Vacuum distillation of a lubricating oil into successively lighter fractions and measurement of their effect in causing surface ignition in an operating engine indicate that surface-ignition harm becomes progressively less as the higher-boiling oil components are removed. This variation in surface ignition harm is believed to be due primarily to changes in oil volatility, as the hydrocarbon composition of the fractions, measured by type analysis, remained uniform throughout the distillation range (*39*).

Effect of Additives. One of the first attempts to solve the preignition problem by additives was the use of tributyl phosphite, claimed in a patent by Campbell (*14*). This compound inhibited the catalytic activity of lead compounds in promoting the glowing of carbon. A later patent issued to Withrow claimed that trimethyl phosphate and trimethyl phosphite also are effective as fuel additives in inhibiting surface ignition due to leaded deposits (*94*). Street, in 1952, ran tests with tricresyl phosphate as an additive in leaded fuel and reported that the phosphorus compound affected the occurrence of lead compounds in the end-gas region of the combustion chamber (*80*).

Many other types of compounds have been evaluated for their effectiveness in suppressing the surface ignition activity of deposits (*12, 84*), and promising results have been ascribed to compounds of undisclosed identity (*73*). However, there are differences in the effectiveness of different phosphorus compounds (*12*).

Tricresyl phosphate was introduced as a commercial fuel additive in 1953 (*33*), and later another phosphorus-containing compound was offered to the industry under the name of ignition control compound (*30*). Almost immediately considerable discussion appeared in the literature concerning these phosphorus-containing additives (*90*). Some workers presented data to show that tricresyl phosphate inhibited the glowing of lead-carbon mixtures in laboratory furnace tests and that, as a fuel additive, it reduced the occurrence of surface ignition in laboratory single and multicylinder engines and in cars on the road (*12, 33, 34, 43*). Tricresyl phosphate also was shown to reduce the tendency

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of spark plugs to misfire by modifying the properties of the deposits which accumulate on the ceramic insulator (*33*, *43*). Other workers pointed out that phosphorus compounds reduce the occurrence of surface ignition but raise the possibility of certain side effects such as valve burning and increased knocking harm (*84*). A major feature of the discussion was the prevalence of surface ignition in cars on the road and lack of agreement among the investigators as to test methods and interpretation of data (*30*, *33*, *84*). An interesting account of the introduction of tricresyl phosphate as a commercial gasoline additive has appeared (*87*).

Causes of Surface Ignition

It is evident that the susceptibility of fuels to surface ignition must be related to the intrinsic ease of ignition of the fuel by hot surfaces and to the effect of the combustion of the fuel on the temperature and nature of the igniting surfaces.

Temperature Required for Ignition of Fuels. LABORATORY EXPERIMENTS. Many workers have measured the temperature required for ignition of fuel by heated surfaces. Holm in 1913 (*40*) determined the minimum ignition temperature of a fuel in air by allowing drops of fuel to fall on a heated porcelain surface of known temperature. Moore in 1917 described a more refined apparatus for measuring spontaneous ignition temperatures of fuels and gave a clear picture of the relation of data obtained in this manner to the surface ignition resistance of fuels in engines (*62*).

Many articles have described the measurement of spontaneous ignition temperatures of various fuels and pure hydrocarbons by a variety of methods (*11*, *25*, *31*, *44*, *83*, *85*, *86*). Jackson gives the spontaneous ignition temperatures of 94 pure hydrocarbons and 15 fuels and commercial fluids. He states that benzene has the highest value of any of the materials tested (*42*). A comprehensive survey of methods of determining spontaneous ignition temperatures of liquid fuels and a tabulation of data is given by Mullins (*64*).

Excellent correlation has been observed between spontaneous-ignition temperature data and knock-rating data in engines for many pure hydrocarbons and blends of hydrocarbons (*29*), because factors that give rise to high-spontaneous ignition temperatures usually result in high octane ratings. The data of Frank and Blackham (*29*) illustrate, however, that there is no simple relation between the spontaneous-ignition temperature as determined in the laboratory and the surface-ignition resistance of fuels in operating engines (Table V). As shown earlier, benzene and toluene differ widely in resistance to surface ignition, and iso-octane is much less susceptible to surface ignition than benzene.

Table V. Spontaneous Ignition Temperatures of Test Fuels

Compound	Spontaneous Ignition Temp., ° F.
Benzene	1192
Toluene	1174
Iso-octane	960
n-Heptane	482

Frank and Blackham point out that materials of construction have an effect on the values of spontaneous ignition temperatures of pure hydrocarbons obtained in different pieces of laboratory equipment (*29*). They observed different spontaneous ignition temperatures for 4-isopropylheptane which they attributed to different catalytic activity of the various metals (Table VI).

Table VI. Catalytic Effect of Metals on Spontaneous Ignition Temperatures of 4-Isopropylheptane

Metal	Spontaneous Ignition Temp., ° F.
Inconel	495
Copper	493
Stainless steel	551
Aluminum alloy	538

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Frank and Blackham also suggest that the effect of metal catalysis on ignition is different for different hydrocarbons (*29*). They believe that hydrocarbons which are ignited by a low temperature mechanism are not readily affected by metal catalysis but that hydrocarbons which ignite at temperatures where pyrolysis occurs may show considerable variation in values of spontaneous-ignition temperature because of the catalytic effect of metals on pyrolysis. Table VII shows that for aromatic compounds, more than for a paraffinic compound, the condition of the surface of the ignition apparatus may make relatively large differences in the observed value of the spontaneous-ignition temperature.

Table VII. Effect of Metal Surface Condition on Spontaneous Ignition Temperature

Compound	Condition of Stainless Steel Surface	Spontaneous Ignition Temp., ° F.
p-Xylene	Heavily oxidized	1310
	Bright metal	1216
α-Methylnaphthalene	Oxidized	1074
	Bright metal	1027
Cetane	Oxidized	455
	Bright metal	457

Other workers have been interested in the effect of size of the hot spot on the temperature required for ignition. Coward and Guest (*20*) determined the area of a hot spot required to ignite a natural gas–air mixture. Using a nickel strip 4.25 inches long and 0.04 inch thick, they varied the width from 0.25 to 1.50 inches. At a mixture ratio of 6% gas in air, the 0.25-inch strip required a temperature of 1960° F. for ignition as compared to 1850° F. for a 1.50-inch strip. Other data on the effect of hot spot area on ignition temperatures have been obtained by Silver, who introduced heated platinum spheres into a fuel-air mixture (*76*). Table VIII gives the diameters and temperatures of platinum spheres required for ignition of a 3% mixture of propane in air.

Table VIII. Effect of Sphere Diameter on Surface Ignition Temperature

Sphere Diameter, Inches	Surface Ignition Temperature, ° F.
1.1	2500
2.0	2260
3.0	2100
4.0	1950
5.0	1900
5.5	1840

These data illustrate some of the factors which make it difficult to correlate the tendency of fuels to ignite on heated surfaces as determined in the laboratory with the ignition tendency on hot surfaces in an operating engine.

ENGINE EXPERIMENTS. Ever since the early experiments of Hopkinson and Ricardo (*71*) investigators have attempted to determine the critical temperature of a hot spot required for surface ignition in an operating engine. The efforts have involved attempts to measure the temperature of metal plugs and small coils of wire inserted in the combustion chamber, as well as spark plugs and other combustion chamber surfaces during engine operation (*75*, *79*, *82*). Spencer describes in detail the difficulty of obtaining reproducible results with hot spots in an engine, especially when the location in the combustion chamber or configuration of the hot spot is changed (*79*). Serruys found that only at extremely low engine speeds and under conditions of very little turbulence did the hot-spot temperature capable of causing surface ignition in an engine approach the spontaneous-ignition temperature of the fuel as determined in the laboratory (*75*).

However, hot-spot temperatures required for ignition of various fuels determined under different conditions agree reasonably well, as shown in Table IX.

The temperatures obtained with the platinum hot spot do not agree well with the temperatures obtained with hot spots constructed of other materials, but data in the literature show that platinum gives unexpected results in this type of experiment.

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Table IX. Hot-Spot Temperatures Required for Ignition

Fuel	Engine	Speed	Hot-Spot Material	Surface Ignition Temp., ° F.	Reference
Benzene	NACA combustion apparatus	500	Nichrome wire	1570	(*79*)
Iso-octane	NACA combustion apparatus	500	Nichrome wire	1570	(*79*)
Methanol	NACA combustion apparatus	500	Nichrome wire	1340	(*79*)
Iso-octane	CFR	1000	Diesel glow plug	1620	(*79*)
Benzene	CFR	1000	Diesel glow plug	1630	(*79*)
Isopropyl alcohol	CFR	1000	Diesel glow plug	1680	(*79*)
69 O.N. fuel-36% benzene	Renault	1250	Metal plug	1680	(*75*)
Iso-octane	CFR	1800	Platinum and platinum plus 10% rhodium thermocouple	2110	(*1*)
Benzene	CFR	1800	Platinum and platinum plus 10% rhodium thermocouple	2070	(*1*)

Coward and Guest have reported (*20*) that under certain conditions platinum must be heated to 720° F. above that of steel to cause surface ignition of a natural gas–air mixture (Table X).

One might expect a platinum hot spot to give a surface ignition at very low temperatures because of catalytic activity. Coward and Guest explain that the oppositely observed effect is due to the fact that the mixture in contact with the surface of platinum is consumed so rapidly that the surface is incapable of propagating a flame, even though its temperature is far above the ignition temperature of the mixture. To check this theory, they determined the amount of preflame combustion in their apparatus by measuring the carbon dioxide formed and found it to be 20 times greater with a platinum surface than with a nickel surface.

Table X. Effect of Metal on Surface Ignition Temperature of Natural Gas–Air Mixture

Hot-Spot Material	Natural Gas in Air, %		
	4.0	9.0	12.0
	Surface Ignition Temp., ° F.		
Platinum	2080	2580	2290
Nickel	1870	1990	2230
Stainless steel	1840	1910	1980
Steel (special English)	1800	1860	1920

Experimentally measured hot-spot temperatures required for surface ignition of iso-octane and benzene in an operating engine are similar in spite of known great differences in actual surface-ignition resistance as measured by other procedures. Alquist and Male (*1*) and Male and Evvard (*57*) concluded that hot-spot temperatures could not be used to characterize the surface ignition resistance of fuels.

Recently Livengood, Toong, Rona, Taylor, and Black used an externally heated hot spot to induce surface ignition in a motored engine (*53*). Under the conditions of these experiments, benzene required a somewhat higher hot-spot temperature for surface ignition than iso-octane, but the difference in temperature was far less than the difference between the spontaneous ignition temperatures of the two hydrocarbons as determined in the laboratory.

Minimum Spark Ignition Energy of Fuels. Determination of the minimum energy required for ignition of fuel by a spark is another way of measuring the intrinsic resistance of a fuel to ignition. Metzler has measured the minimum spark ignition of various fuels. Table XI shows that at atmospheric pressure in a bomb, paraffins, branched

Table XI. Minimum Energy for Spark Ignition of Fuels

Fuel	Minimum Ignition Energy, at 1 Atm., Joule
n-Hexane	0.000248
Cyclohexane	0.000223
Iso-octane	0.00028
Benzene	0.000225

paraffins, cycloparaffins, and benzene of similar molecular weight have essentially the same minimum ignition energies (*59*, *60*).

Calcote and coworkers report that fuel type has a definite influence on the minimum ignition energy; they agree that ignition energies for aromatic compounds are similar to those for linear hydrocarbons containing the same number of carbon atoms (*13*). The results of these laboratory experiments on the relative ease of ignition of fuels by a spark are not in agreement with the known susceptibility of fuels to surface ignition in operating engines. It is known, however, that the minimum energy required for spark ignition of a fuel decreases rapidly with increasing pressure and temperature. For most fuels, the minimum ignition energy varies inversely as the bth power of pressure, where b is approximately 2 (*7*). For temperature, a correlation has been obtained between minimum ignition energy and temperature which has the form $H = Be^{CT}$, where H is the minimum ignition energy, T is the initial temperature of the mixture, and B and C are constants (*26*).

These data suggest that the usual laboratory measurements of minimum spark ignition energies of fuels cannot be correlated with surface ignition of fuels in engines. It is difficult, even in laboratory equipment, to measure minimum spark ignition energies at the temperatures and pressures which exist in a combustion chamber at the time surface ignition occurs because, under these conditions, the energy required for ignition is very small. Such measurements are even more difficult in an engine because of the effect of the cyclic operation of the engine on the test equipment.

Relation between Laboratory and Engine Data. Despite much effort, there has been little success in developing a simple laboratory test procedure with results which correlate with the measurement of surface-ignition resistance of fuels in engines. The data from early engine test procedures did not correlate well, primarily because different investigators were not in agreement in interpretation of their results. Recent results from a number of laboratories using a wide variety of test procedures have shown good agreement in rating a variety of pure hydrocarbons in order of surface-ignition resistance (*16*).

Laboratory test results are not helpful in predicting surface ignition results in engines, because it is difficult to devise a laboratory test procedure which will reproduce sufficiently well the condition to which fuel is exposed in an engine without having the laboratory test device approach the mechanical complexity of the engine.

The actual energy required for ignition of a fuel decreases rapidly as the temperature and pressure of the fuel is increased (*51*). This results, in part, from sensitization of a fuel to ignition by precombustion reactions (*58*).

The turbulent condition of the fuel-air charge in an operating engine and the variation in fuel-air ratio due to incomplete mixing are factors which are important to the occurrence of surface ignition in an operating engine (*79*) but are very difficult to duplicate in laboratory apparatus.

An important factor is the effect of a fuel in heating the combustion chamber surfaces or deposits to sufficiently high temperatures to cause surface ignition. This factor involves the heat of combustion of the fuel, heat capacity of the products of combustion of the fuel (*32*), and the radiation of energy by the burning fuel (*37*). Benzene is known to give higher combustion chamber temperatures than iso-octane (*6*, *79*), even though it has a smaller heat of combustion. This factor may well explain the greater susceptibility of benzene to surface ignition in engines than is observed with iso-octane (*68*).

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Effect of Additives on Combustion of Petroleum-Derived Fuels

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The fuels distilled or refined from petroleum do not always have natural combustion properties which meet the exact requirements of the commercial and consumer equipment in which they are to be burned. This becomes particularly critical when technological improvements in combustion equipment intensify previous problems or cause new ones. One route to the solution of these difficulties has been the addition of chemical modifiers—"additives." Some of these directly affect the combustion processes: antiknock agents for gasolines, ignition accelerators for Diesel fuels, and combustion improvers for heating oils. Others cause beneficial changes in factors that affect combustion, such as surface-ignition inhibitors, other deposit modifiers, and spark-plug–fouling suppressors for gasolines. These and other fuel additives are being used in increasing quantities, not only to solve existing problems, but also so that the better fuels which contain them will enable the manufacturers of combustion equipment (such as automobiles) to continue to improve their products. This paper lists the types of additives which affect the combustion of petroleum-based fuels, describes the development and postulated mechanism of operation of the present commercial additives, and discusses trends in the use of these products.

Crude oils, as they come from the ground, are vastly complex and varying mixtures of hydrocarbons are intermingled with minor proportions of oxygen, nitrogen, and sulfur compounds. As they progress through modern refineries, they are distilled or otherwise separated into products of more discrete properties (boiling range, density, and carbon-atom content of constituent hydrocarbons), but even these products differ in properties from crude oil to crude oil, because of variations in their hydrocarbon constituents—straight and branched-chain paraffins, naphthenes, aromatics, and condensed aromatics.

This variability is sometimes lessened, and sometimes increased by the refining processes to which these products are subjected. Such processes as cracking are used to increase the yields of specific products and often result in improved properties of these products but not necessarily of coproducts. Other processes—e.g., treating or reforming—are designed to improve such specific properties as stability and antiknock value. The effectiveness of all these processes and the extent to which they are used are determined by an economic balance of factors such as the properties of the basic materials, the cost of plants and processing, and the worth to their users of the products and coproducts obtained.

Petroleum products are refined and marketed to serve a vast number of specific uses, but in the main they are employed as fuels and lubricants. As fuels they long ago replaced whale oil and coal-tar fractions; as lubricants they came on the scene just when the demands of industry began to mount. Their advantages are many: fluidity, availability, and low cost, to mention only three. Within surprisingly wide limits, they may be tailored to meet quality specifications. Few industries have done as much with their raw materials as has the petroleum industry.

Nevertheless, there are natural or economic limits to the amount of tailoring possible by use of chemical or physical processes applied to the products per se. There comes a time when these processes can no longer yield products that meet the exacting requirements of the commercial and consumer equipment in which they are to be used. Or there comes a time when these exacting requirements can be met more economically in other ways. Nor does the situation ever become static; it continuously becomes more critical as technological improvements in combustion equipment (including the development of new types) intensify old problems or create new ones.

One route to the attainment of quality or to the solution of combustion difficulties has been the addition to petroleum fuels of small amounts of chemical modifiers, popularly termed "additives." Some of these directly affect the combustion processes; for example, antiknock agents for gasolines, ignition accelerators for Diesel fuels, and combustion improvers for heating oils. Other additives cause beneficial changes in factors that affect gasoline combustion, such as combustion-chamber deposit modifiers (including surface-ignition inhibitors) and spark-plug–fouling suppressors. These and other petroleum-fuel additives are today being used in increased quantities, not only to solve existing problems but also so that the better fuels which contain them will enable the manufacturers of combustion equipment (such as automobiles) to continue to improve their products.

This paper has been prepared as a summary of published information on these combustion-controlling additives, the petroleum fuels in which they are used, their specific functions and postulated mechanisms of operation, their commercial development, and future trends in their use. The literature on these subjects is almost as vast as the products are complex and can be barely touched upon in a single paper; however, some of the basic references are included in the bibliography which is appended. The merits and economics of these materials have recently been discussed by several authorities (*21, 33, 40–42*).

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Gasoline Additives

Gasoline, the prime fuel for automotive engines, has long been a petroleum product susceptible to improvement by use of additives. Chief among these, by far, are the tetraethyllead antiknock fluids, but other additives include deposit modifiers and such noncombustion-controlling substances as antioxidants, metal deactivators, corrosion inhibitors, detergents, and anti-icing agents.

While this paper does not deal with these latter materials, because ideally they do not enter directly into the combustion picture, in actual practice some of them play a large part in determining whether a given combustion-controlling additive may be used commercially in gasoline. Some are designed to prevent or minimize gasoline and/or additive attack on fuel-system parts, intake valves, cylinders, bearings, and the exhaust system, either by maintaining gasoline quality in storage or by modifying the products of combustion. For example, gasoline antioxidants prevent or minimize formation in gasoline of gasoline-insoluble materials which could deposit in and clog fuel-induction systems. Incidentally, additives used for one purpose ideally ought not to affect other problems adversely; this subject has recently been discussed (*24*).

Antiknocks. Antiknock agents are used to improve the natural knock resistance of gasolines used in Otto-cycle gasoline engines, "knock" being the power-robbing, po-

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tentially engine-damaging premature combustion of the unburned portion of the fuel-air mixture ahead of the spark-induced flame front. While many substances have been tested as antiknocks, only fluids containing tetraethyllead have found widespread commercial acceptance. High antiknock effectiveness per unit of cost has been the prime reason for their success, other materials being either more expensive or less suitable for such other reasons as higher engine wear, instability, or poor inductibility.

Antiknocks which contain tetraethyllead were introduced commercially in 1923, ending a period in which the knocking tendencies of existing gasolines were limiting the compression ratios and hence the power and efficiency of engines. The development of these materials has recently been described by Nickerson (*44*); their properties have been reviewed by Edgar (*20*); and their effectiveness in today's fuels and engines has been discussed by Bartholomew (*5*). Today, over 99% of all automotive gasolines sold in the United States contain tetraethyllead.

Despite extensive work both in engines and in laboratory devices of many kinds, no conclusive evidence has yet been presented regarding the precise way in which tetraethyllead controls knocking (*51*). Although it is generally assumed that decomposition of tetraethyllead is a prerequisite for its effectiveness, strong doubt exists as to whether the active agent is a fine dispersion of solid lead oxide (*12*) or whether the inorganic lead compound acts via a molecular dispersion (*22*). Whatever the form of the active agent, it is generally agreed that it operates at least in part by destroying the free radicals which are thought to play an important role in the chain reaction leading to autoignition of the fuel-air charge.

Antiknock fluids containing tetraethyllead also include "scavengers"—organic bromine and chlorine compounds which tend to transform the combustion products of tetraethyllead to forms which are more likely to be vaporized from the engine surfaces. Various combinations of ethylene dichloride and ethylene dibromide have proved effective and economical in the gasolines and engines of each period; one fluid marketed recently has an increased ethylene dibromide content, and for some gasolines this has been shown to reduce both combustion-chamber deposit weight and effects which result from these deposits (octane-requirement increase and surface ignition) and also to increase exhaust valve life (*23*). While scavengers are additives in the correct sense, they are an integral part of tetraethyllead fluids and are usually not considered separately.

Both before and after the commercial introduction of tetraethyllead antiknocks, many other substances have been considered as octane-number improvers. Chief among them are hydrocarbons, amines, and other organometallic compounds.

Hydrocarbons, such as benzene and toluene, are not comparable in antiknock effectiveness to the amines and organometallics and, therefore, must be used in such large quantities for antiknock improvement that they are considered as fuel constituents or blending agents. Certain amines have somewhat higher antiknock effectiveness, but even these cannot compete economically with tetraethyllead (*20*, *49*). Incidentally, their mechanism of antiknock action seems to be reaction with chain-branching free radicals to form more stable molecules and radicals. These do not produce chain-branching and knock-promoting reactions in the time available (*8*).

As regards organometallics other than tetraethyllead and other lead alkyls, only iron pentacarbonyl has received much attention, because of its low cost; in some fuels it is probably the cheapest known source of antiknock increase (*20*). However, the great increase in engine wear which its abrasive combustion products produce makes its use impractical, and there appear to be no prospects for its commercial use (*20*). A new iron compound, dicyclopentadienyliron (ferrocene), also demonstrates the antiknock effectiveness of iron compounds. As an antiknock, it is approximately 50% as effective as tetraethyllead and has other favorable characteristics, but it is not practical for antiknock use for the same reason as iron pentacarbonyl—accumulation of iron oxide in engine cylinders where it has an adverse effect on wear and spark-plug life (*2*).

Organic boron compounds reportedly have some antiknock effectiveness in addition to altering combustion-chamber deposit effects (*35*, *46*). Other compounds showing antiknock properties have recently been reviewed (*50*).

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Deposit Modifiers. In recent years, combustion-chamber deposits have been causing increased problems concerned with engine antiknock-requirement increase, surface ignition, and spark-plug life. Various gasoline additives—chiefly organic phosphorus compounds—have been introduced commercially to combat the latter two problems; some companies have used boron compounds (*46*) or hydrocarbon-base materials (*13*). Other companies have preferred to attack deposit problems by introducing more volatile fuels and lubricants (*26, 31, 32*) found to have lower deposit-forming properties. Periodic removal of deposits has also been attempted in several ways, on a limited scale. Another proposal has envolved in-place combustion catalysts (*45*).

As mentioned, additives to combat spark-plug fouling (leakage of high-tension current through deposits) and surface-ignition (the tendency of deposits to ignite the fuel-air mixture erratically, thereby producing uncontrolled combustion) have received particular attention (*10, 26, 28, 30, 32, 36, 46*). In particular, two phosphorous compounds have been marketed widely—a haloalkyl thionophosphorous compound (*55*) and tricresyl phosphate (*54*). The phosphorous and other elements in these compounds apparently modify the deposits already present or forming, quenching the "glow" which induces surface ignition and rendering spark-plug deposits more highly resistant to spark-current leakage.

Only a few additives have been proposed as general-purpose deposit modifiers or preventers. Boron compounds have already been mentioned (*46*). Use of metal chelates of pentadione (PD) as a "combustion catalyst," said to remove deposits and keep clean combustion-chamber surfaces, was reported in 1949 (*7*) and was disclosed in patents as far back as 1937. More work on octane-requirement increase depressants may be expected.

Other Gasoline Additives. Few other types of gasoline additives have a direct effect on the combustion process. Use of additives to help minimize engine-exhaust emission of unburned hydrocarbons has been suggested as theoretically possible (*42*). Alcohol in alcohol-water injection might possibly be considered an additive; here, the internal cooling effect is important. As mentioned, additives employed for other purposes must be carefully screened for detrimental effects, such as on knocking or surface ignition (*24*).

Diesel-Fuel Additives

Ignition-Quality Improvers. Diesel fuels have found greatly increased use in recent years—so much so that refiners have had to look to cracked distillates from catalytic cracking operations for their extra Diesel fuels. While these cracked distillates have the advantages of relatively high heat content and low pour point, they are inferior in ignition quality (cetane number) to straight-run distillates from the same crudes.

The ignition quality of Diesel fuels is directly concerned with the brief time lag, called ignition delay, which occurs in the Diesel engine between fuel injection and compression ignition, even though the entire period between fuel injection and the end of combustion is only a few thousandths of a second. A certain amount of this delay is desirable, to permit proper mixing of the fuel with the air. A long delay is detrimental, however, because it is followed by excessively rapid burning of the fuel charge, commonly called combustion shock or knock. Relative ignition delay is commonly measured in terms of cetane number. Diesel fuels of inadequate cetane number produce uneven and incomplete combustion, which usually results in smoke and loss of power during engine warm-up, idling, or at high altitudes.

Many compounds have been tested as ignition quality improvers—additives which shorten the ignition delay to a desirable duration. An extensive review in 1944 (*6, 43*) listed 303 references, 92 dealing with alkyl nitrates and nitrites; 61 with aldehydes, ketones, esters, and ethers; 49 with peroxides; 42 with aromatic nitro compounds; 29, with metal derivatives; 28 with oxidation and oxidation products; 22 with polysulfides; 16 with aromatic hydrocarbons; nine with nitration; and four with oximes and nitroso compounds. In 1950, tests at the U. S. Naval Engineering Experiment Station (*48*) showed that a concentration of 1.5% of certain peroxides, alkyl nitrates, nitroalkanes, and nitrocarbamates increased cetane number 20 or more units.

Early in 1952, a blend of primary amyl nitrates was introduced commercially as a Diesel ignition improver. This additive is being used by refiners to upgrade distillates which are low in ignition quality (thereby increasing supplies of Diesel fuels), to increase the flexibility of refining operations, and to permit the marketing of diesel fuels of more uniform quality. Steps in its development and its properties have been reported in the literature (*1*, *18*, *38*).

Other Additives for Diesel Fuels. No other combustion-controlling additives are used at present in Diesel fuels. Although a number of additives have been tested as a means of improving their cold-starting characteristics (*53*), none has yet proved economically attractive as compared with vaporizing certain starting aids directly into the induction air system of the engine immediately prior to cranking. However, since the ignition quality of Diesel fuels is the property which has the greatest effect on the ease with which a Diesel engine will start, it is not surprising that the addition of amyl nitrate and some of the other ignition accelerators improves the starting characteristics of a given fuel. Amyl nitrate is especially helpful in reducing the misfiring period and also the over-all warmup period (*25*).

As regards the suppression of smoke and odor from the exhaust of Diesel engines, it has been found that fuel volatility may be more important in many instances than cetane numbers, although fuels of higher cetane numbers decrease exhaust odors during idling periods (*25*). Incidentally, Diesel-fuel stability additives are becoming of increasing importance; these, however, do not directly affect combustion.

Additives for Jet and Gas-Turbine Fuels

Fuels for jet and gas-turbine engines are today being used in increasing quantities, a trend which is virtually certain to continue at an accelerated pace. Use of these fuels—petroleum fractions ranging from heavy naphthas through kerosine to residual oils, depending on the application—has by no means been free of problems, but so far few of those directly concerned with combustion efficiencies or mechanisms have been amenable to solution by use of additives.

In aircraft jet fuels, for example, especially those for aircraft of the supersonic type, the chief problem so far encountered has been thermal stability prior to combustion. The fuel must be used as a cooling agent, and the resultant exposure to heat accelerates the formation of gum and sediment. These cause plugging of filters and fuel nozzles, and lacquering of heat-exchanger surfaces. Research to date has indicated that some additives are effective in improving jet-fuel stability (*52*), especially if the fuel has first been rigorously refined, but these additives are not combustion improvers in the sense discussed in this paper.

As regards actual combustion of jet fuels, the two critical combustion factors are fuel volatility and hydrogen/carbon ratio. As might be expected, fuels that are too heavy for the spray system and for the combustor design do not burn as well as more volatile fuels. Low hydrogen/carbon ratios also interfere with combustion efficiency, even though straight aromatics have been handled in specially adapted burners (*3*).

Carbon formation is a very real problem, leading as it does to deposits (*4*, *27*). These may cause poor acceleration characteristics, uncertain ignition and spark-plug operation because of carbon accumulation in the dome areas, and decreased liner life caused by warpage resulting from uneven temperature profiles across the combustor liner when carbon deposits are present (*37*).

Smoke (carbon) formation, which apparently is due to incomplete combustion of portions of the fuel-air mixture (i.e., rich combustion), also can pose a serious public relations problem at civilian airports and, by radiant-heat transfer from incandescent carbon particles, can shorten the endurance life of combustion-chamber liners and adjacent parts (*9*). Smoke would also constitute a serious problem in the case of automotive gas turbines, because accumulation of carbon and other nonvolatile fuel components on the intricate passages of the heat exchanger could reduce turbine and heat-exchanger efficiency by reducing heat-transfer rate and increasing the pressure drop across the exchanger. Fuels having low carbon-forming tendencies will be very desirable for the (automotive) gas turbine (*39*).

In practice, the carbon-formation problem has been attacked chiefly by changes in combustor design and by control of fuel constituents and endpoint. However, a recent paper (*2*) states that use of dicyclopentadienyliron (ferrocene) as an additive drastically reduces or eliminates jet-fuel carbon deposits.

Increased problems of deposit formation and corrosion are encountered in industrial gas turbines such as those used in electric power generation and locomotives. Here, residual fuel oil must be used for economic reasons. Ash may deposit and tend to choke the gas turbine, thereby reducing volumetric efficiency. Moreover, vanadium and sodium, two common ash components, cause severe corrosion of super alloys at the high temperatures prevailing in gas turbines. Sulfur content is also significant, because the metal sulfates that form are much lower in melting point than the corresponding oxides and thereby contribute to deposit formation (*17*).

In general, these problems have been attacked by using selected fuels (limited in applicability) by operating at lower temperatures (sacrificing thermal efficiency for longer turbine-blade life), by extracting corrosive agents from the fuels, and by the use of additives. Addition of magnesium compounds (oxide, sulfate, or an oil-soluble compound), alumina, silicates, or other metallic oxides inhibits vanadium attack by forming relatively noncorrosive materials and by lowering deposition through formation of higher melting, more friable ash. These inorganic additives are usually incorporated immediately before consumption, either in solid form or in aqueous solution. Addition at the refinery is feasible only for oil-soluble additives (*9, 17*).

Studies have been made on the effects of additives and diluents on widening the flammability limits and bringing about greater combustion stability in jet engines. While effects were small, it was found that ethyl nitrate and chloropicrin promote flame propagation at rich mixtures, although the latter additive inhibits propagation at lean mixtures, as do carbon disulfide and methyl bromide. The latter increases the minimum pressure for flame propagation (*27*).

Fuel-Oil Additives

In recent years, the middle distillates have been in growing demand as fuel oils and Diesel fuel. As mentioned under the discussion on Diesel-fuel additives, it has been possible to meet this demand only by the inclusion of distillates from catalytic cracking operations. These have higher volumetric heat contents and lower pour and cloud points, but their use has caused problems of stability and compatibility in storage, necessitating use of anti-screen-clogging agents (*14, 41, 47*).

As for similar additives for jet and gas-turbine fuels, the literature is sparse on those distillate fuel-oil additives reported to have definite beneficial influence on actual combustion and is confined largely to claims that certain stability improvers also reduce carbon deposits in preheaters and on burner tips. However, a recent report indicates that ferrocene has recently been groomed for a job as combustion catalyst in home heaters (*15*). As mentioned previously, this substance is reported to have excellent properties for prevention of carbon formation (*2*).

Users of residual fuel oils as boiler fuel encounter much the same problems mentioned under the discussion of these fractions used as heavy gas-turbine fuels; sludging in storage, and corrosion and slagging in boilers. The addition of magnesium, aluminum, or calcium oxides, kaolin plus metallic additives, or silica, prior to combustion, reportedly helps to control the slagging problems. A host of sludge-dispersing agents have been marketed to remedy the corrosion problem (*11, 16, 34, 41*).

Some of these residual-fuel additives also contain rust inhibitors and soot eliminators (*16*).

Patents on Combustion Additives

References cited previously in this paper have dealt largely with the periodical literature. However, the patent art on combustion additives is even more voluminous;

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in fact, too voluminous to include specific citations here. Some idea of its scope can be gained from Table I, which is based on statistical data obtained from a file of machine-sorted punched cards dealing with fuel-additive United States patents (*29*). As a matter of interest, patent references to all types of fuel additives are recorded in this table.

Table I. U. S. Patent Citations to Compounds Usable as Fuel Additives[a]

Affecting Combustion	
Antiknock agents	1586[b]
Ignition accelerators	1575
Combustion improvers	895
Knock inducers	89
Power improvers	81
Cold-starting aids	4
Autoignition inhibitors	2

Affecting Stability	
Antioxidants	8691
Gum inhibitors	4675
Corrosion inhibitors	4577
Sludge inhibitors	4513
Color stabilizers	2750
Detergents	2003
Metal deactivators	1909
Stabilizers	1249
High-temperature stabilizers	1052
Dispersants	834
Tetraethyllead stabilizers	679
Stabilizers for metal carbonyls	209
Surface-active agents	114

Affecting Combustion—Chamber Surfaces[c]	
Deposit preventers or modifiers	2767
Varnish inhibitors	1857
Wear inhibitors	1424
Upper-cylinder lubricants	1103
Scavengers	408[d]
Octane-requirement increase depressants	171
Surface-ignition inhibitors	140
Spark-plug fouling suppressors	68

Affecting Physical Characteristics	
Dyes	423
Foam inhibitors	356
Volatility-solubility improvers	343
Odor inhibitors or masking agents	242
Anti-icing agents	133
Decolorizing agents	97
Odorants	75
Identification markers	48
Freezing-point depressants	15
Flammability suppressors	14

[a] Data obtained from Ethyl Corp. research laboratories' file of machine-sorted punched cards. Each figure is total number of U. S. patent citations to compounds mentioned as serving that specific fuel-additive function. Since a given patent may cite several different compounds and some of these may serve several functions, these totals are larger than the number of separate patents. The actual number of separate patents identified as pertinent is 1879.

[b] Not including tetraethyllead used as such with ethylene dibromide and/or ethylene dichloride scavengers.

[c] Surface is here defined as the exposed area of the cylinder or deposits.

[d] Not including ethylene dibromide and/or ethylene dichloride used with tetraethyllead.

Conclusion

Petroleum fuels, or similar liquid fuels synthesized from natural gas, coal, oil shales, and tar sands, will continue to have great commercial significance so long as fluidity is an important fuel asset, and that is likely to be for a very long time indeed. Just as alloys are often better than their simple metallic constituents, so petroleum fuels fortified by additives are often superior to the basic products themselves.

The number and variety of fuel combustion problems that are still unsolved suggest that many different fuel additives may still come into use. Petroleum refiners will thereby be able to continue to employ a two-pronged attack when improving their products: first, the development of improved refining processes, and second, the use of chemical additives.

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Combustion of Atomized Liquid Propellants

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The applicable theoretical and experimental papers on atomization, evaporation, and combustion of liquid propellants are summarized and applied to the problem of the combustion of atomized liquid propellants. The available reports on ignition delay, performance, and stability limits for liquid propellant combustors are reviewed and the data correlated in accordance with the experimental data and theoretical concepts summarized above. The results of this survey indicate that more rapid ignition, higher performance, and lower stability limits are achieved by fine atomization and that the effects of unstable combustion and erosive burnout of combustion chamber walls are minimized by coarser atomization. Several atomization criteria for optimum performance are proposed as a consequence of this investigation.

The combustion of atomized liquid propellants is characterized by numerous aspects of this complex phenomenon and is dependent upon the several processes which occur prior to the ignition of the combustibles. Thus fuels and combustors are rated in terms of their ignition delay, performance, carbon formation, and stability limits. Because each of these characteristics is affected to a greater or lesser degree by the previous phenomena of atomization and evaporation, this survey considers the processes of atomization and evaporation, as well as laboratory experimental data and theoretical analyses on the combustion of single drops and applies these concepts to the complicated phenomena observed in large scale combustors. Numerous published reports on the combustion of sprays are reviewed, and an attempt is made to correlate the data obtained relative to the macroscopic phenomena by means of published theoretical analyses and experimental data obtained from previous observations with simpler physical systems. Although it is impossible to include each of the reports which have been written on this timely subject, the conclusions presented are intended to give a reliable indication of the effects to be expected in future tests.

Preparatory Processes

Atomization. The first preparatory process to which liquid fuel is subjected prior to its eventual combustion is atomization. As the technical literature abounds with reports and analyses on the general phenomenon of atomization, it is sufficient here to mention several representative surveys, as well as a number of other reports which are directly applicable to the problems peculiar to combustors currently in use. Several

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reasonable correlations of jet disintegration data obtained from experimental tests with single streams were obtained by the present author (*55*), and the scope of this work was extended in a subsequent literature survey (*54*) to include similar correlations of data obtained for other types of atomizers. From this latter survey, it was ascertained that most of the phenomena associated with the process of jet disintegration can be represented adequately by the Weber number of the jet, which is defined as the square root of the ratio of the kinetic energy of the stream to its surface energy. A typical correlation is shown in Figure 1, which indicates that the average drop size varies inversely as the two-thirds power of the Weber number—i.e., inversely as the cube root of the injector pressure drop—with viscosity effects represented by a linear function of the Reynolds' number.

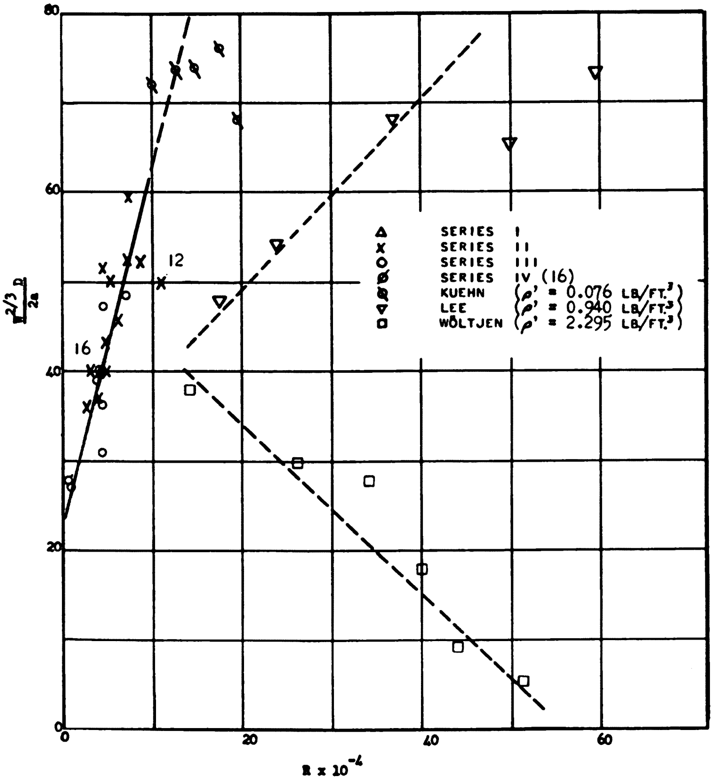

Figure 1. Correlation of drop-size data (Miesse)

An excellent qualitative summary of the atomization process, including superb photographs of the phenomena which occur during air atomization, was presented by Golitzine (*31*). The effectiveness of an air blast, in producing a large percentage of smaller drops, was noted by Joyce (*42*). Longwell (*48*) conducted an extensive investigation on fuel oil atomization and ascertained that the Rosin-Rammler relationship is adequate to express the distribution of drop sizes in the resultant spray. His data showed that the average drop size for conical sprays varied inversely as the 0.375 power of the pressure drop across the injector. Similar studies of fuel sprays, by the staff of the National Gas Turbine Establishment (*62*) indicated that the Sauter mean diameter for a Simplex nozzle varied inversely as the 0.275 power of the pressure drop.

The effect of a low-pressure atmosphere on jet disintegration was studied by Garner and Henny (*21*), who reported a marked increase in average drop size with a decrease in chamber pressure down to 80 mm. of mercury, and by Schmidt (*76*), who noted the formation of fine mists of micron-sized droplets when the vapor pressure of the liquid exceeded the pressure of the surrounding atmosphere. Rodean (*72*) investigated the effect of low temperatures on fuel sprays and found that the resultant increase in viscosity led to larger drops, hence poorer atomization. A similar effect was noted by Bransford and Horstman (*9*), who reported that the fuel pressure required to produce a spray of constant quality increased with an increase in viscosity. In order to facilitate the atomization of viscous fuels, an effective air-blast atomizer was designed by Clare and Radcliffe (*14*), who reported that the drop size thus formed depends mainly on the air-fuel ratio, with a minor effect attributable to the fuel injection pressure.

Evaporation and Ballistics. The second stage in the preparation of a liquid fuel for its combustion is the vaporization of the liquid spray. The laws of vaporization for spherical droplets were established by Frössling (*20*), who noted that the evaporation rate in a moving air stream increased as the square root of the Reynolds' number of the droplet. This law was subsequently confirmed for a large number of different conditions by Ranz and Marshall (*69*), and the results of this latter work were used to develop a theory by El Wakil and coworkers (*16*). The applicability of this law to drops of various nonspherical shapes was established by Hsu, Sato, and Sage (*39*), who noted that any departure from the spherical shape tends to increase the evaporation rate. Sacks (*73*) reported that the rate of evaporation for a kerosine spray is much less than for a drop. An extensive literature survey on the evaporation of drops falling through heated atmospheres was made by Blair (*6*), and the evaporation of fuel drops prior to ignition was investigated by numerous investigators. Longwell, Chenevey, and Clark (*49*) reported that the evaporation rate increases as the ambient pressure decreases, as could be expected from the correlations of Ranz and Marshall.

Kobayasi (*44*) and Nishiwaki (*62*) noted the existence of both a preheat period, during which no change in diameter of the droplet was noted, and a vaporization period. Hottel, Williams, and Simpson (*38*) reported that, whereas the preheat time decreases with the furnace temperature, the vaporization rate remains unchanged. El Wakil and coworkers (*16*) noted a high degree of circulation in the drops during the preheat period and found that the droplets' lifetime increased with the number of carbon atoms and decreased with air temperature.

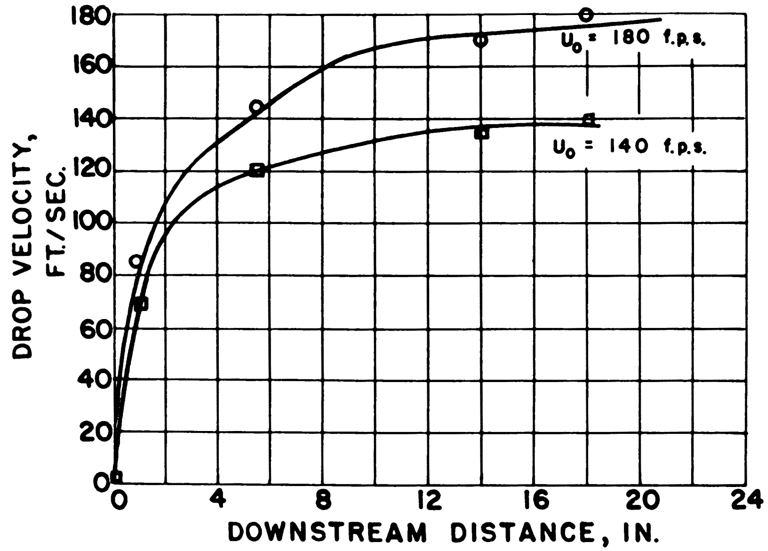

Figure 2. Comparison of theoretical velocity curve with Ingebo's experimental data for a 2,2,4-trimethylpentane spray (Miesse)

The vaporization rates and drag coefficients for 2,2,4-trimethylpentane (iso-octane) sprays in turbulent air streams were determined experimentally by Ingebo (*40*), who reported that the effect of relative velocity on the evaporation rate was represented by the 0.6 power of the Reynolds' number and that the drag coefficient varied inversely with the relative velocity of the drops in the spray. By assuming that the evaporation rate was independent of velocity and the drag coefficient for droplets obeyed Stokes's law, the present author derived a mathematical theory for the ballistics of droplets injected into an air stream for which the velocity varied linearly with distance (*57*) and succeeded in correlating Ingebo's data on velocity variation (*56*). In a subsequent analysis (*53*), the effect of relative velocity on the evaporation rate of a droplet injected into a uniform stream was considered, and a valid correlation of Ingebo's data on drop size *vs.* time was obtained. The correlations of Ingebo's velocity and drop size data thus derived are presented in Figures 2 and 3, which indicate the validity of the corresponding analyses. Ingebo's original work was subsequently extended by Foster and Ingebo (*18*), who noted that the percentage of a spray evaporated varied as the cube root of the distance from injector. These experimental results are shown in Figure 4, which also shows a similar variation calculated from Ingebo's drop size data. The similarity in the correlations is readily observed, thus indicating the validity of determining vapor concentration by droplet evaporation.

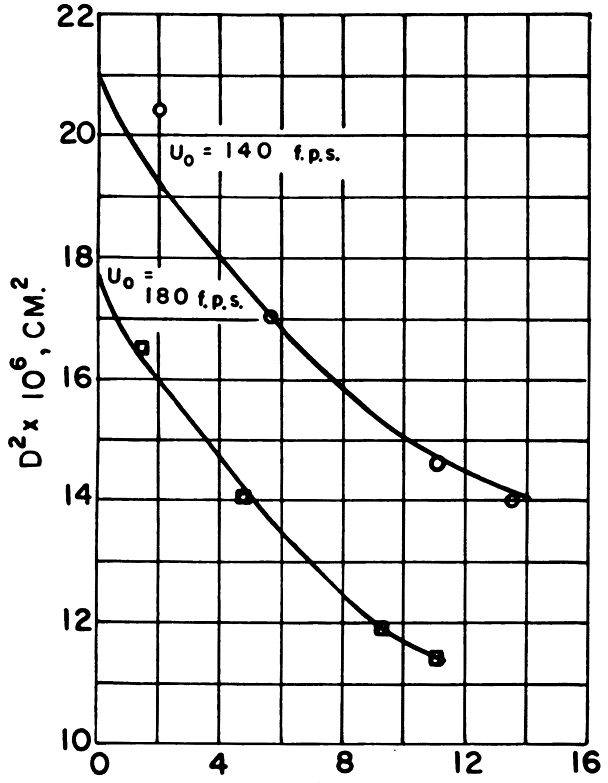

Figure 3. Comparison of theoretical droplet diameter curve with Ingebo's experimental data for a 2,2,4-trimethylpentane spray (Miesse)

An experimental and theoretical investigation (*58*) by the present author was

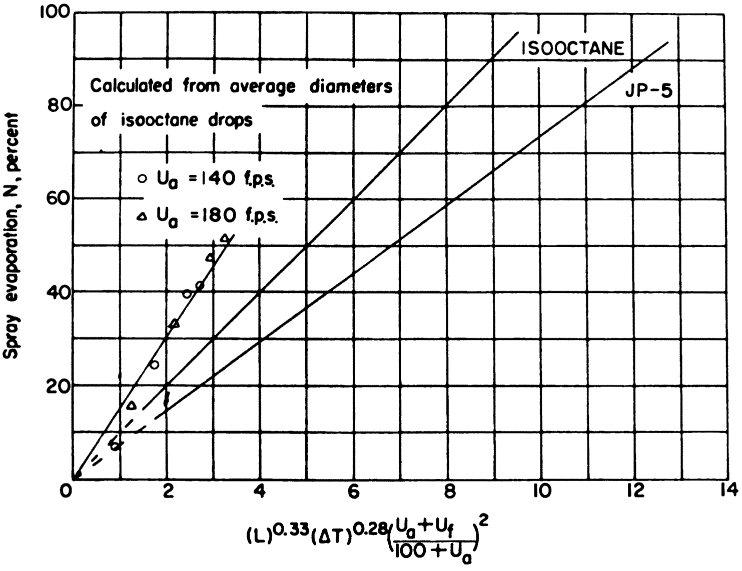

Figure 4. Comparison of variations in percentage of fuel evaporated as determined by gas sampling and average droplet diameters (Foster and Ingebo)

directed toward the determination of the effect of pressure waves, either normal to or parallel with the liquid stream, on the disintegration and dispersion of the stream. Typical photographs of the resultant dispersion and coalescence, for which theoretical analyses were also presented, are shown in Figures 5 and 6.

Combustion Experiments

Single Droplets. The linear variation of droplet surface with time, which was noted for the case of evaporation, was also established experimentally for the combustion process. Godsave (*24*) noted this variation for the combustion of liquid drops suspended from silica filaments, as did also Goldsmith and Perkins (*27*). The same variation was noted for the case of combustion from a porous sphere by Spalding (*77*) and Wise, Lorell, and Wood (*84*): The variation of burning rate as the square root of the Reynolds' number was also noted by the former author, and an increase in the burning rate with an increase in the oxygen content of either the atmosphere or the liquid was noted by the latter authors. Goldsmith (*25*) checked the effect of increased oxygen and air temperatures on the burning of single drops and found that experimental results gave excellent confirmation for the theoretical analysis.

Hall and Diederichson (*36*) noted the variation of burning rate with the fourth root of the ambient pressure, and Spalding (*79*) reported that extinction of the flame occurred at a velocity to diameter ratio of 100 per second for hydrocarbon droplets burning in an air stream. An independent investigation of the effect of air velocity on the burning rate for suspended droplets by Goldsmith (*25*) indicated that a Frössling-type law represented the variation of burning rate with Reynolds' number better than a directv ariation. In a subsequent investigation of the combustion of solid fuel particles, Godsave (*23*) reported the same type of variation in burning rate with the Reynolds' number of the particles.

Kobayasi (*44*) reported that for heavy oil droplets an actual increase in drop size during combustion, due to internal vapor bubbles, occurs. The increase in burning rate, as a function of the product of frequency and the square of amplitude of an imposed vibration of the air field surrounding the burning droplet, was observed by Kumagai

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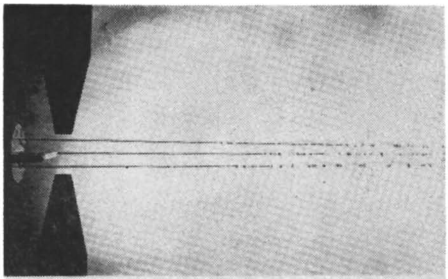
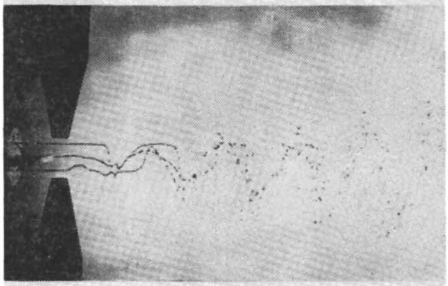
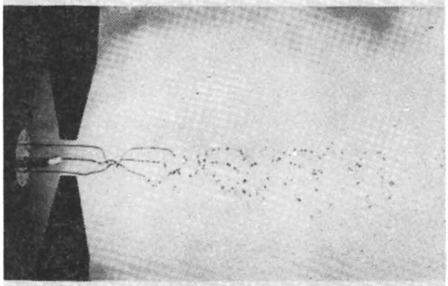


A) f = 0 (UNDISTURBED JETS)



B) f = 200 cps (IN PHASE)



c) f = 200 cps (PHASE OPPOSITION)

Figure 5. Effect of sound waves on jet disintegration (Miesse)

Jet mixing caused by transverse sound waves

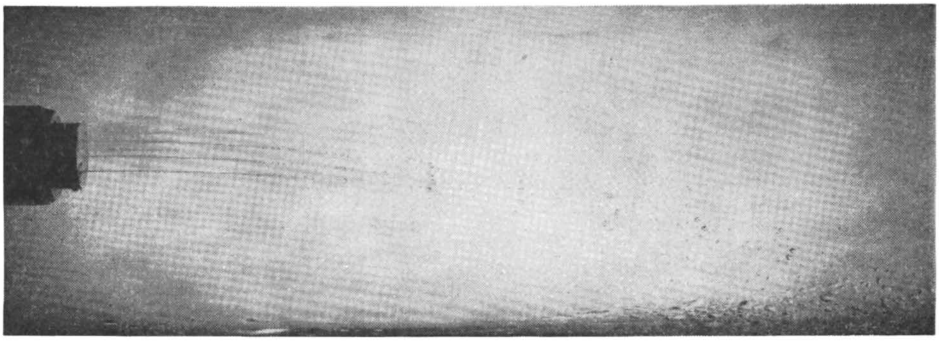


Figure 6. Effect of sound waves on jet disintegration (Miesse)

Coalescence of droplets caused by longitudinal oscillations in a cylindrical chamber and Isoda (*46*). By studying the interference effects during the burning of two stationary droplets, Rex, Fuhs, and Penner (*70*) noted that the burning rate of the droplets increases as the drops approach each other, passes through a maximum, and then decreases as their separation distance is further decreased. This variation, which is apparently due to the relative effects of increased heat supply and decreasing oxygen supply and which differs somewhat for droplets of different sizes, can be correlated by plotting the "droplet burning frequency" (essentially the reciprocal of the lifetime of the droplets) against the separation distance. A typical variation is shown in Figure 7, which indicates that the burning rate of a pair of coalesced droplets is essentially equal to the burning rate of each of a pair of widely separated droplets, as would be expected. The combustion of falling droplets was investigated by Topps (*81*), who reported that the volume burned during a given distance of free fall varied directly as the original volume of the droplet. Similar studies, from which a large quantity of useful information on velocity variation and drag coefficients should be forthcoming, are currently under way at the University of Michigan under the direction of J. A. Bolt.

Among the several theoretical analyses of the combustion of a single droplet, the classical derivation was presented by Godsave (*24*), whose analysis predicted that the mass burning rate should vary directly as the product of flame and droplet radii and inversely as their difference. For flame radii much larger than droplet radii, this theoretical variation reduces to the experimentally observed linear variation of droplet surface with time. A chemical analysis, which extends and generalizes the work of Godsave, was presented by Goldsmith and Penner (*26*), who were able to predict the experimentally observed burning rates with an amazing degree of accuracy.

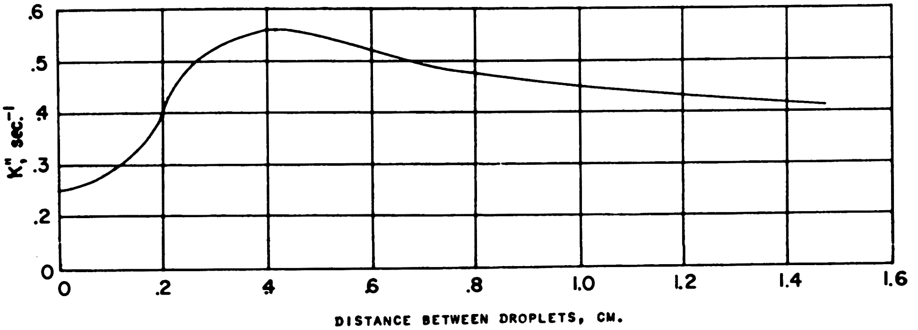


Figure 7. Dependence of evaporation frequency on separation distance (Rex, Fuhs, and Penner)

The burning of liquid strands, which would normally occur in hypergolic streams upstream of the point of jet disintegration, was investigated by McCullough and Jenkins (*51*), who reported that the burning rate, in inches per second, increased as a power of the ambient pressure.

Fuel Sprays. The combustion of fuel sprays has been studied by a number of investigators. The linear variation of average drop surface area with time, as observed previously for single drops, was noted by Bolt, Boyle, and Mirsky (*7*, *8*), and by Burgoyne and Cohen (*11*). The former authors noted that heating of the combustion air did not produce a significant change in the burning rate. The latter authors reported that, for drops below 10 microns in diameter, the combustion was similar to the combustion of fuel vapors, while for droplets larger than 40 microns, burning proceeded from one drop to another; this same tendency was noted by Browning and Krall (*10*). In addition, Bolt and coworkers reported that the burning rate for the fuel spray was about one half of that observed by Godsave for the single droplet, and Burgoyne and Cohen noted that the ratio of flame diameter to droplet diameter was about 19 for a 53-micron droplet, as compared to a ratio of 3 for a 1000-micron droplet, as reported by Godsave. This latter observation is qualitatively in agreement with the observation by Wise, Lorell, and Wood (*84*), who reported that the maximum distance between drop and flame appeared to be constant, independent of the droplet radius.

Applications

Theoretical Analyses. The influence of spray particle size and distribution of spray particle sizes on the combustion of oil droplets was considered theoretically by Probert (*68*), who assumed the Rosin-Rammler expression for size distribution and the linear variation of surface area with time and then proceeded to compute the variation of size distribution due to evaporation and burning. As this analysis indicated that the most important spray parameter is its average size, while the uniformity of its distribution has the greatest effect on the time required for complete combustion of the last few per cent, Probert concluded that the ideal spray should have a small average size and a high degree of uniformity. The theoretical effect of these various parameters is shown in Figure 8. Wolfhard and Parker (*85*) considered the evaporation of kerosine droplets and concluded that there is insufficient vaporization to sustain a flame until the preheating zone of the flame is reached. Their calculations, which are qualitatively confirmed by experimental evidence, indicate that the velocity of the drops at the flame front is approximately equal to the flame speed of the kerosine vapors. The static pressure distribution, leading to adequate length of burning and total burning times for two concentric propellant streams in a bipropellant system, was derived by Charyk, Glassman, and John (*13*). Their theoretical analysis indicated that, for a constant mixture ratio and position, the static pressure increases as the ratio of air to exhaust gas masses decreases; for constant air–exhaust gas ratio and position, the static pressure increases linearly with the mixture ratio of the propellants.

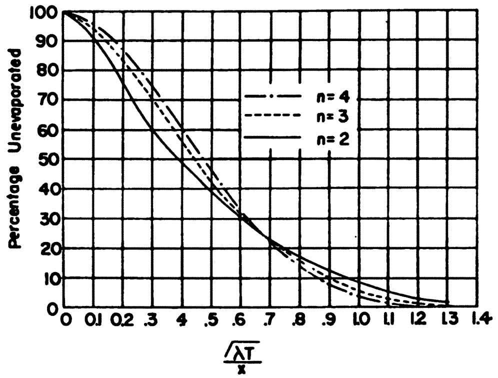


Figure 8. Evaporation and combustion of a spray as a function of uniformity constant *n* (Probert)

By assuming the Langmuir expression for the evaporation of a droplet with the Rosin-Rammler size distribution law, Sacks (*74*) found that the theoretical evaporation rate of a kerosine spray was about 100 times the experimentally observed values. He concluded that the Langmuir expression is based on the single drop and neglects the vapor pressure of the surrounding air, which would tend to inhibit vaporization in a spray. Consideration of the effects of dissociation of combustion products plus the effects of thermal conductivity for the vapors enabled Graves (*33*) to derive a theoretical curve for combustion rate which compared favorably with experimental data. However, the use of Probert's analysis to determine combustion efficiency, yielded efficiencies which were much lower than experimentally observed results.

Use of Godsave's equation for the burning rate of a single droplet, together with

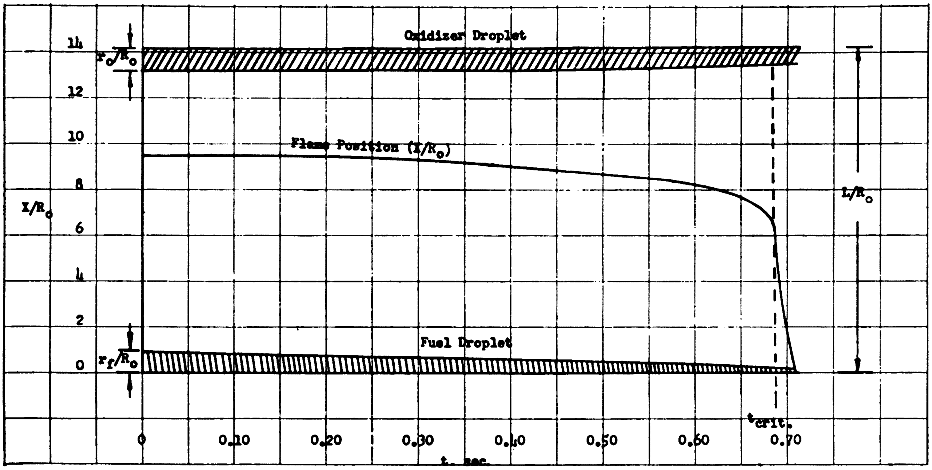


Figure 9. Theoretical variation of flame front position between fuel and oxidizer droplets (Miesse)

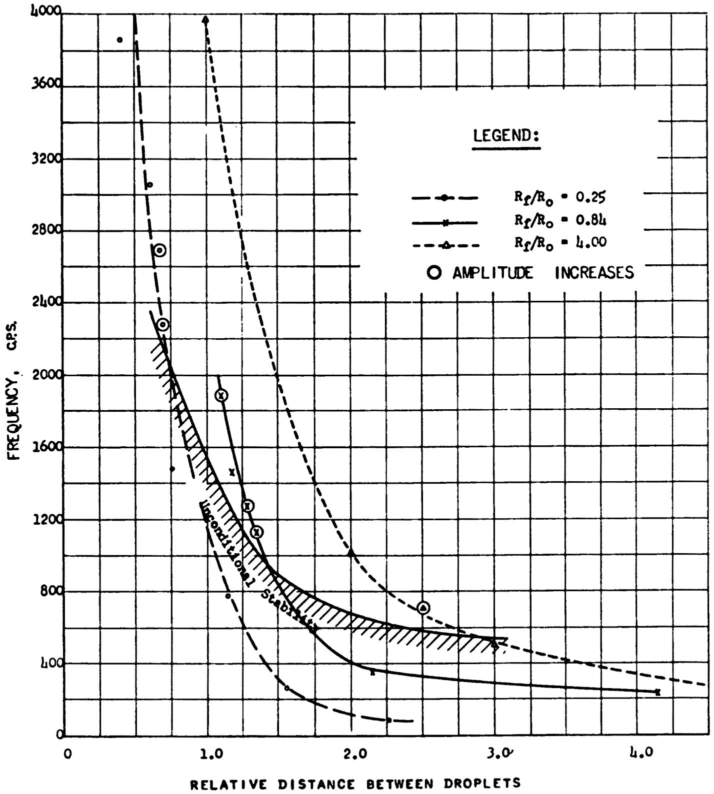


Figure 10. Oscillations of flame front between fuel and oxidizer droplets (Miesse)

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the assumption of a diffusion mechanism for droplet vaporization, enabled the present author to derive a theory of the oscillation of the flamefront between two unlike droplets in a bipropellant system (*59*). This analysis, which was based on the method of small perturbations, permitted the determination of the variation of flamefront position with time, plus the theoretical frequencies and stability boundaries of the oscillating flamefront, as shown in Figures 9 and 10. As a result of this analysis, it was concluded that stability could be increased by decreasing the size of the droplets. In a subsequent analysis (*60*), the stability of the flame front surrounding a fuel droplet burning in an oxidizer atmosphere was analyzed. By assuming that the mass flow rate of the oxidizer vapors into the flamefront was independent of the size of the fuel droplet, the ratio of flamefront to droplet radius should decrease as the droplet radius increases. This theoretical prediction is thus in excellent qualitative agreement with Burgoyne and Cohen (*11*), and, when combined with Godsave's theoretical variation of burning rate with flame front and droplet radii, gives theoretical confirmation of the decreased burning rate for a spray of small droplets, as reported by Bolt and Boyle (*7*).

The trajectory of a burning droplet in a vortex combustion chamber was analyzed theoretically by Havemann (*37*), in an effort to derive the proper design for a vortex combustor, without making allowance for the variation of drop radius due to combustion. The relative effects of decrease in drop size and drag of the surrounding air were considered by the present author in determining the ballistics of an evaporating droplet (*57*), and the experimental evidence available to date indicates that this analysis is equally applicable to the case of a burning droplet.

Ignition Delay. Savic (*75*) presented the hypothesis that circulation, which occurs only in larger droplets, leads to more rapid temperature equilibrium and hence to shorter ignition delays. This hypothesis, however, indicates the opposite trend to that which would be expected, as a number of smaller droplets would provide a larger amount of ignitable vapor than a single large droplet, the volume of which is equal to the sum of the smaller droplets. The theoretical considerations of El Wakil, Uyehara, and Myers (*17*), however, predict the expected effect: Small droplets are heated up much more quickly and are hence prepared for ignition in a shorter time; large droplets have not reached their equilibrium temperature before entering the flame zone and hence require some heat to raise their temperature sufficiently. The theoretical assumption of infinite thermal conductivity, made by El Wakil and coworkers, was subsequently verified

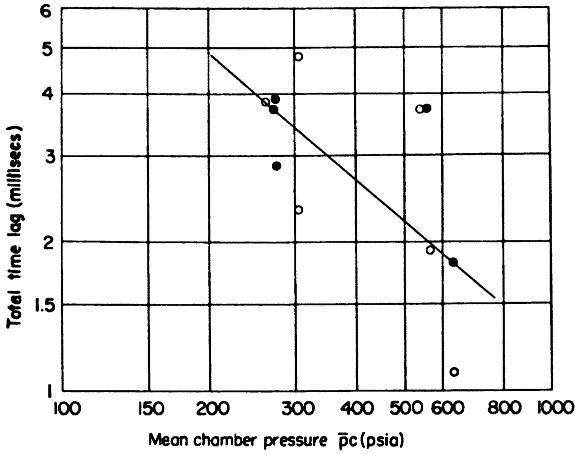

Figure 11. Experimental variation of average total time lag with chamber pressure (Crocco, Grey, and Matthews)

● Frequency, 100 cm. per second

○ Frequency, 50 cm. per second

experimentally (*16*). The safety hazard of propellant accumulation was studied by Barrère and Moutet (*3*), who advocated simultaneous injection of both propellants in a bipropellant system, although an oxidizer lead is not so dangerous as a fuel lead. Their analysis concludes that the ignition delay will increase as the pressure drop across the injector increases and will decrease with an increase in air temperature, or with the addition of active additives to the fuel. The importance of adequate atomization for reducing ignition lags was stressed by Joyce (*42*), who stated that a large portion of the droplets should have diameters of less than 50 microns, and by Koenig and Dandois (*45*), who specified a minimum fuel flow rate of 60 pounds per hour per nozzle in order to obtain ignition and minimize accumulation of propellants. Minimum fuel flows required for ignition were observed to increase with increasing viscosity by Bransford and Horstman (*10*) and Ricci (*71*), who also observed the required flows to decrease with an increase in volatility. Both of these trends give strong support to the thesis that combustion characteristics are strongly dependent upon atomization phenomena.

Mullins (*61*) noted the small (about 20%) effect of either preheating or prevaporizing the fuel, established the validity of the Arrhenius equation for the effect of air temperature, and reported that the ignition delay varied inversely as the chamber pressure. This latter variation was confirmed by Crocco, Grey, and Matthews (*15*), whose experimental results are summarized in Figure 11. The predominant effect of viscosity over volatility or ignitability on relative fuel ignition performance was noted by Kittredge (*43*), who reported that the minimum fuel flows for ignition with jet fuels correlated well with the square root of the dynamic viscosity. Bernard (*5*) observed that the addition of wetting agents decreases the ignition delay by as much as 50%, as the stored energy of the propellants (surface tension times specific area) increases the ignition lag. Gregory and Calcote (*35*) noted that the increase of water to ammonia increased the ignition lag of ammonia-nitric acid combination in all cases, but the addition of water to the acid actually decreased the ignition lag until a minimum value was reached, after which the lag increased sharply.

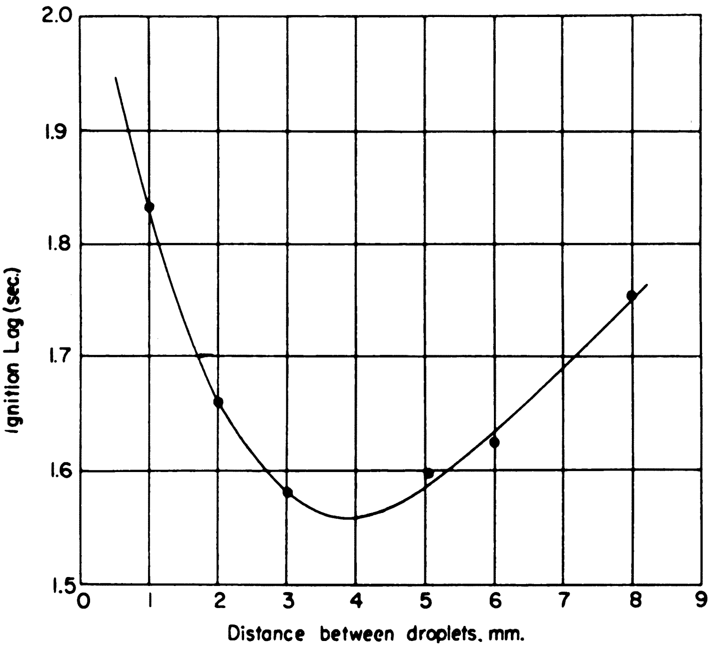

Figure 12. Variation of ignition lag with distance between droplets for cetane at 500° C. (Nishiwaki)

Nishiwaki's (*63*) studies of preheat and vaporization components of ignition lag revealed that an increase in the oxygen content of the fuel decreased the total time lag, while an increase in the diameter of the droplet increased the total lag. The ignition lag for a pair of droplets in close proximity first decreased as the droplets moved apart and then increased as the separation distance became greater. The similarity between this trend and that observed by Rex, Fuhs, and Penner (*70*) for the burning rates of a pair of droplets is striking, as seen by a comparison of Figures 7 and 12. The same preheat-evaporation breakdown of ignition lag was studied by Kobayasi (*44*), who noted that the burning rate increases slightly with temperature, and by Hottel, Williams, and Simpson (*38*), who observed that preheat time decreases with furnace temperature.

Performance. Penner and Datner (*67*) stressed the importance of injector design in the determination of the performance of a liquid propellant combustor. This was borne out by Bellman, Humphrey, and Male (*4*), who noted that both the uniformity of combustion and the specific impulse of their two-dimensional transparent rocket engine were increased by increasing the number of injector orifices. The combined effects of atomization and evaporation were investigated by Lloyd and Mullins (*47*), who reported that efficiency decreases with both the drop size and the atmospheric pressure. Preliminary calculations indicate that the performance decreases linearly with the theoretical average lifetime of the droplets. The requirement of fine atomization for improved combustion efficiency was also stressed by the staff of the National Gas Turbine Establishment (*62*), Koenig and Dandois (*45*), and Sharp (*77*), who added that for poorer atomization an easily cracked fuel is advantageous and that roughness, where it exists, increases with increased volatility of the fuel. Gerstein (*22*) emphasized the importance of good mixing and of minimizing the steps of atomization and evaporation; Graves (*33*) indicated that an increase in the percentage of oxygen in the atmosphere tends to increase the efficiency, as would be expected; and Graves and Gerstein (*34*) reported that the efficiency of a combustor decreased linearly with the volumetric boiling point of the fuel. The detrimental effect on performance of increased liquid viscosity, which results in poorer atomization, was reported by Ricci (*71*) and Bransford and Horstman (*10*).

Wear and Jonash (*83*) reported that for unstable combustion, the highest efficiency was obtained for paraffinic and aromatic fuels with low boiling points. Better efficiency

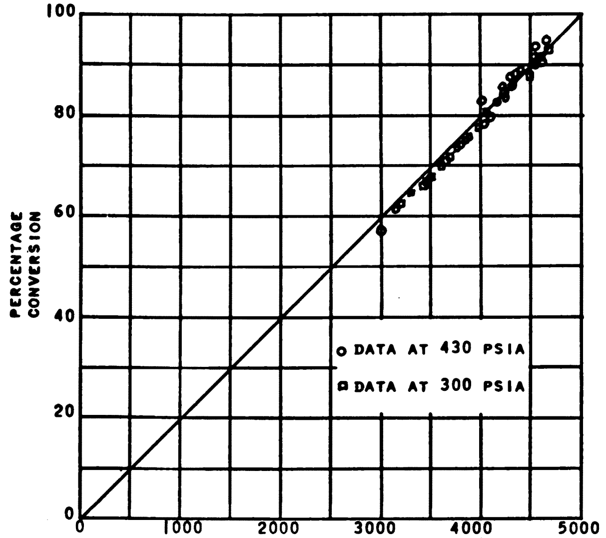

Figure 13. Experimental variation of percentage conversion with characteristic velocity (Trent)

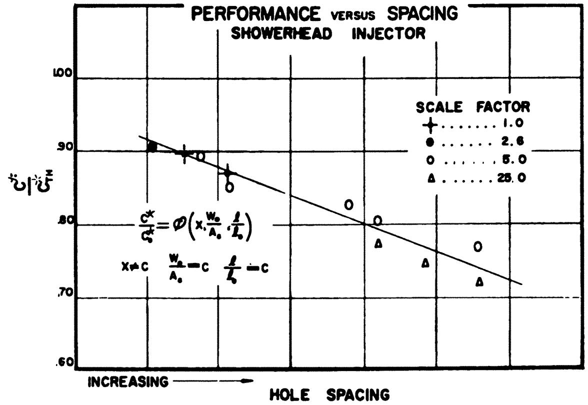

Figure 14. Variation of characteristic velocity with spacing of injector orifices for a showerhead injector (Ross)

was obtained for those fuels with low and medium boiling points, for which the combustion is intermediately stable. For stable combustion, a maximum efficiency of 90% was obtained for all fuels except the aromatic fuels with high boiling point. In his report on flame radiation research, Thring (*80*) reported that an increase in the atomizing agent resulted in a decrease in emissivity, because of greater efficiency and shorter flame: 100% efficiency could be obtained by designing a burner in which the oil is accelerated more efficiently, hence less rapidly.

Similarity criteria for scaling combustors were presented by Penner (*66*), who considered Damköhler's similarity groups and prescribed that the characteristic reaction frequency should decrease as the square of the engine thrust (*65*). Experimental evidence of combustion similarity was presented by Trent (*82*), who found by sampling the combustion gases at various stations in the chamber, that the local value of the charac-

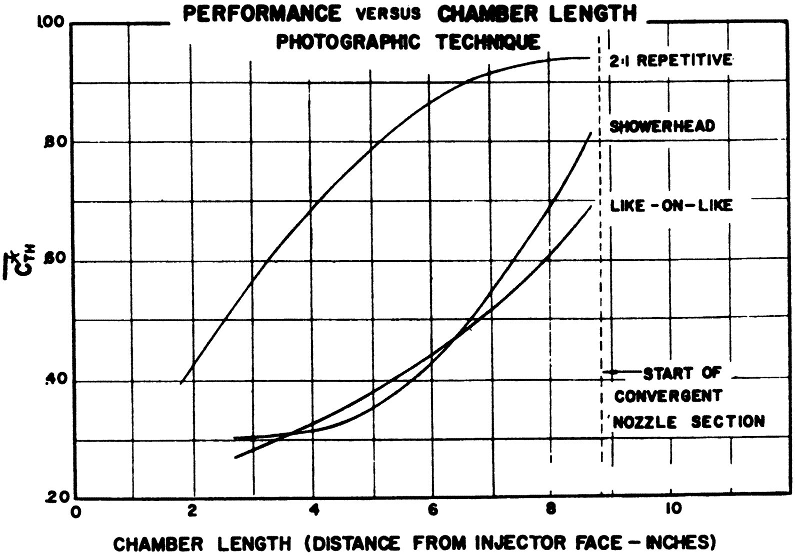

Figure 15. Variation of characteristic velocity with distance from injector face for various injectors (Ross)

Photographic technique

teristic velocity varied directly with the percentage of combustible burned, as shown in Figure 13. Quantitative data on the effect of number of injector orifices and their spacing were presented by Ross (*73*), who showed that the characteristic velocity decreased linearly with the hole spacing, as shown in Figure 14. The variation of performance characteristics with injector type is shown graphically in Figures 15 and 16, which indicate that finer methods of atomization result in higher performance, as indicated above. A theoretical model for predicting performance characteristics, based on these experimental results, is presented below, and indicates that performance variation in the combustor depends on the ratio of reaction rate to vaporization rate, and/or the rate at which the gases are expelled from the chamber.

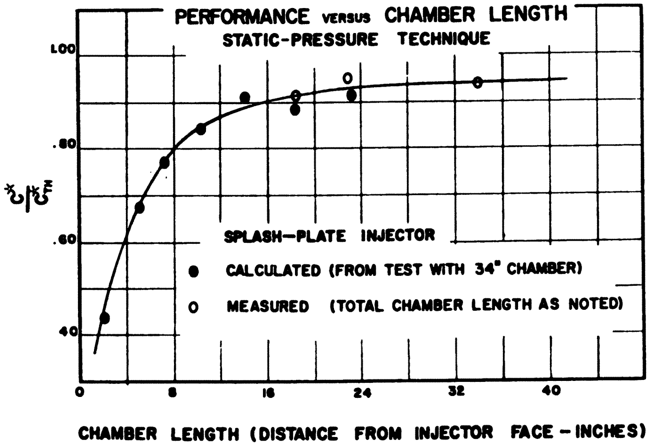

Figure 16. Variation of characteristic velocity with distance from injector face for various injectors (Ross)

Static-pressure technique

Carbon Formation. Fouré (*19*) stated that the factors affecting carbon formation are the functioning conditions of the combustor, the method of injection, the nature of the surface of the combustor walls, and the configuration of the combustor. He found that carbon formation increased with fuel density, boiling point, and the ratio of carbon to hydrogen atoms, and decreased with air/fuel ratio, chamber pressure, and temperature. Barnard and Eltinge (*2*) reported that the smoke point correlates with deposition better than other factors, the relative deposit is increased with the average boiling point of the fuel, and is also increased with the aromatics content of the fuel. Penner and Datner (*67*) summarize the experimental findings by attributing carbon deposition to improper combustion, and Sharp (*77*) notes that carbon deposits are increased by an increase in the atomizer flow number.

Stability Limits. The influence of the quality of atomization on the stability of combustion of liquid fuel sprays was investigated by Anson (*1*), who reported that the fuel-air ratio at the weak limit is increased by increasing the average drop size, as shown in Figure 17, as would be expected from vaporization considerations. Finely atomized spray is conducive to stable combustion at weak limits. Jones and coworkers (*41*) noted that the concentration limits of flammability for very fine droplets are essentially the same as for vapor-air mixtures. Browning and Krall (*9*) reported that the rich blow-off limits for a kerosine mist were much greater than for the vapor and that the mist gave generally a much wider percentage range. The opposite conclusion was reached by Burgoyne and Richardson (*12*), however, in that the mist flame was more easily suppressed by the addition of a particular diluent to the air supporting the combustion, which indicates the possible inhibitive effect of vaporization. Effect of addition of incombustible liquids to oil drops could be explained quantitatively in terms of the thermal

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capacity of the added liquid and the flame-suppressing effect of its vapor. The conditions necessary for flame stabilization in a gas stream with kerosine fuel were investigated by Golitzine (*29–31*). In his first report (*29*), it was concluded that flame stabilization in air streams of over 200 feet per second is possible without plate baffles if the kerosine fuel is injected upstream by means of an air blast atomizer; it was found that an increase in fuel flow rate decreases the optimum blast air-fuel ratio, hence suggests optimum drop size criterion. Using this method, additional fuel may be burned without blast air downstream of the pilot stabilizing zone.

In the second report (*31*), the flame stabilization limits of a baffle in a hot fast gas stream were found to depend to a large extent on the location of the fuel jets upstream of the baffle; a wide range of stable operation is achieved by positioning one fuel jet closely upstream of the baffle, and centrally with respect to it, with other jets located relatively far upstream of the baffle and arranged so as to distribute the fuel in the gas stream. In the third report (*30*), the flame stability limits of kerosine fuel injected upstream into a hot gas stream were found to be narrowed by an increase in gas velocity and a decrease in gas pressure but not greatly affected by gas temperature; limits were widened by an increase in air blast pressure and flow.

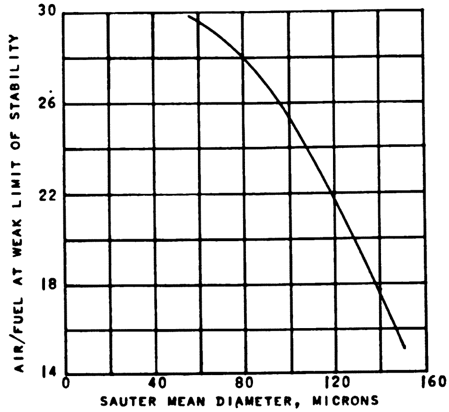

Figure 17. Variation of mixture strength at weak limit of flame stability with Sauter mean diameter of spray (Anson)

Sharp (*77*) and Longwell and coworkers (*49*, *50*) found that greater volatility of the fuel led to a decrease in the lower limit of the fuel-air ratio necessary for combustion, indicating again a minimum vapor concentration criterion. May and Maddocks (*52*) found that the flame was stabilized in the recirculating eddies, the flame supported by vaporization of the liquid deposited on the flame holder. Extinction at the lean limit occurred when the flame holder temperature rose until vapor binding occurred, decreasing the fuel evaporation below the minimum requirement; the rich extinction limit was caused by a reduction in evaporation due to the cooling action of excess liquid. The chief effect of drop size on the flame stability was due to the change in the rate of deposition on the flame holder, which caused cooling of the holder and quenching of the flame; an increase in the fuel volatility by addition of gaseous fuel caused both limits to move to richer mixtures, which is contrary to what might be expected. A decrease in drop size caused a shift of both limits toward richer mixtures, a trend similar to the effect of increased volatility. Heat transfer on the stabilizing rod was concluded to be the major factor in stability.

Bransford and Horstman (*9*) noted that higher viscosity fuels led to an increase in the rich air-fuel limit. The same effect produced by lower velocity injection was reported by Ricci (*71*), who observed the opposite effect of a decrease in ambient pressure. Each of these effects is directly explainable in terms of atomization characteristics. At lower air temperatures Longwell and coworkers (*50*) reported that the range of smooth burning was narrowed by injection of steam into the air stream upstream of the combustor, thus providing a quenching mechanism.

Design Criteria. The experimental study of radiation burner design by Thring (*80*) indicated that a steam-atomized flame gave much lower radiation than air-atomized flame, because of loss of heat to condensed water droplets, and accelerated combustion resulted in less luminosity. Gollin (*32*) reported that extra radiation obtained from burning flame was due to solid matter in the flame but that peak radiation of burning liquid fuel was greater than that of burning pulverized coal. An elegant theory for the design of vortex combustion chambers was presented by Havemann (*37*), who presented a method for determining wall shape and entrance conditions, as determined by the radius, temperature and velocity distribution, and a parameter which is a measure of the stability of a particle in its orbit, being the ratio of the radial derivative of centrifugal force to the radial derivative of viscous drag which opposes this tendency toward centrifugal motion. The design of an air-blast atomizer for use with viscous fuels was presented by Clare and Radcliffe (*14*), who determined experimentally that the flow coefficient for similar swirl atomizers is a function of the Reynolds' number of the flow.

Conclusions

As a result of this survey, the following conclusions can be drawn.

The established correlations and laws of atomization and evaporation are directly applicable to the various combustion problems of ignition delay, performance, stability limits, and design.

Experimental and theoretical information obtained from a study of the single droplet are of great value in understanding the behavior of sprays and the combustion of sprays in general.

Ignition delay, performance, and stability limits can all be considered with respect to the quantity of vapor available for combustion, in that finer atomization and greater volatility lead to shorter ignition delays, higher performance, and leaner stability limits.

The limited quantity of precise knowledge in this very important field should serve to stimulate an extended investigation of the phenomena involved.

Theoretical Model for Predicting Performance

Variation of Performance with Distance from Injector. Consider the basic definition of reaction rate:

$$dw = rW\,dt \tag{1}$$

where dw is the incremental weight (dimensionless) of propellant converted in time dt, r is the reaction rate (assumed to be constant) in pounds of propellant converted per pound of available propellant per second, and W is the (dimensionless) weight of unreacted propellant available. The performance characteristics for the various types of injectors, as depicted in Figures 15 and 16, will depend upon the assumptions regarding the distribution of available propellant W.

VAPORIZED PROPELLANTS. For injectors which produce a very finely atomized spray which vaporizes completely within a short distance from the injector, the gas in the combustion chamber can be considered as a homogeneous mixture of combustibles. Hence the weight of unreacted propellant at any point in the chamber is equal to the total weight of combustibles minus the weight previously reacted:

$$W = 1 - w \tag{2}$$

Substitution of Equation 2 into Equation 1 results in the following first-order linear differential equation for w in terms of the relative axial distance $z = x/L$, where L is the

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length of the combustor

$$\frac{dw}{dz} + \frac{rL}{U}(w - 1) = \frac{dw}{dz} + a(w - 1) = 0 \tag{3}$$

where the parameter a is recognized as Damköhler's first dimensionless group (*66*), and U can be interpreted as the average gas velocity of the system. The solution for Equation 3 is readily obtained as

$$w = 1 - e^{-az} \tag{4}$$

which indicates immediately that the percentage reacted will increase sharply near the injector end of the chamber and then proceed more gradually, as was noted in Figures 15 and 16 for the splash-plate and 2 to 1 repetitive injectors. The parameter a is essentially a measure of the predominance of the reaction rate over the gas velocity, and can be expressed as the product of reaction rate and gas residence time T_g.

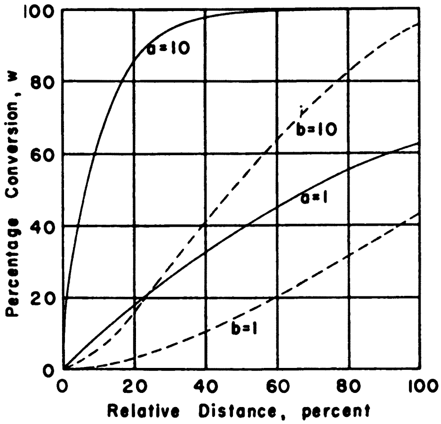

Figure 18. Theoretical variation of performance with axial distance in combustor

Vaporized fuel, $a = rT_g$
Atomized fuel, $b = rT_d$

ATOMIZED PROPELLANTS. For those combustors in which the propellants persist in droplet form for a large percentage of the length of the chamber, it is apparent that the available propellant must be represented as a heterogeneous mass of liquid and vapor in which the vapor concentration will vary with distance from the injector. As Figure 4 shows that the vapor concentration can be determined from droplet evaporation considerations, the equation for available propellant W can be written in terms of the square of the relative droplet diameter $s = (D/D_0)^2$;

$$W = (1 - s^{3/2}) - w \tag{5}$$

Substitution of Equation 5 into Equation 1 then yields

$$\frac{dw}{dz} - \frac{D_0{}^2 r}{\lambda}[w - (1 - z^{3/2})] \tag{6}$$

where λ is the evaporation rate. The solution to Equation 6 can be written

$$w = 1 - s^{3/2} + \frac{3}{2b}(e^{-b(1-s)} - s^{1/2}) - \frac{3\sqrt{\pi}}{4b^{3/2}} e^{bs}(erf\ \sqrt{b} - erf\ \sqrt{bs}) \tag{7}$$

where

$$b = rD_0{}^2/\lambda = rT_d \tag{8}$$

is similar to Damköhler's second dimensionless group (*66*),

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\, du \tag{9}$$

is designated as the error function, and T_d is the droplet lifetime. Thus the performance of a heterogeneous system is characterized by the ratio of the reaction rate to the rate at which combustible vapors are being supplied.

Figure 18 shows several representative curves as determined from Equations 4 and 7; a low value of b results in gradual progressive combustion, as in Figures 15 and 16 for the showerhead and like-on-like injectors. The criterion for a rapid increase in performance as compared with gradual combustion can be expressed by the inequality which is satisfied by larger values of b:

$$\frac{2}{\sqrt{\pi}} e^{-b} < (erf\ \sqrt{b} - erf\ \sqrt{bs})/\sqrt{b} \tag{10}$$

The concept of distribution of available propellant may be of aid in determining the performance characteristics of any combustor under consideration and may thereby prove valuable in the design of future combustors. Most combustors will fit neither of the above cases exactly, as these cases represent extremes. However, any combustion system using atomized propellants can be represented adequately by some combination of the two cases considered above.

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Combustion in Aircraft Gas Turbine Engines

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The requirements of minimum weight, frontal area, and cost, coupled with the requirements of minimum fuel consumption over a wide range of operating conditions, impose rigorous demands on the combustion system of turbojet engines. These systems are evaluated in terms of operable range, heat release rates, combustion efficiency, pressure loss, ease of ignition, outlet temperature profile, and durability. Much empirical and basic research information is available on combustion in the environment found in turbojet engines, and this paper reviews the unclassified portion of this literature and provides a reference bibliography. Summary statements on each of the more important variables influencing combustor operation and design are included, but no attempt has been made to cite all the pertinent literature. The aspects of operable limits and combustion efficiency, smoke and coke, combustor durability, exhaust temperature profile, ignition, and pressure losses are each treated, and an evaluation of the areas for future research is made.

Variations in turbojet engine altitude, flight speed, and thrust require combustion to be maintained over a wide range of inlet air and fuel environment. Furthermore, the combustion must be nearly complete in order to achieve maximum aircraft range. Combustion limits and efficiency are, then, two major performance criteria of the turbojet combustion system. Under conditions very favorable to combustion, the influence of operating, design, and fuel variables are minimized, and only in adverse combustion environment is their influence measurable.

Combustion Limits and Efficiency

Effect of Engine Operating Conditions. Combustor inlet-air parameters (pressure, temperature, mass flow, and velocity) and fuel-air ratio are the primary engine operating variables influencing combustion performance. At least two conditions must change simultaneously, thus hindering the determination of the specific influence of one isolated variable. Enough investigations have been performed, however, to permit trends to be reasonably stated. Different combustion systems will be affected in varying degrees by these operating variables.

COMBUSTOR INLET AIR PRESSURE. The effect of decreasing inlet static pressure has been shown to decrease efficiency at an accelerating rate, decrease maximum stable temperature rise, and narrow the operable fuel-air ratio range (rich to lean blowout

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limits). This pressure effect may be attributed to a decrease in reaction rate and to the narrowing of flammability mixture limits. The lower limits of flammability as found in bench scale experiments (about 1.0 pound per square inch absolute) are, however, at considerably lower pressures than blowout limits for turbojet combustion systems.

COMBUSTOR INLET AIR TEMPERATURE. The effect of decreasing inlet static temperature is similar to the effect of decreasing pressure—i.e., lowered efficiency, lowered maximum temperature rise, and narrowing of the operable fuel-air range. This temperature effect is apparently due to a decreasing rate of chemical reaction with decreasing temperature and changes in evaporation rates of fuel droplets.

COMBUSTOR INLET AIR VELOCITY. Within practical design limitations, increasing velocity results in decreasing efficiency at an accelerating rate, decreasing maximum stable temperature rise, and decreasing rich blowout limits. However, at "off-design" conditions opposite effects have been noted. Apparently there is an optimum value of velocity for each combustor system, and the dependance on design and other operating variables provides a wide range of optimum velocity values among the many combustor systems. Effects of variance in velocity are associated with poor fuel spray characteristics attendant with very low fuel flow rates, variations in fuel-air mixing rate and patterns, and variation in residence time for the fuel-air mixture.

COMBUSTOR OVER-ALL FUEL-AIR RATIO. When, at constant inlet air conditions, fuel-air ratio is increased from a low value, combustion efficiency first will increase at low fuel-air ratios, then not change appreciably at intermediate fuel-air ratios, and finally decrease at high fuel-air ratios. This decrease in efficiency at high fuel-air ratios results in a maximum temperature rise which cannot be exceeded at a particular operating condition. This can result in an altitude operational ceiling for the turbojet engine (*26*). Fuel-air ratio effects are attributed to poor fuel atomization and vaporization at low flows which "leans out" the burning fuel-air mixtures; at high fuel flows better atomization and vaporization results in "over-enrichment," shifting the zone of optimum fuel-air mixture downstream into a higher velocity region of the combustor. The fuel-air ratio effect is analogous to the velocity effect in that an optimum range exists for any combustion system, and, depending on air admission and fuel injection characteristics, combustion efficiency may be sensitive or insensitive to changing fuel-air ratios. The best combustor would, of course, provide a high, flat efficiency curve over the desired fuel-air ratio range at any inlet conditions encountered in operation of the engine.

Combustion performance of turbojet combustors is adversely affected by decreasing pressure and temperature and by increasing velocity. Also, the narrower the fuel-air ratio range required over the spectrum of engine operation the easier it is to design a chamber providing maximum efficiency. Thus, increasing altitude, decreasing engine rotor speed, and increasing air loading (mass per flow area) are factors detrimental to combustion performance while increasing flight speed, increasing compression ratio, and decreasing air loading are favorable to combustion performance.

Effect of Design Variables. Absolute efficiency and maximum temperature rise values vary with combustor design for given operating conditions. The design of turbojet combustors would be made easier if the exact, independent contribution of each of the basic processes of combustion could be evaluated. Unfortunately, at present, such an evaluation is not possible. Many design variables have been studied, however. These are: combustor shape and size; air admission features such as total area, size, shape, and distribution of openings; and fuel-injection factors such as atomization, spray pattern, location of nozzles, and the use of fuel vaporizers. A number of these variables are considered here. Although they are discussed separately, they are not independent of each other, nor do the separate processes occur in separate distinct zones in the combustor.

COMBUSTOR SIZE. The question of whether combustor volume is the limiting factor in altitude operation can be answered by comparing heat release rates measured in simple flames and homogeneous reactors with those obtained in engines. Simple flames and reactors give rates of the order of 7×10^8 B.t.u. per hour per cubic foot per atmosphere

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(*70*). This is much greater than combustor heat-release rates (*40*) currently required in engines (4 to 8 $\times 10^6$ B.t.u. per hour per cubic foot per atmosphere) so that only about 10% of the combustor volume would be required at 65,000 feet altitude. However, at the present state of combustor development, the combustor cross section should still be made as large as possible without exceeding the diameter of the other engine components. With regard to combustor length, the requirements of minimum engine weight and cost demand as short a length as practical. Typical values of ratio of length to diameter for turbojet combustors are 3 to 5.

COMBUSTOR SCALE. The need for a proper testing technique to determine the thermodynamic behavior of geometrically scaled combustors for experimental development is obvious. From a consideration of the basic processes, a technique has been developed that appears experimentally to be a reasonable working compromise (*179*). This technique consists of testing models at pressures inversely proportional to their linear dimension with no change in flow velocities, fuels, fuel-air ratios, and temperatures. A half-scale model would be operated at twice the normal full-scale pressure while holding other variables constant. This technique provides better similarity between combustors of the prevaporizing type than between liquid atomizing combustors. Scaling of atomizing combustors by this technique is more complex because of the differences in fuel weight flows and spray-path lengths between the model and its larger prototype. It is necessary then to test the model with a scaled atomizer to ensure a constant fuel pressure differential. To cover full operating range, a series of atomizers would be required (*150*).

COMBUSTOR AIR ADMISSION. An important design consideration is, of course, the primary combustion zone where low velocities and reverse flows must be provided in order to allow sufficient time for initiation and completion of burning. This air admission system is based not only on the requirements of the burning process but also on other factors such as coke deposition, ignition, outlet temperature patterns, and durability. The primary zone is generally assumed to occupy the first one third to one half of the total combustor length, the remainder being devoted to dilution of the combustion products to the desired outlet pattern. About 20 to 30% of the total air flow is required for combustion, and this amount of air is usually added gradually in this primary liner length. These percentages of primary air required for maximum efficiency and limits vary directly with fuel-air ratio; that is, more air is desired in the high fuel-air ratio range and less air in the low range. Studies with controlled separate primary-air admission indicate that the minimum primary fuel-air ratio is about 0.05 for best performance (*141*). Studies have also shown that the ratio of air-inlet hole area to burner exit area and the angle of liner wall to the axis affect efficiency and performance. These factors affect the air admission through their effect on over-all pressure drop through the combustor system; only in systems with very high pressure drops is the fraction of total air passing through openings in liner walls at a given station directly proportional to the fraction of total open area at the station.

Primary zone size is important with regard to efficiency and limits also. Within practical limits, a larger primary zone cross-sectional area will provide the best performance (*138*). Possible reasons are: lower velocities, less wall impingement by fuel, larger zone of low velocity, and less wall quenching of chemical reactions. The best axial distribution of open area of a combustor will depend on required operating conditions, the pressure loss characteristics, and the shape of the air entry ports. It will also depend on fuel-injection and fuel-volatility characteristics, as these factors will affect the amount of vapor fuel present at any location. If proper burning environment is to be obtained, these factors must be matched, and compromises in performance must be expected.

FUEL ADMISSION AND RELATED FACTORS. If it is important to admit the air gradually in the upstream end of the combustor, it is likewise important to admit the fuel gradually, as both air and fuel must be matched to achieve the correct mixtures. In atomizing combustors, the nozzle is usually near the upstream end of the combustor. However, fuel is effectively distributed along some length of the combustor because it is not instantaneously vaporized and mixed with air at this upstream station. (In vaporizing-type combustors the vaporizer outlet is usually immersed some distance into the primary zone.) When operated in still air, the injector geometry, injector pressure drop, and fuel characteristics influence the sizes of the droplets and their distribution. These spray characteristics are modified when the injector is operated under the dynamic conditions found in combustors, and it then becomes difficult to evaluate the influence of a specific spray variable on combustion performance. Nevertheless, much research, both empirical and basic, has been devoted to determining the effects of fuel injection variables on combustor performance.

A method of estimating the density distribution of various size drops in the combustor primary zone was presented in one investigation (*28*). At sea-level conditions, droplet evaporation times were calculated with vapor diffusion theory. Percentage of spray evaporated was seen to be related to combustion efficiency, and, when the residence time was less than evaporation time, efficiency decreased. A small capacity nozzle will provide the highest combustion efficiency at low fuel-flow rates, and at high fuel-flow rates a large capacity nozzle will provide the best performance (*100*). The values of maximum temperature rise were found to increase with increase in fuel-nozzle size. At low temperature-rise values, high pressure differentials across the nozzle give the best efficiency performance. However, as temperature rise is increased, high-pressure differentials result in premature blowout, while lower-pressure differentials give increased temperature rise with increased combustion efficiency. Thus, a minimum quality of atomization is required at all conditions, but it is possible to produce sprays that have such small droplets that they give mixtures that are too rich to burn.

Wide cone angles of nozzle sprays have also been shown to provide maximum efficiencies and limits in a combustion system, especially at low fuel-air ratios (*133*). There is an optimum nozzle size (that is, optimum vapor fuel-air mixture) for a given combustor design, fuel, and operating condition. A nozzle design having only one orifice system would provide optimum performance through only a portion of the total operating regime of an engine (12 to 1 range of fuel flow rate is required in current engines). This has led to the development of duplex nozzles, which combine the components of two individual nozzles of different size, variable-area nozzles (*62*), and spill-return nozzles (*24*). The latter two nozzles provide finely atomized sprays over a flow range of 15 to 1 or greater.

The importance of fuel vaporization has been determined by using both liquid and vapor fuel (propane) in a turbojet combustor. The combustion efficiencies at high altitudes were less affected by changes in altitude with the vapor fuel. However, it was shown that vapor fuel distribution was very important as performance was markedly affected by poor vapor distribution. The importance of controlling the atomization and vaporization steps in the combustor process are evident. Vaporizing-type combustion chamber designs have been compared at altitude conditions in terms of their efficiency performance (*168*). Geometrical design (effectiveness of vaporizer) and vapor fuel distribution were shown to be important.

The effect of design variables on efficiency and limits can be summarized as follows:

Total combustor volume and primary zone volume should be as large as possible within the limits imposed by other engine components and pressure-loss characteristics.

A strong reverse flow is required to bring hot combustion products into contact with fresh fuel-air mixture and provide maximum residence time.

Fuel injection should give at least a minimum quality of atomization which is tailored to the air admission to produce fuel-air mixtures near stoichiometric.

These effects suggest interesting design variations, such as a change in air admission proportions with operating condition or premixing air and vaporized fuel to proper mixture concentrations just prior to injecting into a variable combustion volume governed by the operating condition.

Effect of Petroleum Fuel Properties. Three primary requirements must be met by practical fuels for aircraft turbojets. These requirements are: They must be available in large quantities at low cost, they must produce satisfactory performance in all types of engines, and they must be suitable for aircraft fuel systems. Petroleum fuels vary in volatility, chemical composition, and concentrations of minor nonhydrocarbon compo-

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nents. The first two of these variables can influence both combustion efficiency and operable limits. However, there are interrelationships between fuel and engine hardware variables which permit engines to be designed for optimum performance with one or another type of fuel.

FUEL VOLATILITY. Combustion efficiencies are substantially 100% with fuels of widely different volatility at sea level–high pressure conditions. However, as altitude is increased, efficiencies usually decrease with decreasing volatility. As volatility enters directly into the vaporization rate of fuel droplets, increasing volatility has an analogous effect on performance as increasing atomization. Better lean limits are usually obtained with more volatile fuels, but maximum stable temperature rise values decrease. Thus, higher engine operational ceilings are frequently obtained with less volatile fuels.

Efficiency has been shown to be a function of the 50% boiling temperature of the fuel with both liquid atomizing and prevaporizing combustors, but if the 50% temperature doesn't exceed 480° F., efficiencies are not greatly affected (*69*). This means that varying volatility over the range provided by present jet fuel specifications will not result in large efficiency losses or lowered altitude engine ceilings. Proper selection of combustor air and fuel admission can eliminate volatility effects, and it is probable that higher boiling fuels will be utilized efficiently in the future.

FUEL CHEMICAL COMPOSITION. Comparisons of efficiencies obtained in combustors operated at severe inlet-air conditions with fuels having different chemical composition have shown that normal paraffins were best, isoparaffins were intermediate, and aromatics were worst. Fuels line up in the following arrangement with regard to maximum stable temperature rise: normal paraffins, olefins, cycloparaffins, aromatics, and isoparaffins (best to worst, respectively). Fuel-air ratio influences this relationship, however, as benzene gives the richest blow-out limits (*109–113*). This anomaly suggests that aromatic-rich fuels would provide the highest engine altitude ceilings. In one investigation benzene did produce slightly higher limits than isoheptane, but with a high-boiling aromatic solvent, the limits were much lower (*100*). In general, chemical composition (within the range permitted by jet fuel specifications) would have little effect on efficiency or altitude ceilings of turbojet engines.

Correlating Factors. One of the principal objectives of the worker in the field of combustion is the development of correlations that will predict or estimate the performance of combustion systems. In recent years a number of factors have been explored, but because of the complexity of the over-all process no exact treatment connecting all the factors has been found.

A correlating function reflecting both fuel volatility and composition was found to relate fairly well with combustion efficiency (*35*). This factor,

$$\frac{1/\log 50\% \text{ boiling point}}{\sqrt{\text{specific gravity}}}$$

was obtained empirically in a combustor operated at altitude conditions with 13 fuels.

Such fuel characteristics as flame speed, spontaneous ignition temperature, quenching distance, and minimum ignition energy are fundamental properties that may account for the effect of fuel structure on combustion efficiency. Maximum flame speed has been found to be related to combustion performance. Fuels with high flame velocities generally provide high maximum, stable temperature-rise values, wide blowout limits, and high efficiencies. No definite quantitative correlation has been established between combustion efficiency and flame speed, however (*34*). As fuels with high flame speeds also have small quenching distances and low ignition energies, performance might relate inversely to these properties. Physical variables, such as viscosity and surface tension effects on fuel atomization, may also be related to performance in atomizing combustors.

Reasonable correlations of combustion efficiency with fuel spray momentum and spray energy in two different combustors have been shown to hold over a range of altitude–engine idling conditions (*133*). As different curves were obtained with different injector nozzles, spray-cone angle was thought to be a factor. Further work showed that efficiency did correlate closely with expressions representing the spray momentum or energy, provided the cone angle was constant and allowance was made for inlet air velocity to the $^2/_3$ power and inlet temperature to the $^5/_4$ power.

Several investigators have suggested that chemical-reaction kinetics control the performance of both ramjet and turbojet combustors (*4, 96, 139*). Second-order reaction equations were assumed to be the over-all rate determining step, and the influence of combustor inlet-air pressure, temperature, and velocity on combustion efficiency could be explained in terms of their effects on these second-order reactions. Combustion efficiency has been shown to vary inversely with a reaction-rate parameter of the form

$$\frac{W_f}{(p^{1.8})(A_b)(D_o)}$$

where

W_f = fuel flow rate, thousands of pounds per hour
p = pressure, atmospheres
A_b = cross-sectional area of burning zone, square feet
D_o = length of burning zone, feet

with fuel-air ratio as an independent variable (*15*). This correlation apparently holds over the range of temperature, pressure, and velocity values covered. Analyses of this type provide a basis of comparison between combustor designs and reduce the amount of test data necessary to evaluate any given design.

Smoke Formation and Coke Deposition

Coke deposits are sometimes found on interior surfaces of the turbojet combustor, and smoke is often noticed in the exhaust gases—both factors are undesirable. Coke may deposit on nozzles and affect spray patterns, it may partially block air entry holes, short out ignition sources, and reduce combustor life by promoting liner warping and cracking. Smoke does not appreciably affect combustion efficiency or combustor life, but is bothersome in flight operations. Several theories about the mechanism of coke formation have been advanced. The soft, sooty deposits are thought to form when high-boiling residuals and polymerized products are mixed with gas-phase smoke, and the hard, striated deposits may originate from thermal cracking in the liquid phase of that fuel which impinges on the liner walls.

Effect of Engine Operating Conditions. The interdependence of the operating variables again renders the direct determination of the influence of one variable on combustor deposits difficult. The situation is similar to the determination of the effect of these variables on combustion efficiency and limits.

COMBUSTOR INLET-AIR PRESSURE. Increased pressure accelerates smoke formation in both laboratory flames and combustors. Coke deposits are, in general, affected similarly. A leveling-off in deposit rate has been found once the pressure is increased to 2 to 3 atmospheres. This is attributed to increased rate of erosion with increased air density. Coke deposition would be expected to increase with pressure because smoke forms more readily at the higher pressures and because the evaporation of fuels is retarded.

COMBUSTOR INLET-AIR TEMPERATURE. Inlet-air temperature has little or no effect on smoke formation. The influence of inlet-air temperature on coke deposition is a complex process depending on design, fuel used, and operating conditions. Different investigators have reported decreases, increases, maxima, and minima. The different basic processes resulting on coke deposition are important at different temperature levels. If the inlet-air temperature is above the temperature at which coke will burn, coke will not deposit on the hot metal surfaces.

COMBUSTOR INLET-AIR VELOCITY. Inlet-air velocity effects on both smoke and coke deposition are similar to inlet temperature effects—i.e., depending on operating and design variables, smoke and deposits may increase or decrease with increase in velocity. Velocity can increase coke deposition, for a given combustor design, by increasing recirculation of air currents that would cause more fuel impingement on walls

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and lower wall temperature. Conversely, it can decrease deposition by increasing air scrubbing action which lowers fuel contact time on metal surfaces and increases erosion.

COMBUSTOR OVER-ALL FUEL-AIR RATIO. In general, coke and smoke both increase with increasing fuel-air ratio, although some investigations have shown that smoke can attain a peak point beyond which it decreases. However, the location of this peak value was variable and dependent on other factors. These fuel-air ratio effects can be attributed to more fuel wash on surfaces, richer local fuel-air ratios, and increased thermal cracking of the fuel. Increased burning and erosion might lower coke and smoke formation, however.

DURATION OF TEST. The amount of deposit depends on length of run time, with deposit weight increasing linearly with time in the initial stages. A maximum weight is attained, however, as the rate of build-up decreases with time.

Coke and smoke formation was found to increase up to an equilibrium level with increasing pressure, fuel-air ratio, and time of test. Variation in velocity and temperature produced conflicting results, with smoke and deposits increasing or decreasing, depending on operating conditions and design of the combustor.

Effect of Combustor Design. Combustor designers must consider the factors that cause coke deposition and smoke formation. Local fuel-rich regions should be minimized, especially near metal surfaces. This means that the impingement of liquid fuel on combustor liners should be eliminated, large fuels droplets avoided, and local burning zones kept near stoichiometric proportions. Several investigators have shown that coke deposition was drastically reduced by providing air jets which supply an "air wash" along liner walls or around nozzles (*168*). The effect of smaller nozzle capacity (better atomization) has been shown to cut deposition. Use of fuel prevaporizing hardward devices decrease deposits because of elimination of liquid fuel in contact with cooled surfaces and better fuel distribution. Design of prevaporizing combustors is more critical in one respect, however, as lack of complete vaporization (with high-boiling fuels) can result in more deposition than a comparable atomizing combustor (*88*). Also, if the coke accumulates in the vaporizing device itself, the resultant decrease in fuel flow can cause failure of the device. While the most certain way of eliminating coke and smoke is to avoid having local fuel-rich regions, combustion efficiency and stability at high altitudes may be sacrificed as a result of this lean operation. Combustor design is, then, a compromise of several factors with coke and smoke formation only one of these factors.

Effect of Petroleum Fuel Properties. One of the earliest fuels problems to be recognized in turbojet combustor development was the coking problem, and, consequently, numerous investigators have obtained data showing the effect of various fuel properties on deposition.

FUEL VOLATILITY. Smoke formation is less dependent on fuel volatility than on other fuel factors, such as hydrocarbon type. Data indicate that smoke decreases slightly with increasing volatility. In general, the more volatile fuels caused less coke deposition. High front-end volatility was shown to decrease deposits, as the addition of light components to a bad fuel resulted in less deposition. Increase in volumetric average boiling point resulted in a considerable increase in deposition at constant hydrogen-carbon weight ratio. This effect of volatility is associated with increased rates of vaporization which provide smaller fuel droplets and less contact time between surfaces and liquid fuel. Eliminating the vaporization process does not eliminate deposition, however, as gaseous propane also formed some deposits (*101*).

FUEL CHEMICAL COMPOSITION. For pure compounds, the smoking tendency varies as follows:

Aromatics > alkynes > mono-olefins > *n*-paraffins

The smoking tendency of the average aromatic is roughly 10 times that of olefins and 20 to 30 times that of the paraffins (*138*). Coke deposition is also affected by fuel type, with all investigators reporting that aromatics greatly increased coke deposition, especially the high-boiling aromatic compounds. For this reason, U. S. fuel specifications limit the aromatic concentrations to 20 to 25% for present jet fuels (*8, 9*). Information concerning the effects of normal paraffins, isoparaffins, and cycloparaffins indicates that these fuels all have about the same coke-forming tendencies, and the amount deposited is considerably less than with aromatic fuels. Olefins are about the same as paraffins depositwise, with some tendency to produce slightly more deposits. These differences in performance of the fuels are also reflected in the hydrogen-carbon ratio, and the fuel with the lower ratio produces the most coke.

MINOR NONHYDROCARBON COMPONENTS. Sulfur compounds and gum (insoluble or soluble) are present in jet fuels and can affect coke formation. The effects of sulfur are not always consistent, but, in general, sulfur is not considered to be a problem until 1% or more is present. However, no more than 0.4% of sulfur is permitted in current fuels specifications. Gum causes a small increase in coke deposits, but this effect is insignificant for fuels meeting gum specifications.

Additives have been shown to effect decreases in coke deposits. Small amounts of organometallic compounds and commercial fuel-oil additives have been shown to decrease coke weight. Metallic compounds in excess can result in increased deposition because of the metal oxide, and some of these compounds have also been reported to cause metal corrosion, as have sulfur compounds. Results of investigations with additives to inhibit coke formation are not conclusive enough at present to justify their acceptance.

A volatile, paraffin fuel will deposit the least amount of coke. Decreasing volatility increases coke deposition but has little effect on smoke. Increasing aromaticity increases both coke and smoke. Minor components have no effect within the maximum permitted by fuel specifications.

Evaluation of Fuel Properties with Coke Deposition. Considerable effort has been spent in the development of a test based on either fuel properties or bench-scale apparatus which will correlate with the coking performance of fuels in engines and provide a control method for fuel specifications. As few planned engine data are available, much of the effort has been to relate the results to single-combustor testing.

FUEL PROPERTIES. Hydrogen-carbon ratio, aromatic content, American Society for Testing Materials (ASTM) distillation temperatures, gravity, and aniline point are the properties that have been used alone or in combinations to indicate the coke-forming tendency of a fuel. Two of these relations are discussed below.

Hydrogen-carbon ratio and volatility were related (*177*) to deposits as follows:

$$\text{Weight of deposits} = \frac{\log (N_c/N_H + C_1)}{C_2} + \frac{T}{C_3} + C_4$$

where C_1, C_2, C_3, and C_4 are constants; N_c/N_H is the ratio of carbon atoms to hydrogen atoms; and T is ASTM 10% distillation temperature, in ° F. In general, deposit weight increased with the value of this equation but with considerable scatter.

Another relation (*202*) with the same properties (National Advisory Committee for Aeronautics (NACA) K factor) is:

$$\text{Log of combustor deposits} = a + bK$$

and

$$K = (t + 600)(0.7)\,\frac{H/C - 0.207}{H/C - 0.259}$$

where a and b are constants; t is volumetric average evaporated temperature, ° F.; and H/C is hydrogen-carbon weight ratio. The deposits from many fuels have been precisely estimated by this relation; however, some fuels give wide variations. Many other relations have been used as a means of relating deposits to the fuels. Examples are: aniline-gravity constant, Universal Oil Products (UOP) characterization factor, and high-boiling aromatic content.

BENCH-SCALE APPARATUS. Laboratory combustion devices include flame-plate, pot-burner, and Institute of Petroleum Technology (IPT) wick-lamp apparatus. Small-scale combustors could be considered laboratory equipment, but results obtained with them have been discussed herein along with full-scale combustor results. Results obtained with the laboratory devices show that coke forming tendencies among various fuels are not consistently predicted with any of the three. However, a relation called smoke volatility index has been developed with the smoke-lamp which is used to limit the coke-forming tendencies of JP-3 and JP-4 jet fuels in U. S. military specifications. This index is given by:

$$SVI = s.p. + (0.42)\ (\text{Volume \% boiling below 400° F., ASTM})$$

where SVI is smoke volatility index and $s.p.$ is smoke point in millimeters. The percentage boiling below 400° F. is a volatility term, and the smoke point is a measure of chemical composition. Smoke volatility index, smoke point, and NACA K factor have been compared by means of controlled tests using 10 fuels, and no one of these factors was markedly superior to the others in predicting the deposition tendencies of the fuels.

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Combustor Durability

Life of the combustion system in an engine is quite important, as the operational time between overhauls is usually controlled by the combustor. Combustion liner failures are due to corrosion and erosion, pressure-differential loading, and induced vibrations acting on metal structures that are stressed by a high-temperature environment and high thermal gradients (*204*). Heat is transferred to the metal surfaces by both radiation and convection, and it has been estimated that about 0.5% of the heat released by the burning fuel is transferred by radiation and about 1% by convection (*15*). The major portion of this heat is removed by the dilution air flowing on the outside surface, the remainder by radiation to the outer housing. The exact temperature of a liner is determined then, by a balance of these heat flows.

The variables that increase liner temperatures are higher air temperatures (both inlet and outlet), higher air pressures, and higher flame emissivities caused by suspended particles. Liner temperatures obviously will increase with increasing inlet-air and exhaust-gas temperatures. At constant air and gas temperature they will also increase with increasing pressure and with fuels that increase flame emissivity. The pressure effect is observed on both convective transfer rates and on flame emissivity, but this effect is modulated by the fact that the rate of cooling to the dilution air is increased. Increase in coke deposits might increase thermal gradients in the metal.

Liner life can be lengthened by use of more suitable materials, possibly by the use of refractory coatings, by improved cooling, by reducing thermal gradients, and by reducing pressure loading (lowered pressure loss). Liners are now generally cooled by film cooling; that is, dilution air flow on outside wall surfaces while the inner surfaces are shielded from the combustion by a thin layer of air. Such methods employ louvers, holes, and sections laid in a stepwise fashion (*150*). Transpiration cooling through porous walls has been shown to be very effective (*46*); however, this method has not been used in practical engines because of the lack of suitable porous materials, the ease with which these pores are fouled, and the need for relatively high pressure drops to get adequate coolant flows.

Exhaust Gas Temperature Pattern

Thrust increases with increasing combustor outlet temperature. However this temperature is limited by the maximum temperature (currently near 2000° R.) which the highly stressed turbine blades can stand. There is also an optimum temperature pattern which arises from the difference in stresses between blade root and tip. To obtain this pattern requires a stable and steady burning primary zone. Achievement of a proper temperature pattern is then contingent upon a combustor design that will perform well over the range of fuel and operating conditions expected (*168*). Further adjustments must be made in the dilution section of the combustor, and area, size, shape, and pattern of air openings are important (*108*). However, little quantitative information is known concerning this dilution process, and control of exhaust-gas patterns is achieved with cut and try methods.

Ignition

Starting of turbojet engines is more difficult at altitudes or at low ambient temperatures on the ground. Altitude ignition is required after flame-outs or with multiengine aircraft where all engines may not be operated at all times.

Basic studies have shown that minimum ignition energies for hydrocarbon-air mixtures increase as pressure is decreased and velocity and turbulence level of flow past igniting source is increased. Fuel-air ratio was also shown to be important, and the least energy was required where the mixture was slightly richer than stoichiometric (*184–188*). Ignition studies in combustors have produced parallel results, with energies required for ignition, although much greater than those required in the basic studies, decreasing as pressure and temperature increased and velocity decreased. However, pressure was shown to be less important than velocity, at least in the range of practical values encountered in a particular turbojet engine combustor. Fuel volatility was important, with the more volatile fuels igniting with less fuel flow and at lower pressures for a given spark energy. Increased fuel atomization would help, then, by providing increased fuel evaporation. The quantitative influence of these variables depends on the design of primary-air admission, location of ignition source, and design of the ignitor. Ignition of turbojet combustors, in a practical sense, is largely a matter of correct ignition system, fuel injector, and combustion chamber design.

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Combustor Pressure Loss

Loss in total pressure of the working fluid passing through a turbojet engine results in a decrease in engine cycle efficiency and an increase in engine fuel consumption for a given thrust. The over-all total pressure loss in the average combustion system is about 5% at design conditions (*28*). Pressure losses occur as a result of abrupt changes in flow cross-sectional area, partial blockage by flame stabilizing devices, friction, the turbulence required to mix gases, and increases in momentum through heat addition. Pressure loss is increased with increasing inlet-air velocity and with the amount of fuel burned. Geometric factors are important, too, and an increase in the ratio of liner diameter to outer housing diameter has been shown to increase pressure loss, with pressure loss rising rapidly when the liner diameter reaches about 80% of the housing diameter. This factor is in conflict with the environment desired for high combustion efficiencies as the volume available for burning should be as large as possible. Other geometric factors, such as total air passage area, placement of air openings along liner walls, and convergence of liner and outer housing walls are equally important in that they control the proportions of air in the liner at any given point and the local fuel-air mixture concentrations. Inasmuch as pressure loss should be kept low as possible, compromises are necessary, and in the final stages of development combustor designs are usually evaluated by empirical methods.

Future Exploration Areas and Requirements

Highly successful turbojet combustors have been developed through the use of both fundamental principles and "cut and try" empiricism. The latter approach is costly and time consuming, and it is likely that better combustors could be developed more easily if the exact contribution of each of the several basic processes influencing combustion were known. Therefore, there is a need for a better understanding of these processes and for correlations of this understanding with performance.

Higher flight speeds will increase combustor inlet temperatures, and cooled turbine designs will permit higher combustor outlet temperatures. The increased inlet temperature, coupled with the demands for increasing thrust per unit frontal area, will require burning in higher velocity air streams and with increased heat release rates per unit combustor volume. Higher velocities and heat release rates will require lower combustor pressure losses to maintain present cycle efficiencies. Structural durability at the higher wall temperatures may become more troublesome. As low pressure ratio engines will probably still be needed, the combustion efficiency problem at high altitudes will continue to be of interest.

Aerodynamic heating will present problems concerning the thermal stability of fuels, as they will probably be used as a heat sink on aircraft. The fuels will be susceptible to evaporation and thermal decomposition at the temperatures and duration of time to which they will be exposed. Considerable effort (*25, 81, 102, 135*) is now being devoted to this field.

Subject Listing

This is a breakdown, by subject, of the reference material listed in the following Bibliography

Bibliographies	(*56, 132, 144*)
Historical and design background	(*36, 38, 40, 43, 84, 120, 156, 164, 172–174, 180, 183, 194, 196, 206, 210, 216*)
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General reviews	(*35, 54, 55, 69, 95, 139, 168*)
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Diesel Fuel Combustion

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The combustion of Diesel fuel is discussed by considering each phase of the process and pointing out, insofar as possible, the effects of important fundamental variables. In the Diesel engine, fuel is burned intermittently under exceedingly heterogeneous conditions. Physical processes are involved in the formation of a combustible fuel-air mixture and in transporting oxygen into inflamed regions to complete combustion. Chemical processes are involved in the ignition of the fuel-air mixture and in the subsequent reactions that occur during combustion. These processes are discussed in relation to such applied problems as ignition delay in the engine, the characteristics and performance of fuels, smoke, odor, and products of incomplete combustion. The complexity of the Diesel combustion process frequently necessitates qualitative generalizations to explain the observed phenomena. This is illustrated in discussing the design of combustion chambers. Developments in combustion chambers in which fuel is impinged on hot surfaces are described. In certain applications, Diesel engines operate on both gaseous and liquid fuels. Accordingly, the basic considerations in dual-fuel combustion are presented.

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In the Diesel engine, fuel is burned intermittently under exceedingly heterogeneous conditions. Accordingly, as pointed out in many reviews and texts (*9, 11, 17, 19, 31, 43, 44, 71, 81, 101, 107, 118, 119, 130, 132*), in the combustion of Diesel fuel we are dealing with a complex system in which gases, liquids, and solids are present; in which extreme concentration and temperature gradients exist; and in which a steady state is never reached. To simplify the discussion of such a complex system, the individual physical and chemical processes occurring during each stage of combustion must be considered.

In Diesel fuel combustion, the physical processes include: metering and transportation of fuel and air into the combustion chamber, vaporization of fuel, mixing fuel vapor with air, and provision of an environment favorable for rapid chemical reaction. The chemical processes include: self-ignition or autoignition of the fuel-air mixture, and extensive chemical reaction to liberate the potential energy in the fuel. The accomplishment of these processes is the basic consideration in the design of the Diesel engine.

Certain operating characteristics of the Diesel or compression-ignition engine result from the nature of the combustion process. In particular, the engine operates over a comparatively wide range of over-all fuel/air ratios because fuel and air are not premixed. At a given speed the range is from approximately 0.01 pound per pound (580% excess air) at no load to about 0.055 pound per pound (20% excess air) at full load. Excess air is essential to ensure complete combustion and avoid smoke production.

Over-all fuel/air ratio is an important variable with which data on combustion performance may be correlated. In the four-stroke cycle engine the over-all fuel/air ratio is almost exactly equal to the average fuel/air ratio in the cylinders during combustion. However, in the two-stroke cycle Diesel engine the over-all fuel/air ratio is considerably less than the average fuel/air ratio during combustion because some of the air blows through the cylinder and enters the exhaust system during the scavenging process. In both types, over-all fuel/air ratio is only an indication of average conditions existing during combustion because local concentrations of fuel may range from 0 to 100%.

Combustion in the Diesel Engine

In any combustion process there are at least three basic requirements: formation of a mixture of fuel and air, ignition of the fuel-air mixture, and completion of combustion of the fuel. In the Diesel engine these requirements are met as indicated diagrammatically in Figure 1 (*43*, *44*). Formation of the fuel-air mixture is accomplished by the disintegration of the fuel jet, the dispersion of droplets of fuel in air, the vaporization of fuel, and the mixing of fuel vapor with air. Ignition occurs as the result of preflame oxidation of the fuel, the rate of which rapidly accelerates, eventually culminating in the initial flammation of a local region. After ignition has occurred, the mixture inflames and combustion may proceed as indicated in Figure 1, either by the rapid oxidation of mixtures of fuel and air or by the oxidation of products of thermal decomposition of the fuel. Incomplete combustion may result either from the failure of the combustible to

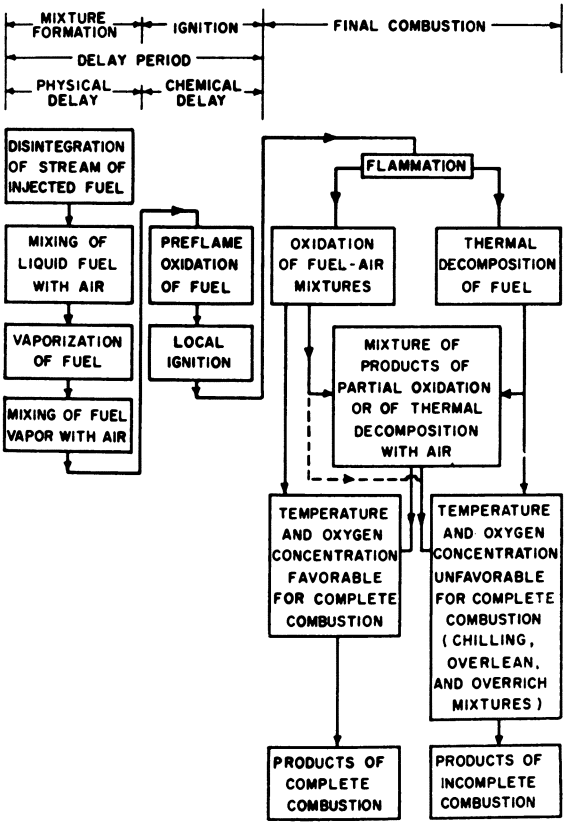

Figure 1. Outline of combustion process in Diesel engine

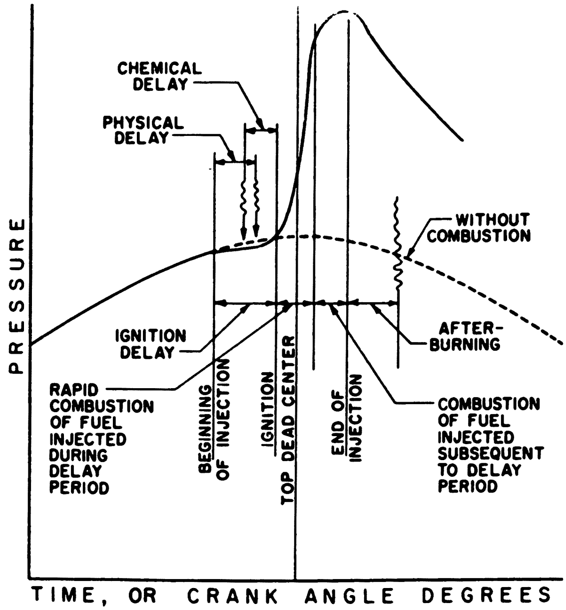

Figure 2. Schematic representation of stages of Diesel combustion in relation to indicator card

find oxygen under conditions favorable for reaction or from the chilling or quenching of combustion reactions before their completion. These steps in the combustion process have chronological significance for a particular fuel particle. However, many of the individual steps proceed concurrently because fuel is being injected while combustion is in progress.

The outline of the combustion process shown in Figure 1 is the outgrowth of the studies of many investigators (*9, 10, 43, 61, 105, 106, 112, 118, 137*). Several of these (*9, 105*) considered the process as occurring in four stages: the delay period, which represents the time elapsed between injection and ignition; the period of rapid combustion, during which the fuel injected during the delay period burns; the period of controlled combustion, during which the rate of combustion depends upon the rate at which fuel being injected finds air for combustion; and the period of afterburning, during which unburned combustible from the earlier stages completes its combustion. The concept of these different stages is very helpful in relating the combustion process to what is observed on an indicator card, as illustrated in Figure 2.

Ignition Delay

Ignition of the fuel in the Diesel engine is manifested by a rapid rise in pressure, as indicated diagrammatically in Figure 2. The time elapsed between the start of injection and the start of rapid pressure rise is referred to as ignition delay (*59*), which is an arbitrarily defined fuel characteristic. The beginning of fuel injection is a logical and generally accepted reference point for the beginning of the delay period. However, the choice of a condition to fix the end of the delay period is arbitrary. Nevertheless, all reasonable choices give ignition delays that do not differ greatly in a particular experimental environment. Consequently, ignition delay or ignition lag is useful in characterizing fuels.

For purposes of discussion, ignition delay is frequently divided into physical delay and chemical delay (*11, 41, 44*), although it is recognized that the two cannot be separated. Physical delay includes time lags in the injection system and the time required for heat and mass transfer processes to form a combustible mixture of fuel vapor and air.

Chemical delay occurs as a result of the time required for preflame reactions to accelerate and lead to ignition of a combustible mixture of fuel vapor and air.

Mixture Formation. The passage of fuel through the injection system is the first step in the formation of a fuel-air mixture. Flow is intermittent, and pressures may range from 100 to 1500 atmospheres, depending upon the type of system. Thus, the metering and delivery of the fuel are affected by pressure waves, the compressibility of the fuel, and the elasticity of the system. Flow under transient conditions in Diesel fuel injection systems has been studied and analyzed (*35*, *143*) and methods have been developed for measuring the rate of fuel flow (*34*, *136*) under these same conditions.

The first contact between fuel and air is made by a continuous jet of liquid fuel. The disintegration of this jet into droplets has been studied (*24*, *36*, *79*, *86*, *90*, *98*, *111*, *122*) and reviewed (*53*), and it is affected by the velocity of the jet, the frictional drag at the interface between the jet and the air, the density of the air, and the surface tension and viscosity of the fuel.

Drop size distribution is a measure of the effectiveness of the atomization process. Depending upon the design of the injection system, drop sizes may range from 1 to 60 microns (*118*). The distribution of drop sizes follows the Rosin-Rammler law (*104*). Average drop size decreases with increases in jet velocity and in density of the air into which fuel is injected (*118*). The largest drops are found at the center of the disintegrating jet and the smallest at the periphery (*86*).

Vaporization begins as soon as fuel comes in contact with air (*42*, *126*). The first theoretical analysis of droplet evaporation (*137*) showed that under conditions existing at the end of compression in a Diesel engine, drops having a diameter of 10 microns or less will be vaporized in less than 0.6 milliseconds. Recent extensive theoretical studies (*41*) have shown that vaporization of atomized fuel in a Diesel engine occurs under conditions approaching single droplet vaporization at the periphery of the spray and under adiabatic saturation conditions at the center of the spray. These studies also showed: The difference in the rate at which high-volatility and low-volatility fuels receive

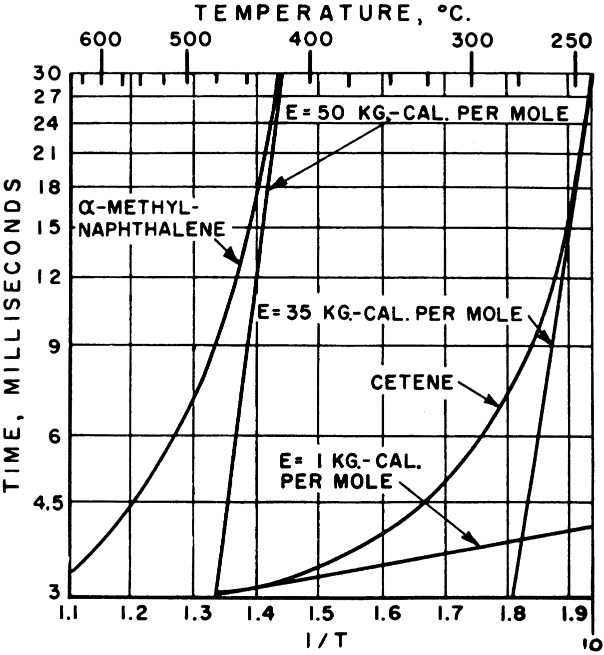

Figure 3. Effect of temperature on ignition delay of α-methylnaphthalene and cetene [after Jost (*71*), data of Mueller (*94*), and Wolfer (*139*)]

heat is less than might be expected from differences in volatility; under adiabatic saturation conditions low-volatility fuels can attain the proper combination of temperature and vapor/air ratio required for self-ignition as well as, or even more readily than, high-volatility fuels; and the time required for the physical processes leading to mixture formation (physical delay) is not a negligible fraction of the total ignition delay.

Fuel-air mixtures in Diesel engines have been characterized (*12*) in relation to their fineness (micromixture), which includes degree of atomization and evaporation, and in relation to distribution of fuel in air (macromixture), which refers to the degree of homogeneity of the fuel-air mixture throughout the combustion chamber.

Autoignition. The autoignition of Diesel fuels has been studied by measuring the total ignition delay of the fuel, either in an engine (*125, 127*) or when injected into a constant volume bomb (*30, 50, 67, 74, 88, 97, 124*), or by measuring ignition temperatures (*69, 70*). The results of such studies are discussed generally on the basis of total ignition delay, although methods have been suggested for separating the effects of physical and chemical delay in both bombs and engines (*41, 43, 44, 142*).

Work on the autoignition of Diesel fuels has been concerned primarily with the measurement of total ignition delay and comparatively no attention has been paid to the rate and nature of the preflame reactions leading to autoignition. The results of one investigation (*55*) have shown that aldehydes and peroxides are formed when fuel is injected into the hot compressed air in an engine. Evidence of two distinct reaction mechanisms was obtained: low-temperature reactions occurring during the delay period at about 350° C., in which aldehydes and peroxides were formed and reached a peak concentration at the time of ignition; and high-temperature reactions occurring after ignition which were manifested by a second peak in the concentration of aldehydes and peroxides. The heat released in preflame reactions of fuels injected into a constant volume bomb has been calculated (*66*). Although extensive data are lacking on the preflame reactions of Diesel fuels, there is information available on the preflame reactions of fuels in the gasoline boiling range. The results of such studies can be applied, qualitatively, to the autoignition of Diesel fuels.

TEMPERATURE. The ignition delay of most Diesel fuels decreases as the temperature increases (*50, 67, 94, 139*). In certain temperature ranges highly-branched and cyclic compounds are exceptions (*50*). If it is assumed that the chemical delay is long in relation to the physical delay at low temperatures, then it is possible to estimate an apparent over-all energy of activation of the preflame reactions, as indicated in Figure 3 (*71*). Results similar to those shown in Figure 3 can be represented by an empirical relationship (*43, 44*) of the form:

$$\text{Total ignition delay} = C_1 e^{C_2/T} + C_3 e^{C_4/T}$$

in which C_1, C_2, C_3, and C_4 are suitable positive constants, and T is the absolute temperature. A study of Figure 3 shows that the ignition delay is determined primarily by the rate of the preflame chemical reactions at lower temperatures and by the rate of the physical processes of vaporization and mixing at the higher temperatures.

PRESSURE. The effect of pressure on ignition delay has been determined generally by injecting Diesel fuel into a constant volume bomb (*50, 139*). Interpretation of results is complicated (*50*) by the fact that a change in pressure changes other important variables: partial pressure of oxygen, which effects the rate of preflame reactions; air density, which changes the spray pattern and affects local fuel concentrations; and, depending upon the experimental apparatus and procedure, other variables in bomb tests. An increase in pressure decreases ignition delay with moderate to high temperatures (800° to 1400° F.) but increases ignition delay for many fuels as the temperature approaches the minimum for autoignition (*50*). Over a comparatively narrow range of pressures and temperatures ignition delay is related to these variables by a formula (*119*) of the form:

$$t = \frac{c(e^{b/T})}{p^N}$$

which can be derived from chain reaction theory.

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CONCENTRATION OF FUEL. In any homogeneous chemical reaction, the concentration of reactants is an important factor affecting the rate of reaction. However, this factor is indeterminant under the heterogeneous conditions existing in the Diesel engine at the time of ignition, because the combustion chamber contains local concentrations of fuel ranging from 0 to 100%. Ignition occurs in some region where the local concentration of fuel is optimum. This is generally in the envelope of the spray.

Many factors affect the local optimum fuel concentration, and it is not surprising, therefore, that conflicting results have been obtained on the effect of over-all fuel/air ratio on ignition delay. In one instance, ignition delay passed through a minimum in the range of air/fuel ratios between 15 and 35 (*129*). However, other tests show no significant difference in the ignition delay in the range of over-all air/fuel ratios from 10 to 365 per pound (*114*). Recent studies (*50*) in a constant volume bomb have shown that ignition delay is affected markedly by fuel/air ratio at low temperatures when ignition delay is long and, therefore, there is adequate time to approach a homogeneous mixture. Under such conditions over-all fuel/air ratio is a measure also of local fuel/air ratio. At higher temperatures comparatively little effect of fuel/air ratio on ignition delay was observed (*50*) because under these conditions the over-all fuel/air ratio has little or no relation to the local fuel/air ratio where ignition occurs.

Comparatively little data are available on the minimum local fuel/air ratio below which ignition will not occur under the conditions existing in a Diesel engine. The existence of such a minimum fuel/air ratio for ignition and flame propagation has been suggested (*5*) and is indicated by photographs (*89*) of combustion in a Diesel engine. In one of these photographs taken with early injection (43° before top center), and with one eighth of the full load fuel (probably less than 0.01 fuel/air ratio), ignition was not obtained.

The minimum fuel/air ratio for ignition is analogous to the lower limit of flammability. It is important in Diesel fuel combustion because partial oxidation will occur in local regions in which the concentration of fuel is less than the minimum or lower limit, but these regions will not ignite or inflame. Consequently, products of partial oxidation giving rise to odor, and possibly deposits, will appear in the exhaust. This is discussed in a subsequent section.

MOLECULAR STRUCTURE. Recent studies (*50*) on the effect of molecular structure on ignition delay have shown that for a homologous series ignition delay decreases as the number of carbon atoms in the molecule increases and that for a given number of carbon atoms the normal paraffins exhibited the shortest ignition delays of the hydrocarbons tested. In these studies data were obtained also on isoparaffins, 1-olefins, naphthenes, and aromatics. The results of these studies agree qualitatively with data obtained in previous investigations of the autoignition characteristics of pure hydrocarbons in the boiling range of Diesel fuels (*73*, *102*) and gasolines (*83*, *131*).

FUEL RATING. The autoignition characteristics of commercial Diesel fuels are determined in the CFR engine by matching, under standard test conditions, the ignition delay of the unknown fuel with the ignition delay of a reference fuel (*3*). The primary reference fuels are mixtures of cetane and α-methylnaphthalene. The result of such a procedure gives the cetane number, which is the percentage by volume of cetane in the particular mixture of cetane and α-methylnaphthalene that matches the ignition delay of the unknown fuel. This method of fuel rating is the outgrowth of extensive studies (*60*, *120*) of methods for determining the ignition quality of fuels in engines. Cetane number is useful in placing fuels in the proper order with respect to the ease with which they may be ignited by compression and also as a basis for correlating data on certain fuel performance factors in engines (*2*).

Cetane number cannot be used as an absolute measure of ignition delay in a particular engine, because the relation between cetane number and ignition delay depends upon the type of engine and the engine operating conditions (*43*, *44*). The importance of environment is emphasized by recent studies (*50*) of the ignition delay of pure hydrocarbons in a constant volume bomb which showed: Ignition delay determined at a fixed temperature and pressure is not uniquely related to the cetane number of fuels composed of a

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wide range of hydrocarbons of different structure, and cetane number may be misleading in predicting autoignition characteristics of a fuel under conditions which differ markedly from those under which the number was determined. The cetane number of Diesel fuels is interrelated with other physical properties of the fuel, such as boiling point, viscosity, and gravity (*7*), and thermal stability (*12*). These interrelationships must be considered in correlating data on combustion performance with cetane number (*1, 27*) to make sure that the effects observed are not due to changes in one of the interrelated fuel properties. Cetane number may be estimated from other fuel properties (*141*). Properties other than cetane number are important (*16, 57*) in evaluating fuel performance in engines, particularly when heavy fuels are used (*15, 128*).

IGNITION ACCELERATORS. The rate of the preflame reactions of the Diesel fuel may be increased by the addition of ignition accelerators (*4, 21, 100*). Numerous compounds have been proposed (*13*), but of these amyl nitrate is the only one that is commercially available. The effectiveness of ignition accelerators depends upon molecular structure. One investigation (*56*) showed that the response of paraffinic fuels was greater than that of paraffinic-aromatic fuels, whereas naphthenic fuels had the lowest response. The same study showed that ignition accelerators were in general more effective when added in the vapor phase to the intake air than when added to the fuel in the liquid phase. Other investigators (*29*) have found that vapor-phase addition is more effective than liquid-phase addition in reducing cold starting temperatures. Increasing the cetane number of the fuel by the addition of an ignition accelerator does not necessarily improve cold starting, because it has been shown (*96*) that the addition of *tert*-butyl peroxide increases the cetane number but has little effect on minimum cold starting temperature.

The mechanism of ignition acceleration by small additions of additives has been explained on the basis of chain reaction theory (*21*). It has been suggested (*56*) that vapor-phase additions are more effective than liquid-phase additions because of the initiation of preflame reactions during the compression stroke.

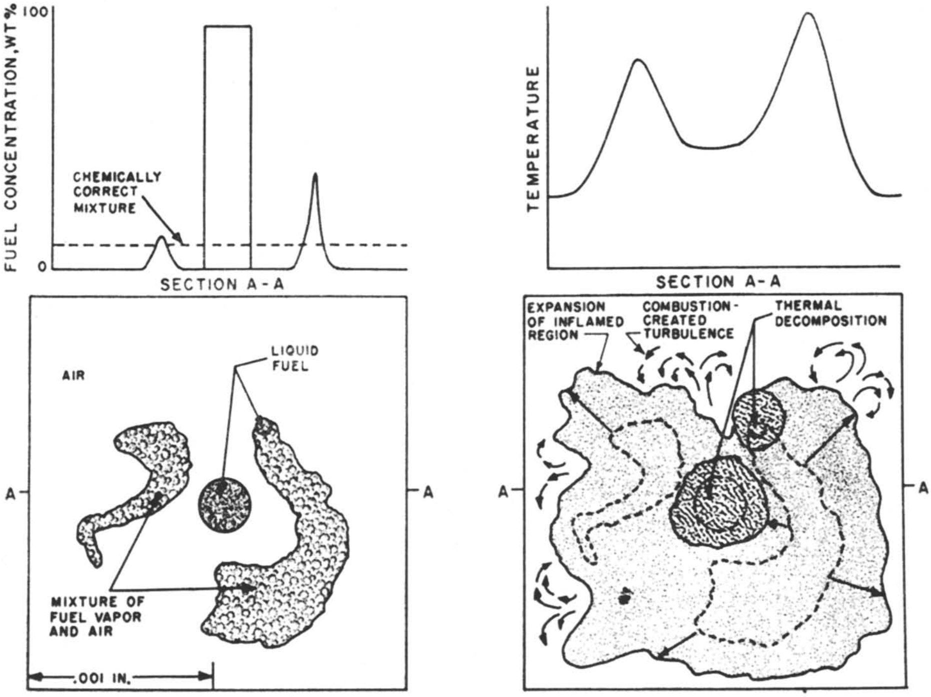
Flammation

Flammation, or the period of rapid combustion, starts when a small local region has ignited and is on the verge of spreading throughout the fuel-air mixture. The familiar physical manifestation of flammation in the Diesel engine is the rapid rate of pressure rise (*110*) which is indicative of the rapid rate of chemical reaction. Many excellent pictures (*25, 61, 89, 113, 115, 116*) of ignition and flammation in the Diesel engine have shown that ignition starts in a local region at the periphery of the spray and that a highly luminous flame containing incandescent carbon particles spreads rapidly throughout the combustion chamber. At the instant of flammation the combustion chamber contains droplets of fuel, mixtures of fuel vapor and air, and also air containing practically no fuel, as shown diagrammatically in Figure 4*a* for a small segment of the combustion chamber. After ignition, this small region might appear as shown diagrammatically in Figure 4*b*. Following ignition, flame propagates through continuous regions in which the fuel/air ratio is in the flammable range. Adjacent regions containing a mixture of fuel vapor and air will ignite either by contact with the advancing flame front from an ignited region or by autoignition as a result of the rapid increase in temperature and pressure resulting from the flammation. Unvaporized fuel in the vicinity of an inflamed region may undergo extensive thermal decomposition, producing products that must be further mixed with air. Similarly, regions in which there is a deficiency of air also produce some products that must be further mixed with air before oxidation is complete. When flammation occurs, further mixing of the fuel and air is promoted by combustion-induced turbulence, as illustrated diagrammatically in Figure 4*a*.

The extreme heterogeneity of the combustion process is illustrated in Figure 4 by the concentration gradients, the temperature gradients, and by the presence of three different phases during the flammation period. The existence of such conditions has been demonstrated experimentally by high-speed photographs (*76*), by sampling combustion chamber gases (*40*) at different parts of the cycle and at different positions in the combustion chamber, and by tests (*45, 49*) in which gaseous combustibles were added to the intake of a Diesel engine in concentration below the lower limit of flammability.

The course of combustion reactions during flammation has been studied (*78*) by the application of gas analysis techniques (*40*), by absorption spectra (*76*), by temperature measurements during combustion (*95, 133–135*), and by the analysis of indicator cards (*25, 99, 110, 112*).

Turbulence is extremely important in promoting both rapid reaction during flammation and completeness of combustion. In the Diesel engine, turbulence is induced by the combustion process itself or by the design of the combustion chamber. Studies of the effect of air motion during flammation have shown that as the rate of air swirl increases, the rate of pressure rise increases under a given set of conditions (*130*). If it is assumed that increases in engine speed produce greater turbulence (*80*), then data are available (*44, 135*) showing that a fourfold increase in speed resulted in a threefold increase in the average rate of reaction during the flammation period.



4a 4b

Figure 4. Schematic representation of fuel distribution and mechanism of flammation in small local region in combustion chamber of Diesel engine

When the rate of energy release in the first stages of flammation is so high that the mechanical system is not capable of converting this energy to useful purposes, some of the energy is dissipated in thermal, frictional, and vibrational effects with an attendant audible knock (*12, 120*). The conditions under which knock occurs depend on both engine and fuel characteristics, and it is very difficult to make generalizations. There are, however, basic factors that determine whether knock will occur: the quantity of fuel present when flammation occurs, the distribution of the fuel at the instant of flammation, and the point in the cycle at which flammation occurs. If flammation occurs in the vicinity of top dead center, it is apparent that more fuel will be present in the case of fuels having long ignition delays, and therefore the tendency to knock will be greater. Fuel distribution is an important consideration (*44*) because local rates of reaction are affected by local concentrations of fuel. The point in the cycle at which flammation occurs is important because it determines whether the piston is tending to increase or decrease the rate of pressure rise.

Rate of pressure rise is used as a rough criterion of knock. At rates less than 30 pounds per square inch per degree of crank angle, combustion is generally smooth; at 50 pounds per square inch per degree the engine may knock; and at rates greater than 100 pounds per square inch per degree, knock is almost certain to be observed (*44*).

Knock is sometimes referred to as "uncontrolled burning," and many operating variables affecting it have been summarized (*44*). In general, operating conditions that would tend to induce knock in the Diesel engine would tend to eliminate knock in the spark ignition engine.

Products of Incomplete Combustion

Products of incomplete combustion originate as shown in Figure 5 (*47*). Although generally present in low concentrations in the exhaust gases, they are of considerable importance (*47, 63*) because some of these products are responsible for the smoke and odor emitted by Diesel engines. In addition, certain products of incomplete combustion, along with products of combustion of sulfur in the fuel, are responsible for engine deposits and wear (*84*).

Carbon monoxide is generally present in the exhaust in concentrations less than 0.1% by volume and originates from locally overlean and locally overrich regions (*47*).

Aldehydes are usually present in part-per-million concentrations (*44, 62, 138*) and are partially responsible for the odorous and irritating properties of Diesel exhaust gas (*33, 138*). Removal of aldehydes (*33*) produces significant reduction in odor and irritation. Aldehydes are products of partial oxidation, and their concentration in the ex-

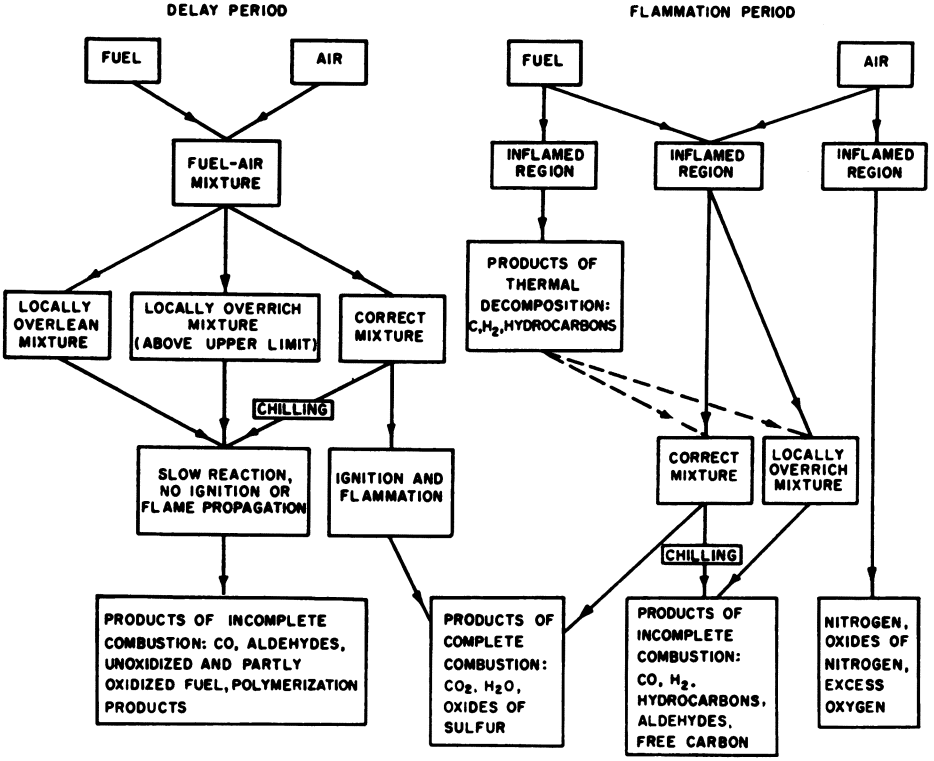


Figure 5. Origin of products of combustion of Diesel fuel

haust gases is generally greatest at light loads, where local overleanness and chilling are most pronounced. Other oxygenated organic compounds have been identified (*48*) in the exhaust gases from Diesel engines at light loads.

Smoke originates from two sources within the engine: (*44*, *123*) unburned or partly oxidized fuel, which appears in the exhaust gas as a liquid aerosol, and unburned carbon which has been formed by thermal decomposition of the fuel and which has not reacted with oxygen. The first type of smoke (cold smoke) (*123*) is generally observed at light loads and low fuel/air ratios and is a result of local overleanness or of chilling combustion reactions. The second type of smoke (hot smoke) (*123*) predominates at high fuel/air ratios (high loads) and is a result of thermal decomposition and incomplete oxidation in locally overrich regions. The coexistence of both smoke components has been demonstrated experimentally by cooling the exhaust gases from a Diesel engine and collecting the condensate (*39*, *75*, *77*).

Engine operating variables (*121*, *123*) and fuel quality affect smoke formation. Improved mixing of fuel and air at the instant of flammation minimizes the tendency for combustion to occur under locally overrich conditions and therefore minimizes smoke. Addition of auxiliary fuels to the intake can reduce the tendency to smoke (*37*). As injection is advanced, less smoke is produced (*76*); however, if injection is advanced too far, smoke production may be increased because of spray impingement and eventual misfire (*123*). A short ignition delay generally increases smoke production because a larger portion of the fuel is injected into an inflamed mixture (*76*). Fuel volatility is an important consideration in smoke production (*76*, *123*); in general, the more volatile fuels produce less smoke. Considerable information is available on methods for measuring the smoke (*65*) from Diesel engines and on the effect of fuel characteristics (*22*, *140*), injection characteristics, and operating conditions (*64*, *121*, *123*) on the smoke produced by diesel engines.

The exhaust gases from Diesel engines contain both oxides of sulfur (*23*, *144*) and oxides of nitrogen (*44*, *58*) in comparatively low concentrations. These constituents, along with other products of incomplete combustion, form deposits (*72*) which have been studied in relation to corrosion (*26*) and wear in Diesel engines (*8*, *18*, *20*, *28*, *52*, *84*, *91*). The production of oxides of nitrogen by Diesel engines is of interest in connection with air pollution, because it has been shown that these compounds enter into smog-forming reactions.

Unburned hydrocarbons are found in very low concentrations in the exhaust gases from Diesel engines (*51*). The fraction of fuel appearing as unburned hydrocarbons in the exhaust is greatest at light loads, where it may be as high as 12% (*51*).

Combustion Chambers

The foregoing discussion has demonstrated the importance of distributing liquid fuel, mixing fuel vapor with air, and maintaining control of combustion. These objectives are achieved in the development of combustion chambers by: making the spray pattern conform to the shape of the combustion chamber (*6*, *106*), providing primary turbulence (air movement prior to ignition) to assist the formation of a fuel vapor air mixture (*106*), and providing secondary turbulence (movement of the inflamed mixture) after ignition (*106*). Combustion chamber design involves a series of compromises, and with the present status of our knowledge it is necessary to test various designs to determine the optimum for a particular set of conditions. Among the other factors that may influence the selection of a particular design (*109*) are the rated, full-load, brake mean effective pressure; the brake specific fuel consumption; torque characteristics; idling characteristics; ease of starting; insensitivity to fuels; ruggedness and maintenance.

In the development of the Diesel engine (*117*) the design of the combustion system has played an important role. Several combustion chamber shapes are presently in use. These include the open chamber (*38*, *54*, *68*, *82*), the precombustion chamber (*24*, *32*, *92*, *108*), the turbulence or air-swirl chamber (*32*), the air cell, and the energy cell (*32*). In all of these fuel is vaporized by transferring heat from the air charge to the fuel. In a recently developed combustion system (*87*) the fuel is sprayed on a hot surface which

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furnishes heat for vaporizing the fuel at a controlled rate. The fuel vapors are swept from the surface by air swirl. By controlling the vaporization and mixing of the fuel, the rate of reaction is controlled to such a degree that the engine is known as the "whisper engine." Some of the basic considerations in this system have been pointed out recently (*42*).

Dual-Fuel Combustion in Diesel Engines

Dual-fuel combustion as applied to the Diesel engine signifies the simultaneous combustion of gaseous and liquid fuels. When a Diesel engine operates as a dual-fuel engine, the gaseous fuel predominates and generally mixes uniformly with the intake air. The liquid fuel is injected into the compressed homogeneous gas-air mixture and furnishes a source of ignition for this mixture. Dual-fuel engines may use any type of gaseous fuel (*14*), but natural gas is most frequently used, and in areas close to pipelines considerable savings can be effected through the substitution of cheap natural gas for Diesel fuel.

In dual-fuel combustion the lower limit of flammability of the combustible gas in the compressed gas-air mixture is an important consideration (*46*). If the concentration of gas is greater than the lower limit, flame propagates throughout the gas-air mixture, and the attendant rapid rate of energy release may result in engine operating difficulties and knock. If the concentration of gas is below the lower limit of flammability, the gas does not react completely with oxygen unless it is in or immediately adjacent to an inflamed or high-temperature region. The fraction of gas reacting increases with an increase in either liquid fuel oil ratio or concentration of gas and is affected by type of engine and engine speed.

Combustion in dual-fuel engines has been reviewed (*93*) and studied experimentally (*46, 85, 93*).

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Future of Combustion Research

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Most investigations in combustion research indicate a deep and fundamental curiosity about the nature of the combustion process. Workers in the applied science field usually become enthusiastic supporters of the patient, fundamental work of the scientist. Frequently the solution to technical problems is reached by the use of empirical methods. The investigator, trying to reach one of these solutions, grabs at all straws—his imagination makes grist of all that he can find to pour into it. Yet the most recent findings of the kineticists may not indicate what to try next.

To comprehend the value of fundamental scientific work one must look back and weave the strands together. Sometimes the threads are very evident. For example, the battle of Britain was won in considerable part by the use of planes which were products of combustion research. The interrelationships of supercharging, compression, and fuel properties and composition in the reciprocating engine had been partially explored at that time. The Germans seemed to apply these principles but slowly at first. The British put this knowledge to work immediately as did the petroleum industry in the United States in those frantic days of producing tremendous quantities of fuel.

It was the threads of information supplied by the fundamental researchers of the twenties and thirties which enabled such advancement. The combustion studies of pure hydrocarbons in reciprocating engines was sufficient (though far from complete) to direct their efforts. Valuable research had been done by the fundamental American Petroleum Institute projects, where antitrust considerations keep many wary of digressing from truly basic research. With a combination of fundamental knowledge, process details, and personal imagination, it was possible to solve fuel problems when the solution was so sorely needed. From the psychological standpoint it is important to realize that only by the interaction of these three was a solution possible. Fundamental research is the slowest and hardest part to achieve and frequently its usefulness is not obvious at the time it is being done.

The enormity of the problem confronting us in the area of energy has been dimly outlined in the past 6 years or so. The density of our present civilization seems bound to it. It appears more and more likely that this civilization will approach such a grand scale that energy requirements will be astronomical.

Hubbert (*2*) shows a graph of the estimated world use of the available fossil energy by combustion. The area under the curves represents the 50×10^{18} kcal. of energy thought to be available. Consumption patterns are shown by curves *A* and *B*. The small black space at the lower left hand corner shows the energy which has been burned so far. From this it is seen that fundamental and applied combustion research has a tremendous payoff potential in the near (100 years) future.

The differing rates of consumption of the two curves emphasize that combustion efficiency can play a major role in the life of this resource. Curve *A* shows a twofold increase in consumption by the year 2000, but the Paley report 3 years later shows a fourfold increase (*3*). Neither of these take into account the rapid spread of modern civilization into the backward nations. There we find 80% of the world's population. If they approach the western level of consumption, the energy requirements will leap tenfold above the estimate. Only the use of nuclear energy can hope to achieve this result. Even with that source it is not inconceivable that we will exhaust the economic com-

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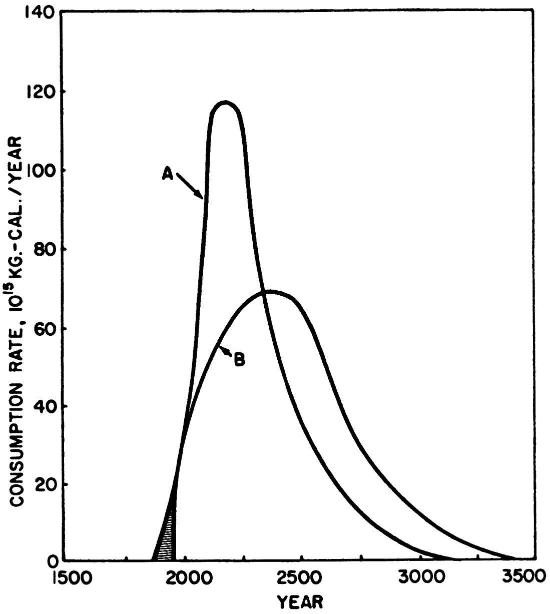

Figure 1. Rate of consumption of total energy available from fossil fuels (2)

bustible material in 75 to 100 years. Our well-being and freedom will be based on the highly intelligent use of the combustible fossil resources. It is intriguing to realize that the solution of the problems of low-cost fuel for a 12 to 1 compression ratio engine, or of the mechanism of highly turbulent combustion, can have an effect so far-reaching.

Our technical researchers will no doubt improve the efficiency factor as well as the preformance indices. Today the average direct efficiency of the use of available energy in fossil fuels is not above 25% and well below 25% when considering energy cost of obtaining and converting it (*1*). The improvement in efficiency is the most important challenge before the combustion research today.

Many of the problems in combustion research stem from the difficulty of burning in combustors at high speeds and altitudes. The advances in this field have been tremendous. The jet-turbine combustor will release 500 times the energy for a given space as the stationary boiler furnace. Its operating problems have been overcome (with the usual partial aid of fundamental combustion research) so that the limiting operational altitudes of aircraft are well above 50,000 feet and the speeds are supersonic.

More of our universities must take a teaching and research interest in the accumulated knowledge from combustion research by offering additional professorships and courses, at least at the graduate level. We need a continuation of the present level of fundamental research in combustion and a significant improvement in organization and distribution of the knowledge.

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