

94. *The Spontaneous Ignition under Pressure of the Simpler Aliphatic Hydrocarbons, Alcohols, and Aldehydes.*

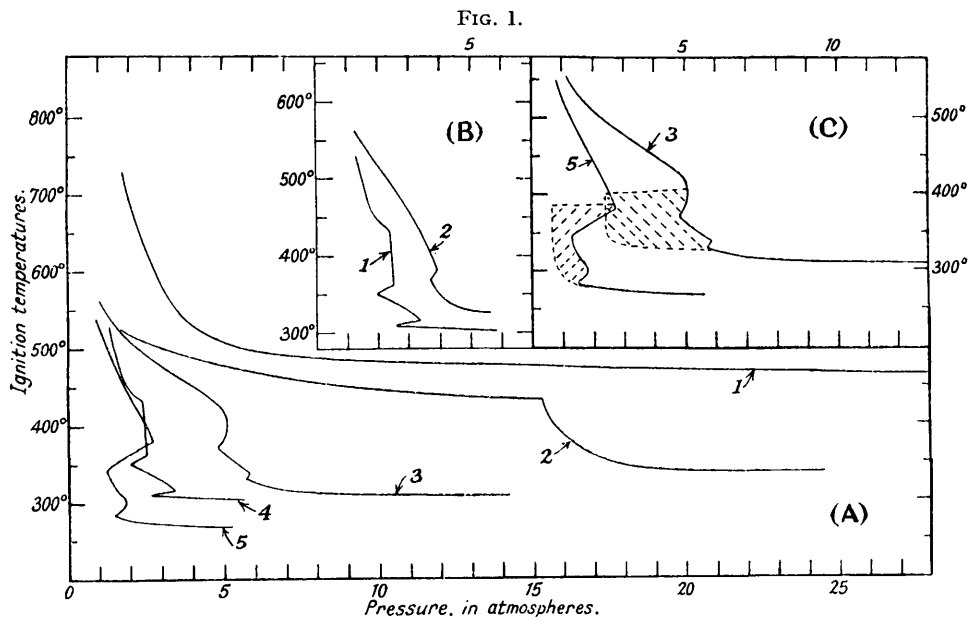
By G. P. KANE, E. A. C. CHAMBERLAIN, and D. T. A. TOWNEND.

IN recent years, investigations designed to throw light on the problem of "knock" in internal combustion engines have led to the recognition that the processes involved in the combustion of complex hydrocarbons are by no means simple. For instance, Edgar and his collaborators (*J. Amer. Chem. Soc.*, 1929, **51**, 1875, 2203, 2213; 1934, **56**, 102), who studied the slow combustion of mixtures of higher paraffins, etc., with air in a flow system, found that, although initial oxidation commenced at 150—200°, becoming active between 250° and 270°, in which range the products were luminescent, and then mildly explosive between 270° and 300°, yet at higher temperatures the combustion was less intense until about 500° had been reached. Similar observations were made by Pease (*ibid.*, 1929, **51**, 1839; 1934, **56**, 2034; 1935, **57**, 2296). Subsequently, Prettre (*Bull. Soc. chim.*, 1932, **51**, 1132; cf. also Emeléus, J., 1929, 1733) made an extensive investigation into the luminescent and cool-flame phenomena associated with the slow combustion of a wide range of combustibles at atmospheric pressure. Among the paraffins, cool flames were not observed with methane and ethane; rich mixtures of propane, pentane, hexane, heptane, and octane, however, gave rise to them in a temperature range usually between 230° and 300°, above which normal inflammation did not occur until temperatures above 600° had been reached. Amylene and amyl alcohol were the simplest olefin and alcohol, respectively, to exhibit cool flames; aldehydes and ether, on the other hand, readily gave rise to them.

More recently, while studying the influence of pressure on the reactivity during slow combustion of butane-air mixtures, Townend and Mandlekar (*Proc. Roy. Soc.*, 1933, *A*,

141, 484) observed that on the attainment of a critical pressure, which varied somewhat with mixture composition, ignition occurred abruptly in a temperature range below *ca.* 350°, which in later experiments was recognised as that in which only cool flames are normally observable. It was also recognised that the critical pressure referred to was related to the critical compression ratio for the incidence of "knock" in engine practice.

The influence of pressure on the spontaneous ignition of the paraffins and other combustibles has since been systematically studied (*ibid.*, 1933, A, 143, 168; 1934, A, 146, 113; 1936, A, 154, 95); in Fig. 1, A, the ignition-point curves for corresponding mixtures with air of methane, ethane, propane, butane, and hexane (curves 1, 2, 3, 4, and 5, respectively) have been plotted side by side for easy comparison. It will be observed that, whereas the curve for the methane-air mixture fell smoothly and showed no evidence of a lower system even at pressures up to 30 atm., and that for the ethane-air mixture showed



A. Curves 1, 2, 3, 4, and 5 are for 13% methane, 10% ethane, 5% propane, 3.8% butane, and 2.7% hexane, respectively, in air.
 B. Curves 1 and 2 are for 3.8% butane and isobutane, respectively, in air.
 C. Curves 3 and 5 are as in A, but with cool-flame areas shaded.

a sharp inflexion at about 15 atm. (430°), beyond which a simple lower system was superposed on the higher one, yet with all higher paraffins an abrupt fall occurred, two pressure minima of ignition being observed, one at about 280—330° and the other at about 340—370°. Another matter of importance, particularly having regard to the relation between these observations and the known knocking propensities of the hydrocarbons concerned, was that, as the paraffin series was ascended, not only did the minimum pressures requisite for ignition in the lower range progressively decrease, but the pre-ignition time-lags were also materially reduced; for instance, with propane, lags of the order of 3—5 seconds were reduced to less than 1 second with hexane. Also, to illustrate the difference in behaviour between a normal and an *iso*-paraffin, in Fig. 1, B, curves have been drawn for 3.8% mixtures of butane and *iso*butane (curves 1 and 2, respectively).

Moreover, with the members containing three or more carbon atoms, there were fairly well-defined pressure and temperature limits within which cool flames were propagated, those for the propane- and the hexane-air mixture being illustrated by the diagonally shaded areas, Fig. 1, C. When a pressure adequate for true ignition in this temperature range was attained, a two-stage process occurred, the full ignition following rapidly after the formation of a cool flame.

In considering the complex chemical processes involved in the combustion of the higher paraffins, three main conditions have therefore to be taken into account, *viz.*, (1) that giving rise to cool flames, in our own experiments somewhere in the temperature range *ca.* 280—410°; (2) that ultimately resulting in true ignition in the products arising after the passage of cool flames, there being usually two distinct zones of activity between 280—330° and 340—370° severally; and (3) that occurring above the upper temperature limit for cool flames, *i.e.*, above about 410°. It is now generally agreed that conditions conducive to (1) are mainly responsible for "knock"; the low-temperature combustion has been examined chemically, as well as by absorption spectra, and correlated with the chemical state of the charge in an engine before the passage of flame, by Egerton, Ubbelohde, and collaborators (*Proc. Roy. Soc.*, 1933, *A*, 142, 26; 1935, *A*, 152, 354; *J.*, 1932, 661; *Phil. Trans.*, 1935, *A*, 234, 433). Knock itself probably involves essentially the processes occurring in (2), which become intense at sufficiently high pressures.

Also, there is little doubt that the processes occurring in cool flames are chain reactions and are probably associated with the presence of peroxides, aldehydes, or other active intermediate species. Aldehydes play an important rôle with the simpler hydrocarbons (*cf.* previous papers), but with higher members other substances also are probably concerned. Egerton and his collaborators have regarded primary peroxides as mainly responsible, and Newitt's recent discovery of the formation of mixed ethers in the slow combustion of olefins (*Proc. Roy. Soc.*, 1936, *A*, 157, 348) suggests another type of intermediate substance known to promote reaction (Kane and Townend, *ibid.*, in the press). The upper temperature limit for cool flames has generally been ascribed to the thermal instability of some material essential to the process and its breakdown may also involve chain reactions, but further investigation on the matter is necessary.

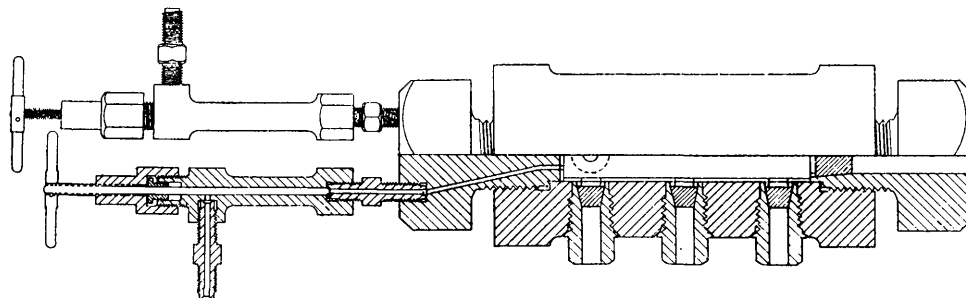
In recent discussions relating to the mechanism of the processes occurring in the low-temperature range, it has been inferred from Prettre's work that the substitution of a hydroxyl group in a paraffin would necessarily decrease chemical reactivity. It will be readily appreciated, however, from the cool-flame ranges already illustrated, that this would be a difficult issue to decide from isolated experiments carried out solely at atmospheric pressure, and as the matter is of great interest in regard to the theory of hydrocarbon combustion generally, we decided to investigate it more closely. The experiments described herein relate to the simpler corresponding paraffins, alcohols, and aldehydes containing one, two, or three carbon atoms; with these materials chemical reactivity has been found to ascend in the order named.

It should be added that, owing to the great violence usually associated with ignitions of combustible-oxygen media, our experiments have been restricted in the first place to mixtures made with air.

EXPERIMENTAL.

Explosion Vessel.—The explosion vessel (Fig. 2) is that most recently developed for use in these investigations. It was constructed of nickel-chromium steel, and provided with an

FIG. 2.



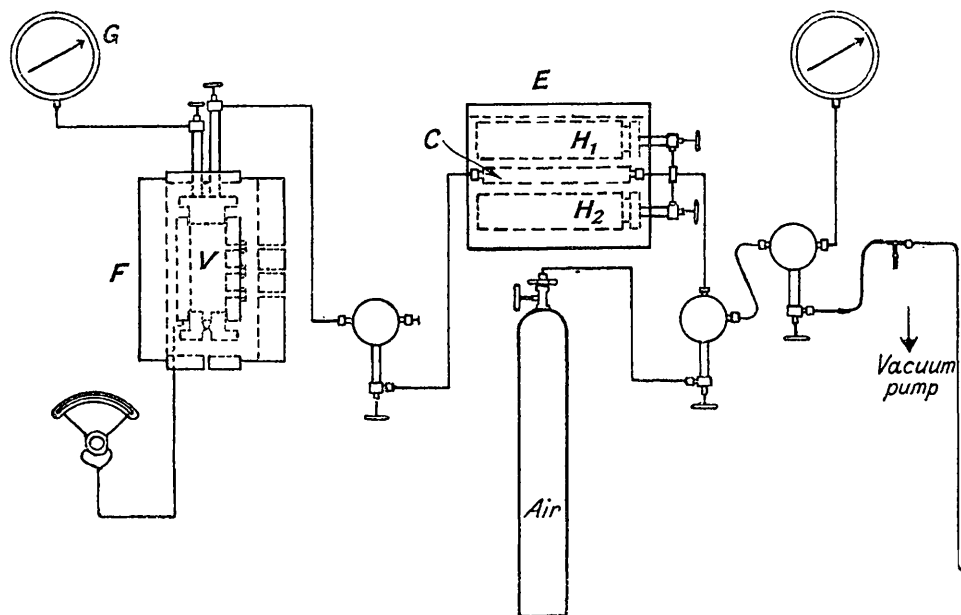
internal cylindrical cavity 15 cm. long and 3.6 cm. in diameter, closed at one end by a plug fitted with inlet and outlet valves, and at the other by a plug, either blank or alternatively provided with a quartz window, as actually shown, or with a disc recording manometer. Three

plugs for windows were also placed along a horizontal axis down one side of the vessel. The valve stems were grooved to within $\frac{1}{4}$ in. of their seats, and bull-nosed so as to allow rapid admission of the gaseous mixture to the explosion vessel, and they were long enough to allow easy operation from without the heating furnace, the stuffing boxes being packed with grease-free asbestos impregnated with graphite.

Procedure.—The vessel was mounted in a well-lagged electric furnace *F* (Fig. 3), which could be maintained constant at any experimental temperature.

Two pressure nickel-steel vessels H_1 and H_2 , fitted with slow control valves and constructed to withstand a pressure of 1000 atm., were used as storage vessels for the hydrocarbon-air mixtures, half-inch glass balls introduced into each cylinder facilitating rapid and thorough mixing of the constituents. A capacity vessel, *C*, from which the gas mixtures were rapidly released into the explosion vessel *V*, at the experimental pressure, and the pressure vessels H_1 and H_2 were separately housed in a well-lagged electric heater *E*, fitted with an automatic

FIG. 3.



Filling System.

temperature regulator, so adjusted that the combustible-air media under pressure were maintained homogeneously in the vapour phase. All connections and valves were wound with asbestos-covered nichrome wire, so that the system could be heated to any desired temperature up to 200° . In the case of aldehyde-air media, where storage would be undesirable, the mixtures, owing to the low b. p. of the combustibles concerned, could be made up separately for each experiment in the capacity vessel *C*, and after 30 seconds' agitation, they were released into the explosion vessel.

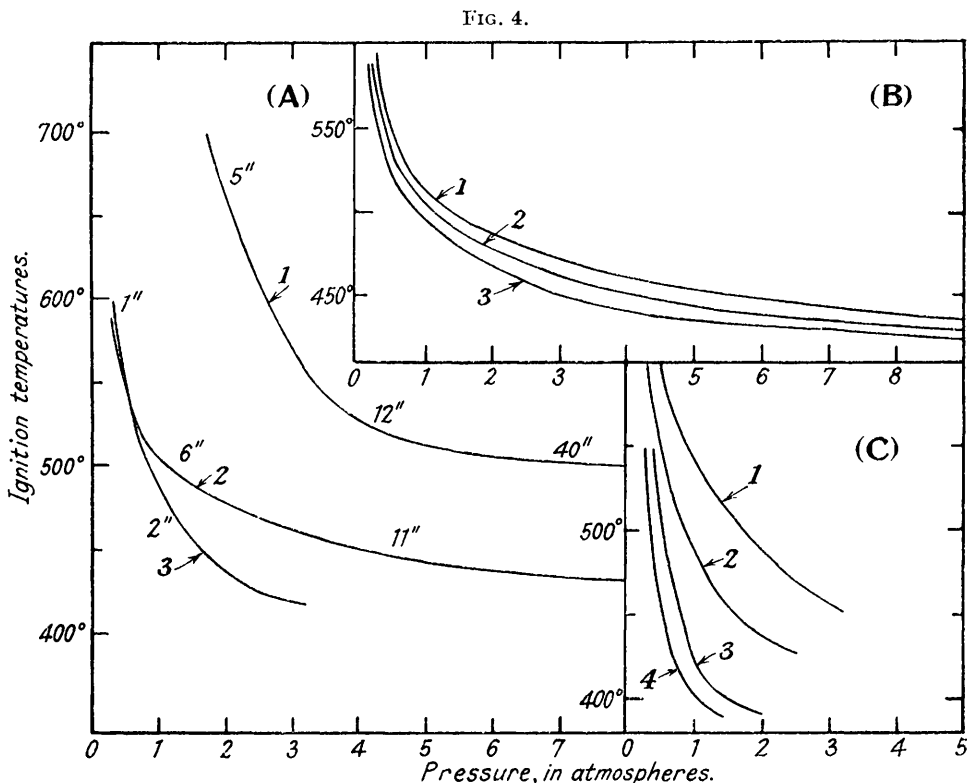
To determine an ignition point, the filling pressure was gradually raised until spontaneous ignition occurred, and then varied more carefully so that a critical value could be obtained; this pressure was usually located within 0.1 atm. above 5 atm., within 0.05 atm. between 1 and 5 atm., and within a few mm. of mercury at pressures below atmospheric. The occurrence of an ignition was conveniently recorded by the kick imparted to the Bourdon gauge *G*; cool flames normally gave rise to a mild pressure pulse which was easily recognised after some experience of the work. Both types of ignition were also readily distinguishable by visual observation through the quartz windows; moreover, the cool flames gave rise to intermediate products strongly aldehydic in character.

Results.

A. Methane-, Methyl Alcohol-, and Formaldehyde-Air Mixtures.—An account of the influence of pressure on the spontaneous ignition points of methane-air mixtures has been given else-

where (*Proc. Roy. Soc.*, 1936, *A*, 154, 95), and their general behaviour may be judged from curve 1, Fig. 4, A (cf. also curve 1, Fig. 1), relating to a 10% mixture.

Observations with methyl alcohol (A.R. sample, dried with sodium in the usual way and fractionated, b. p. 64–65°) were restricted to three mixtures containing severally 8, 12, and 18% of the combustible (curves 1, 2, 3; Fig. 4, B). Reproducible results were not easily obtainable with the mild-steel liner usually employed in these investigations, and it was therefore replaced by one of silica. The ignition points fell progressively with increase of pressure, the general behaviour simulating that observed with methane-air mixtures, except that the time-lags (small figures along the curves) were much shorter, and the corresponding ignition pressures much lower, than with the parent hydrocarbon.



A. Curves 1, 2, and 3 are for corresponding mixtures with air of methane, methyl alcohol, and formaldehyde.
 B. Curves 1, 2, and 3 are for 8%, 12%, and 18% methyl alcohol-air mixtures.
 C. Curves 1 and 2 are for 8% and 16% formaldehyde-air mixtures; curves 3 and 4 are for 8% and 16% formaldehyde-oxygen mixtures.

Formaldehyde was prepared from paraldehyde by the method of Trautz and Ufer (*J. pr. Chem.*, 1926, 113, 105), an apparatus similar to that of Spence and Wild (*J.*, 1933, 1193) being used, and a special filling system being adopted so that the mixtures could be made up directly from the depolymerising apparatus. Four mixtures were investigated containing 8 and 16% of formaldehyde in air, and 8 and 16% of it in oxygen (curves 1, 2, 3, 4, respectively; Fig. 4, C). The ignition-point curves again fell quite smoothly, the ignition pressures and corresponding time-lags being now much less than with either methane- or methyl alcohol-air mixtures.

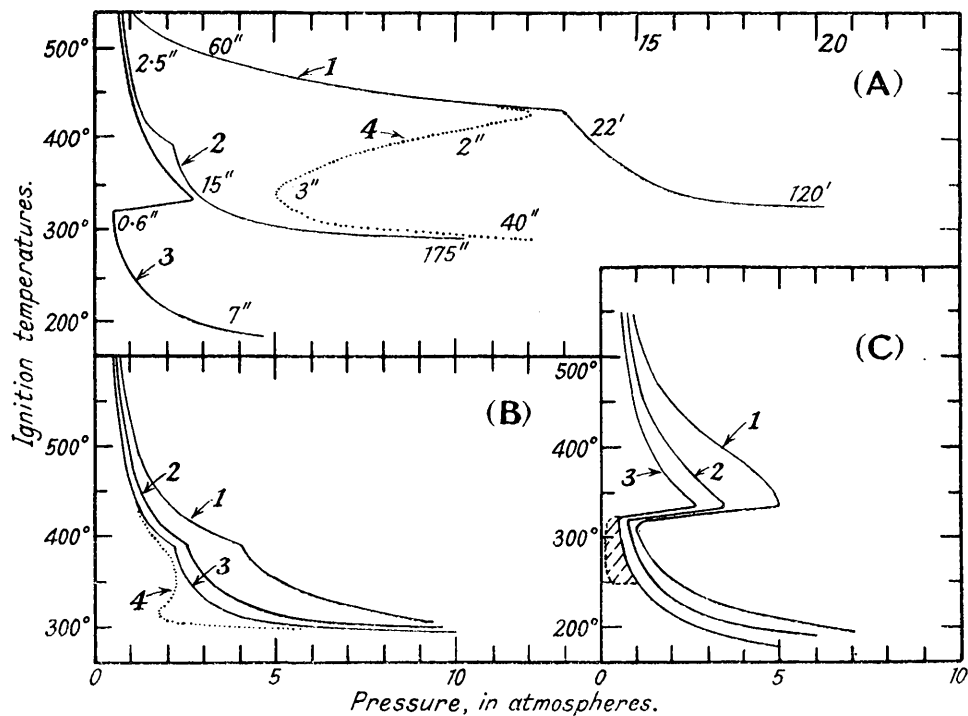
The ease of ignition of the three materials is best compared by reference to the curves for corresponding mixtures shown in Fig. 4, A. A small allowance must be made for the silica liner employed with the methyl alcohol-air mixtures, for this had the effect of lowering the ignition points by some 20° at the low and 5° at the high pressures, as compared with determinations in a mild-steel vessel.

It should be particularly noted that none of the curves shows any sign of the development

of a lower ignition system and they are typical of those of non-knocking fuels; moreover, they are in agreement with the recent observations of Bone and Gardner (*Proc. Roy. Soc.*, 1936, *A*, 154, 297) on the relative reactivities of equimolecular methane-, methyl alcohol-, and formaldehyde-oxygen mixtures in a static system.

B. *Ethane-, Ethyl Alcohol-, and Acetaldehyde-Air Mixtures.*—In Fig. 5, A (also cf. Curve 2, Fig. 1), the ignition-point curve (No. 1) for a 13% ethane-air mixture is reproduced and needs no further comment. The dotted curve No. 4 shows the influence of the addition of 1% acetaldehyde to this mixture (cf. *ibid.*, p. 103), and in our opinion provides strong evidence that the imposed lower system with ethane-air mixtures arises when temperature and pressure conditions allow of an adequate rate of formation and survival of acetaldehyde.

FIG. 5.



- A. Curves 1, 2, and 3 are for corresponding mixtures with air of ethane, ethyl alcohol, and acetaldehyde; curve 4 is as 1, but with addition of 1% acetaldehyde to the mixture.
 B. Curves 1, 2, and 3 are for 4%, 6.5%, and 9% ethyl alcohol-air mixture; curve 4 is as 3, but with addition of 1% acetaldehyde to the mixture.
 C. Curves 1, 2, and 3 are for 5%, 7%, and 10% acetaldehyde-air mixtures: shaded area denotes cool-flame limits.

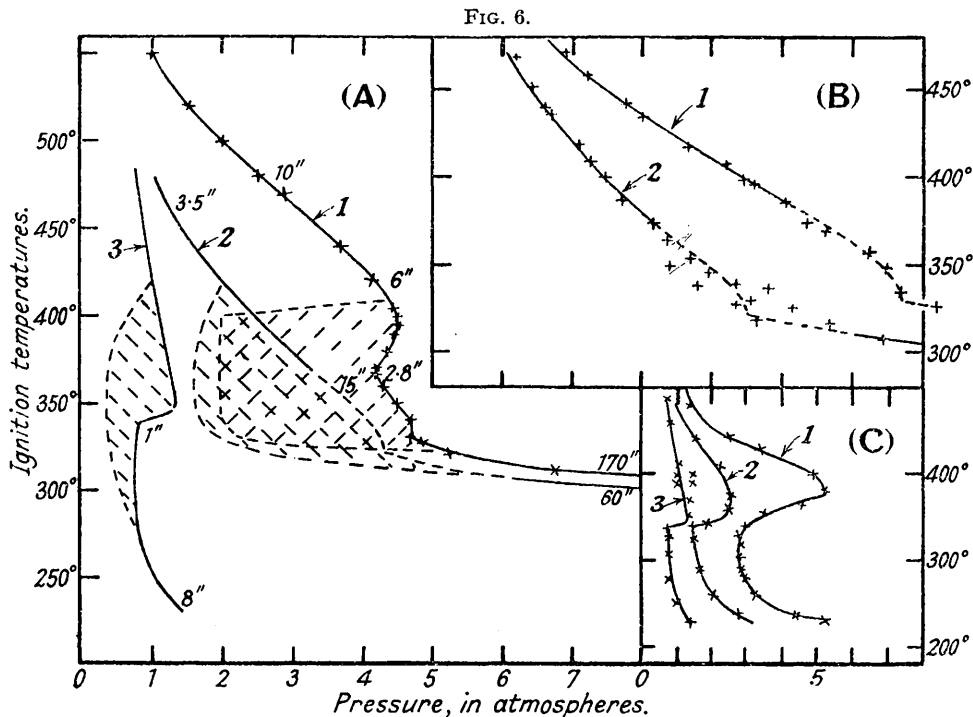
The influence of pressure on the ignition points of air-ethyl alcohol (dried in the usual way and fractionated; b. p. 78–79°) mixtures is shown by the curves 1, 2, 3 (Fig. 5, B) for mixtures containing respectively 4, 6.5 (theoretical), and 9% of the combustible. They are similar in form to those of ethane, with an inflexion in the curves at about 395°. The addition of 1% of acetaldehyde to a 9% ethyl alcohol-air mixture had an effect very similar to, but less marked than, that of a corresponding addition to the 13% ethane-air mixture, indicating that the survival of acetaldehyde probably plays a like rôle with both media. Although no cool flames had been observed with ethane-air mixtures, we were uncertain whether the alcohol-air mixtures gave rise to them under pressure, for although a mild pressure pulse was observable in certain circumstances, it was not possible to correlate this with a travelling flame, the mixture being merely luminescent; we would therefore leave the question an open one.

The opinion that the low-temperature system was connected with the formation of acetaldehyde found strong support when the ignition-point curves for acetaldehyde (b. p. 21°)-air mixtures were determined, as may be seen from curves 1, 2, and 3, Fig. 5, C, relating to 5, 7, and 10% mixtures, respectively. Cool flames were also now definitely observed for the first

time within the range shown by the dotted boundary curve, which relates to the 10% mixture (No. 3). Moreover, the ignition-point curves reveal a strong negative temperature coefficient of reaction at about 330°, and this seems characteristic of the upper pressure minima found in corresponding curves for all the higher paraffins and certain other combustibles.

A comparison of the three corresponding curves for ethane, ethyl alcohol and acetaldehyde (Fig. 5, A; curves 1, 2, and 3 respectively) leaves little doubt as to the order of ease of ignition of the three materials; it also appears almost certain that acetaldehyde is in some way responsible for the lower ignition system observed with ethane and ethyl alcohol.

C. *Propane-, Propyl Alcohol-, and Propaldehyde-Air Mixtures.*—Propane in admixture with air is the simplest paraffin to give rise to cool flames, and its ignition-point curves are the



- A. Curves 1, 2, and 3 are for corresponding mixtures with air of propane, propyl alcohol, and propaldehyde. Shaded areas denote cool-flame limit.
 B. Curves 1 and 2 are for 3% and 7% propyl alcohol-air mixtures.
 C. Curves 1, 2, and 3 are for 3%, 5%, and 10% propaldehyde-air mixtures.

first to show two pressure minima in the low-temperature system typical of all higher paraffins (curve 1; Fig. 6, A); moreover, the processes operative in its combustion in the low-temperature system may be regarded as typical of those of knocking fuels, although it may well be that these processes are augmented when higher paraffins are concerned. It is of interest, therefore, to examine the respective behaviours of propane and propyl alcohol, for if the same order of reactivity be maintained as with the simpler paraffins already considered, ease of ignition in the lower system would seem likely to be attributable to some intermediate product common in each oxidation.

In Fig. 6, B, curves 1 and 2 relate respectively to the ignition of 3 and 7% purified *n*-propyl alcohol (b. p. 96.5–97.5°)-air mixtures. A main interest lay in the question as to whether propyl alcohol would exhibit pressure minima, as found with propane. No definite conclusion could be drawn regarding this, however, as ignitions in the range 320–360° were found to be very sensitive, and often gave different values in successive experiments; this difficulty was not overcome by replacing the mild-steel liner by silica. The broken lines, however, indicate very nearly the minimum pressures requisite for ignition in this range. Nevertheless, the values obtained were quite adequate to indicate that the propyl alcohol mixtures were more easily ignitable than those of propane, as may be seen by comparing curves 1 and 2, Fig. 6, A. It will also be observed that cool flames were propagated at somewhat lower pressures.

Propaldehyde (b. p. 50°)-air mixtures (Fig. 6, C) showed characteristics not unlike those observed with acetaldehyde, but the lower ignition system extended to rather lower temperatures.

Although the comparison between the behaviour of the three materials is not so well defined as with the ethane series, it is clear that propyl alcohol is certainly *not* less easily oxidised in the lower temperature range than propane, but it may be unwise, on the other hand, to assume that the curves justify the conclusion that the formation of propaldehyde is entirely responsible for the low-temperature combustion of both the alcohol and the hydrocarbon.

DISCUSSION.

There are few data in the literature concerning "knock" ratings of the materials examined in this investigation, but there is general agreement between our own results and the extant observations, as may be seen from the following table :

No. of C atoms in molecule.	Critical compression ratios.		
	Paraffin.	Alcohol.	Aldehyde.
1	non-knocking		
2	14.0	7.5	both
3	12.0	—	knock

With propyl alcohol, for which no figures are available, however, although the minimum pressure for ignition in the lower range is intermediate between those of propane and of propaldehyde, we should not anticipate its knock-rating to conform to the same order; for the time-lags were much longer with the propyl alcohol between 330° and 430° than with propane. Moreover, their decrease with increase of pressure was very much less than with the paraffin, a most important consideration in correlating the knocking propensity of a fuel with ease of ignition in the lower system.

We have not yet been able to compare the respective behaviours of corresponding materials containing four carbon atoms. An attempt to determine the ignition points of amyl alcohol was only partly successful, as the ignitions were often unreproducible; it was quite clear, however, that with five carbon atoms the rate of reaction was greater with the paraffin than with the alcohol, and this is in agreement with the finding of Layng and Youker (*Ind. Eng. Chem.*, 1928, **20**, 1048), who contrasted the oxidation characteristics of heptane and heptyl alcohol. It appears probable, therefore, that a change over in the respective ease of oxidation of parent hydrocarbon and alcohol occurs with about four carbon atoms in the molecule, and the recent suggestion of Ubbelohde (*loc. cit.*) with regard to the possible function of cyclic substances in the combustion of higher hydrocarbons may possibly be of relevance in this connection.

In general, our results seem to indicate that, although intermediately formed aldehydes play an important rôle in the combustion of the lower paraffin hydrocarbons, yet their influence may be less important than that of other substances in the case of higher paraffins.

SUMMARY.

A brief account is given of previous investigations upon the influence of pressure on the spontaneous ignition of paraffin hydrocarbon-air media, indicating the relationship between ease of ignition in a low-temperature system at *ca.* 300—350° and the knocking propensities of the fuels concerned as observed in engine practice.

In recent discussion of the chemical processes occurring in the low-temperature system and giving rise to knock, it has been assumed that aliphatic alcohols are less reactive than their parent hydrocarbons. It is now shown that, in the ethane series, ease of ignition is in the order aldehyde > alcohol > paraffin; in the propane series the same order is found, but the time-lags for the alcohol are greater than for the paraffin. With paraffins containing five or more carbon atoms, the order (from both the authors' experiments and others) is paraffin > alcohol.

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