10 mole % of hexane, about 50% of the hexane and 22% of the ethylbenzene were converted.

In experiment 11 the hexane content of the feed was increased to 50 mole %. This experiment was made at a low temperature level, under which conditions 28% of the ethylbenzene and 56% of the hexane were converted. On the basis of the ethylbenzene reacting, the yield of benzaldehyde was increased considerably, as shown in Figure 6.

Isopropylbenzene. This compound readily oxidized at temperatures above 500° C. at atmospheric pressure. The major products of the reaction consisted of styrene, α-methylstyrene, acetophenone, and benzaldehyde. The relative proportions produced are given in Figure 1. The composition of a typical organic layer product as determined by distillation is presented in Figure 7. The distillation was carried out under reduced pressure (20 mm. of mercury) using a glass-packed column having about six theoretical plates, and operated at a reflux ratio of about 5 or 10 to 1.

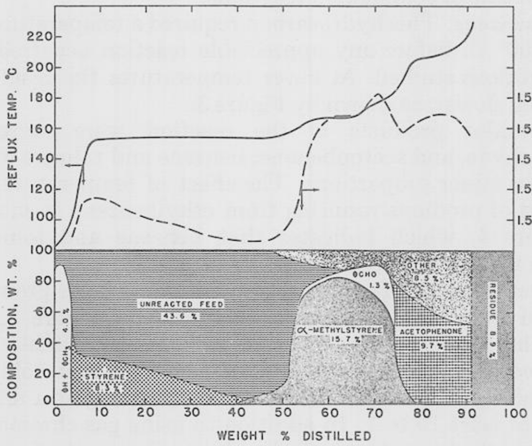

Figure 7. Distillation of isopropylbenzene products

The reaction products were identified by gas chromatographic procedures as well as by the preparation of known derivatives as outlined under ethylbenzene.

Diisopropylbenzene. This compound readily oxidized to give styrene and oxygenated derivatives as principal products. Although none of the individual compounds were identified, the presence of isopropylstyrene, isopropyl-α-methylstyrene, and carbonylic compounds was indicated on carefully distilling portions of the liquid product. The relative proportion of each product in the distillate was estimated on the basis of the unsaturation and carbonyl content of the various boiling ranges. The data are summarized in Figure 1.

ACKNOWLEDGMENT

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Flame Luminosities of Hydrocarbons and Hydrocarbon Mixtures Burned in the Gas Phase

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DURING THE COMBUSTION of a hydrocarbon fuel in a jet engine, the extent to which microscopic carbonaceous particles form in the flame can substantially affect engine performance (*6*). Incandescent carbonaceous particles increase the rate of radiant energy transmission to the walls of the combustion chamber, resulting in increased wall temperatures. Excessive wall temperature shortens combustion chamber life, and incomplete combustion of the fuel represents a loss in fuel efficiency, leading to decreased range and payload. Therefore advantages could accrue from use of a jet fuel with little tendency to form carbon in the flame. Although carbon formation can also be controlled by modifications of engine design such as premixing techniques or varying fuel-air ratio, accompanying space, weight, or other penalties may make it impractical.

This investigation was undertaken in connection with a project to study the feasibility of cooling very high speed aircraft by means of an endothermic reaction of the fuel prior to combustion. A number of endothermic reactions of hydrocarbons have been under consideration for this purpose, including aromatization, cracking, depolymerization, dehydrogenation, and isomerization. In evaluating each reaction one of the criteria has been the burning characteristics of the products, particularly the luminosity.

The carbon-forming propensities of fuels have usually been measured and compared by determining the maximum rate at which each fuel could be burned in a specially designed apparatus (*3, 4, 5*) without smoking. The figure of merit may be the actual limiting burning rate or the corresponding flame height. In some cases smoking characteristics have been determined by measuring the percentage of light transmission for a fixed rate of combustion. Recently the Luminometer (Model 02L-18, Erdco Engineering Corp., Addison, Ill.), has been developed, which measures the tendency of a substance to form carbon in a flame during combustion by a measurement of the flame luminosity. Thus far the instrument has been used only with liquid fuels.

The goals of the present work were (1) to evaluate the instrument for comparing luminosities of fuels burned in the gas phase; (2) to compare the luminosities of some potential endothermic fuels with the products that would be formed by reaction—e.g., cyclohexane *vs.* a 3 to 1 molar mixture of hydrogen and benzene; and (3) to develop a more basic understanding of the factors determining the luminosity of flames of simple hydrocarbons as measured in the Luminometer. Of particular interest was the extent to which knowledge of the separate components would make possible general predictions of the luminosities of fuel mixtures and fuels mixed with diluents.

Operation of Luminometer. The fuel is burned on a wick in an apparatus similar to an alcohol lamp. The flame size (rate of burning) is adjusted so that radiant energy is dissipated at a specified rate, determined by a photocell, that is the same for all fuels studied. (This is an arbitrary standardized reading of 45 in the usual test.) A highly luminous flame consequently will be adjusted to burn relatively slowly; a less luminous flame, to burn much more rapidly. The instrument reading comes from a thermocouple located over the flame and at a standard distance above the base of the flame. The temperature read by this thermocouple clearly increases with flame height. Consequently, if flame height is adjusted to a fixed radiant energy dissipation rate, this temperature, conventionally expressed in degrees Fahrenheit above ambient, is a measure which varies in some inverse way with the luminous nature of the flame.

EXPERIMENTAL

A drawing of the essential parts of the Luminometer is shown in Figure 1. The wick (for liquid fuels) dips into a fuel reservoir, while the flame is contained in a chamber to permit stability and eliminate drafts. Since the fuel is not premixed with air and the fuel flow rate is low, a laminar diffusion flame results. Flame height can be regulated by manually raising or lowering the wick. The photocell, located behind the flame, is connected to a battery-powered amplifier and meter which indicates the flame luminosity level in arbitrary units over a linear scale. The response of the 935 phototube is greatest for orange light of wave length 5000 to 6000 A., but it is reasonable to assume that this is representative here of the total radiation spectrum.

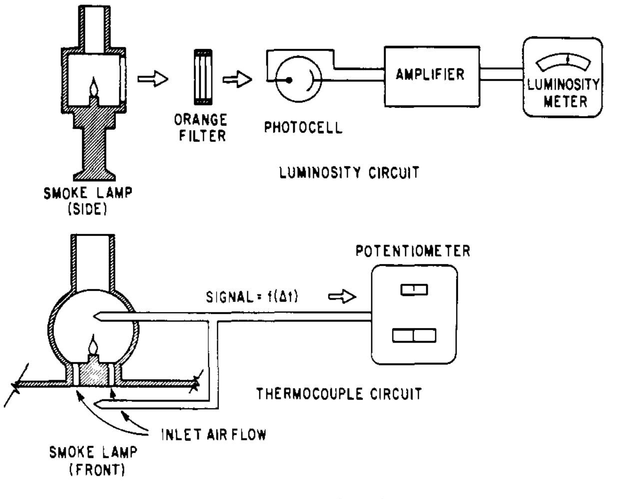


Figure 1. Essential parts of Erdco Luminometer

COURTESY ERDCO ENGINEERING CORP.

An iron-constantan thermocouple is located a short distance above the flame tip and another thermocouple measures ambient temperature. The temperature elevation (ΔT) above ambient is read directly from the potentiometer connected to these two thermocouples. To minimize daily variations caused by atmospheric changes in humidity, air entering the combustion area was first dried by passage through a tube packed with anhydrous calcium sulfate. No corrections were applied for minor changes due to variations in atmospheric pressure.

No change in the Luminometer itself was required to burn gaseous fuels, other than removal of the wick from the fuel supply tube and suitable modifications to permit direct piping of vapor to the instrument. Three methods of supplying vapor were developed (Figure 2).

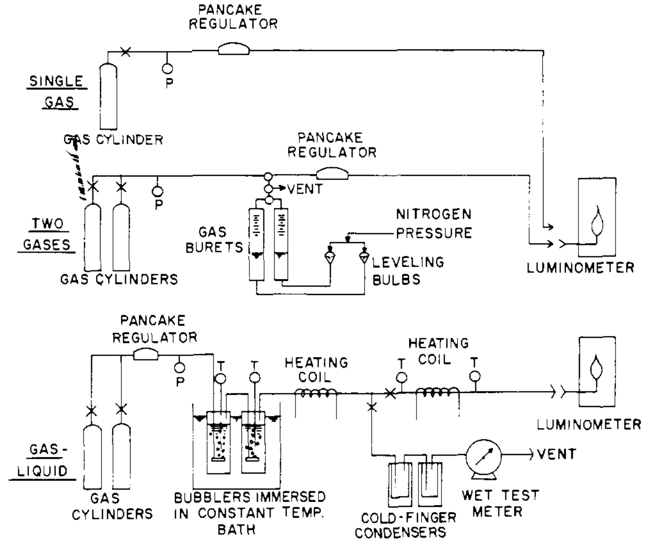


Figure 2. Modification of Luminometer for use with gaseous fuels

The very small flow rates of gas required must be carefully controlled, since any irregularity in the flow rate causes the flame to fluctuate and makes accurate luminosity determinations impossible. A conventional, two-stage reducing valve was incapable of maintaining the required gas flow rates of approximately 1 liter per hour at a pressure slightly above atmospheric. However, a fine, even, and easily controlled flow of gas was achieved by incorporating a large, low-pressure pancake regulator, a sensitive needle valve, and a pin-point-sized orifice into the system.

When a single gas was studied, it was piped directly from the storage cylinder through the pressure-regulating devices, and then into the Luminometer. Mixtures of two or more gases were prepared by introducing the component gases in the desired proportions into two 1000-ml. burets and mixing the gases thoroughly by repeatedly cycling them between the two burets. Nitrogen pressure on the leveling bulbs forced the gas mixture through the regulator and into the Luminometer.

To prepare a mixture of a gas and a substance normally liquid at room temperature, the liquid was placed inside two bubblers immersed in an oil bath. The gaseous component was passed through the usual pressure-regulating devices and through the two bubblers in series. Composition of the vapor mixture could be determined by passing the vapor through two cold-finger condensers in series and a wet-test meter. It was established that this composition was almost exactly that predicted for saturation, using vapor pressure data from the literature. The composition could be closely controlled by regulating the temperature of the oil bath. To prevent condensation, the lines carrying the gas from the bubblers to the Luminometer were heated to a temperature above that of the bubblers.

Although the Luminometer yields results in the form of temperature differences, it has been customary to express fuel luminosities as Luminometer numbers (LN). For liquid fuels the two references are Tetralin (ΔT = 214° F.) and iso-octane (ΔT = 480° F.), so that the Luminometer number for a test fuel is defined as

$$\text{LN} = \frac{\Delta T_{\text{test fuel}} - \Delta T_{\text{Tetralin}}}{\Delta T_{\text{iso-octane}} - \Delta T_{\text{Tetralin}}} \times 100$$

All values of ΔT are obtained at a meter reading of 45. ΔT and Luminometer number both increase with decreasing fuel luminosity.

Luminometer numbers are not identical for the same substance when determined in the gas and liquid phases. It is more convenient to use as reference fuel substances which are gaseous under ambient conditions. Accordingly, a new gas phase Luminometer number scale has been used here, based on acetylene (ΔT = 303° F.) and ethylene (ΔT = 716° F.). The Luminometer number for gases is therefore defined by

$$\text{LN}_{\text{AE}} = \frac{\Delta T_{\text{test fuel}} - \Delta T_{\text{acetylene}}}{\Delta T_{\text{ethylene}} - \Delta T_{\text{acetylene}}} \times 100$$

RESULTS

The degree of accuracy and reproducibility of gas phase luminosity determinations was first established by running several gases each day, with every attempt being made to eliminate variables that might lead to fluctuations. The results are presented in Table I in the form of ΔT values and Luminometer numbers (LN_{AE}), including average values and mean deviations. The greatest variation from day to day comes from fuels which are relatively nonluminous and therefore the most difficult to measure accurately.

Luminosity data were obtained on a number of pure hydrocarbon gases, as well as mixtures of two gases, as shown in Table II, which also contains values for a number of compounds run in the liquid phase. Values for LN_{AE} and conventional Luminometer numbers have been calculated in each case. LN values indicate the approximate relationship of gaseous fuels to the more familiar liquid fuels and must be considered as approximate only, since they are based on the assumption that gas and liquid phase readings on the same compound are identical. This is not exactly correct.

The vapor phase luminosities of mixtures having a component normally liquid at room conditions were investigated with mixtures of nitrogen, hydrogen, and ethylene with benzene and Tetralin (Figures 3 and 4). The temperature of the oil bath was varied from 24.2° to 73.3° C., which produced mixtures ranging from 12 to 82 mole % benzene. Tetralin concentrations between 3.5 and 85.3 mole % were produced by varying the bath temperature between 98° and 200° C.

To obtain a vapor phase Luminometer number for benzene, the three curves of Figure 3 were extrapolated to zero diluent concentration—i.e., 100% benzene. The value of −10.7 so obtained corresponds to a ΔT of 259° F. The ΔT for liquid benzene, as determined with the conventional wick, was 247° F. Similarly, the Tetralin-ethylene curve of Figure 4 was extrapolated to 100% Tetralin, to obtain the gas phase Luminometer number of pure Tetralin. The approximate LN_{AE} value of −2 so obtained corresponds to a ΔT value of 295° F., compared to the liquid phase (wick) ΔT value of 214° F.

Gas phase readings of Tetralin presented a number of difficulties due primarily to the high boiling point of the compound and its strong tendency to form carbon by decomposition upstream of the Luminometer, as well as during combustion. Condensation of Tetralin in the lines leading from the bubblers to the Luminometer caused much flame instability. To eliminate this problem these lines were heated to such a temperature that the Luminometer flame chamber itself overheated, yielding erroneous readings and necessitating the introduction of a correction factor.

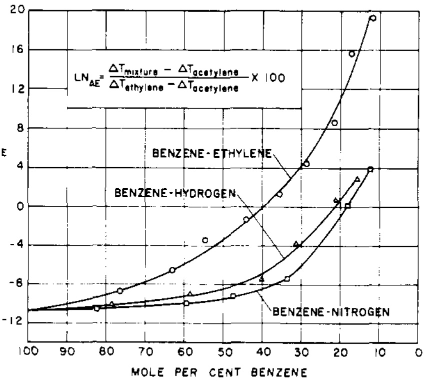
Table I. Gas-Phase Luminosity of Selected Hydrocarbons

Luminometer ΔT values and calculated Luminometer numbers, LN_{AE}

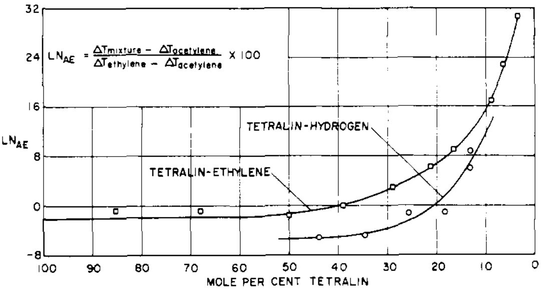
		Date													
Fuel		10/21	10/27	10/28	11/4	11/5	11/6	11/9	11/10	11/17	11/18	11/19	11/23	Av.	Mean Dev.
Acetylene	ΔT	300	304	301	307.5 309	305.5	308.5	305	303	298	296	303	300	303	±3
Ethylene	ΔT	681	738.5 743	720 727	732 738	736	730.5	722 719	703.5 704	717 717	679.5	696	690	716	±16
Cyclopropane	ΔT	394	404	407	418.5 418	419.5	410	410 403	397	412	391	402	395	406	±8
	LN_{AE}[a]	24.7	22.9	25.1	25.8[b]	26.5	24.1	24.4[b]	23.5	27.2	24.8	25.2	24.3	24.9	±0.9
Propylene	ΔT	421	436	439	440.5 439	444	437	437	441	439		425	416.5	435	±7
	LN_{AE}[a]	31.7	30.2	32.6	30.8[b]	32.1	30.5	31.8	34.4	33.6		31.0	29.9	31.7	±1.1
Isobutane	ΔT			626	641 639				604				598	622	±16
	LN_{AE}[a]			76.9	77.7[b]				75.2				76.4	76.6	±0.8
Butadiene	ΔT			322	327				331				329	327	±3
	LN_{AE}[a]			5.0	4.4				7.0				7.4	6.0	±1.2
1-Butene	ΔT				423 421				418				406	417	±5
	LN_{AE}[a]				26.6[b]				28.7				27.2	27.5	±0.8
Barometric pressure, mm.		780	752.9	777.0	767.7	768.8	766.8	770.6	771.6	761.8	767.7	763.5	771.6		

[a] Luminometer numbers as calculated from ΔT values and based on ethylene (100) and acetylene (0) as standards.

[b] Average of two runs on same day.



← Figure 3. Vapor phase Luminometer numbers of several benzene-gas mixtures



→ Figure 4. Vapor phase Luminometer numbers of Tetralin-gas mixtures

Tetralin flames also tend to deposit carbon on the thermocouple, leading to low temperature readings. These difficulties were responsible for the much greater uncertainty of the data and of the extrapolated value for 100% Tetralin vapor.

In an attempt to develop a method of predicting Luminometer numbers of mixtures from known values of the pure components, a series of luminosity determinations involving various n-butane-1-butene mixtures was performed. These data, as well as those shown in Figures 3 and 4, were analyzed in several ways. The presence of a small portion of the more luminous component makes the mixture more luminous than would be predicted on any simple additive rule based on mole fraction or weight fraction. The extent of this enhanced luminosity effect varies with different systems, however, so no reliable generalized curve was developed. A plot of log ΔT as a function of mixture composition on a weight per cent basis gives curves that are most nearly linear, which makes interpolation and extrapolation somewhat easier. Figure 5 shows curves plotted in this fashion for the n-butane-1-butene and benzene-ethylene systems.

Table II. Luminosity of Selected Hydrocarbons

Test Fuel	ΔT, ° F.	LN_{AE}[a]	LN[b]
Propane (extrapolated)[c]	1322	246	416
n-Butane (extrapolated)[c]	990[d]	166	292
n-Hexane[e]	951	157	277
n-Heptane[e]	858	134	242
n-Octane[e]	795	119	218
n-Undecane[e]	696	95	181
n-Tridecane[e]	659	86	167
Isobutane[c]	622[d]	77	154
Iso-octane[e]	480[d]	43	100[f]
Cyclopropane[c]	406[d]	25	72
Cyclohexane[e]	572	65	135
Decalin[e] (decahydronaphthalene)	361	14	55
Ethylene[c]	716[d]	100[f]	189
Propylene[c]	435[d]	32	83
1-Butene[c]	417[d]	28	76
Isobutylene[c]	391	21	67
Butadiene[c]	327[d]	6	42
Butadiene-hydrogen[c] (1:1.01)[g]	348	11	50
Butadiene-hydrogen[c] (1:2.01)[g]	395	22	68
Acetylene[c]	303[d]	0[f]	33
Acetylene-hydrogen[c] (1:1.04)[g]	407	25	73
Acetylene-hydrogen[c] (1:2.02)[g]	516	52	114
Acetylene-hydrogen[c] (1:2.94)[g]	623	77	154
Acetylene-nitrogen[c] (1:1.01)[g]	375	17	60
Acetylene-n-butane[c] (1:1)[g]	589	69	141
Benzene[e]	247	−14	12
Ethylbenzene[e]	240	−15	10
o-Xylene[e]	231	−17	6
m-Xylene[e]	226	−19	5
Tetralin (tetrahydronaphthalene)[e]	214	−22	0[f]

[a] $$LN_{AE} = \frac{\Delta T_{\text{test fuel}} - \Delta T_{\text{acetylene}}}{\Delta T_{\text{ethylene}} - \Delta T_{\text{acetylene}}} \times 100 = \frac{\Delta T_{\text{test fuel}} - 303}{716 - 303} \times 100.$$

[b] $$LN = \frac{\Delta T_{\text{test fuel}} - \Delta T_{\text{Tetralin}}}{\Delta T_{\text{iso-octane}} - \Delta T_{\text{Tetralin}}} \times 100 = \frac{\Delta T_{\text{test fuel}} - 214}{480 - 214} \times 100.$$

[c] Gas phase reading using modified Luminometer. [d] Average of two or more determinations. [e] Liquid phase reading using conventional wick procedure. [f] By definition. [g] Mole ratio of gaseous compounds in mixture.

The luminosity of a series of iso-octane–Tetralin and Decalin-undecane mixtures of various concentrations was determined in the liquid phase using a wick (Figure 6).

To obtain a clearer picture of the significance of Luminometer numbers as a measure of flame luminosity, it is desirable to have a correlation between the temperature rise, ΔT, and the burning rate at the standard rate of radiation emission. Burning rates for a number of pure gases, and mixtures of two or more gases, were determined by measuring the volume of gas burned in a given time while maintaining the luminosity level in the Luminometer continuously at 45. Naturally, substances burning with highly luminous flames in general attain a luminosity level of 45 with a lower burning rate than compounds burning with less luminous flames. Molar rate of burning does not correlate with ΔT, but the relationship between burning rate in mass per unit time and ΔT (or Luminometer number) brings all the data for the wide variety of hydrocarbons studied onto a single smooth curve. A plot of this curve is shown in Figure 7, which contains data obtained from gases or gas mixtures. The correlation probably reflects the fact that the heat of combustion per unit weight does not vary greatly among different hydrocarbons.

DISCUSSION

Studies of the origin of carbonaceous particles in flames have been reviewed recently by Gill(*2*), who gives extensive reference to the literature. Among recent detailed studies, Hunt (*3*) reports information on smoke point for a large number of compounds, from which generalizations were developed between smoke point and molecular structure. Schalla, Clark, and McDonald (*4, 5*) related smoking tendency to hydrocarbon type and method of burning and also considered the mechanism of carbon formation in some detail.

The effect of molecular structure on luminosity as measured by the Luminometer is similar to that reported previously for the effect on carbon formation as measured by the smoke point (*3, 4, 5*). Luminosity increases with increasing molecular weight within a homologous series. There is an especially sharp rise in Luminometer number as the molecular weight decreases to the low molecular weight hydrocarbon gases. The luminosity of methane and ethane is so low, and the flame so hot, that its measurement is beyond the limits of the Luminometer. Luminosity increases with increased branching of the molecule and also with increased unsaturation. Aromatic and acetylenic compounds burn with particularly luminous flames.

Figure 7 makes it apparent that the mass burning rate

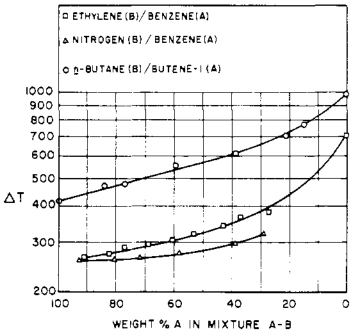


Figure 5. Vapor phase luminosities of benzene-ethylene, benzene-nitrogen, and *n*-butane–1-butene mixtures

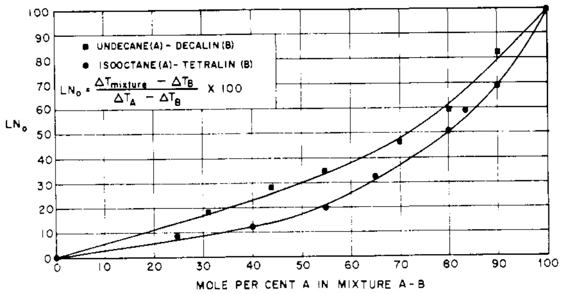


Figure 6. Liquid phase Luminometer numbers of undecane-Decane and iso-octane – Tetralin mixtures

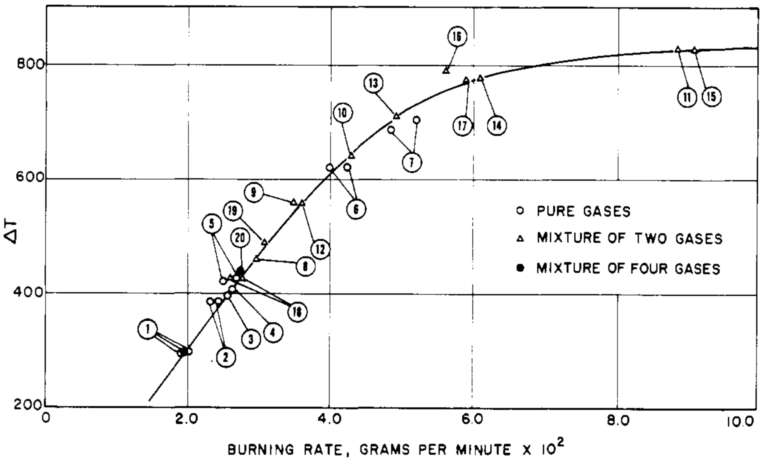


Figure 7. One simple curve of luminosity vs. mass burning rate correlates all gaseous fuels and fuel mixtures studied

Numbers in parentheses represent mole fractions

1. Acetylene
2. Isobutylene
3. Cyclopropane
4. 1-Butene
5. Propylene
6. Isobutane
7. Ethylene
8. *n*-Butane (0.39), butadiene (0.61)
9. *n*-Butane (0.61), butadiene (0.39)
10. *n*-Butane (0.75), butadiene (0.25)
11. *n*-Butane (0.90), butadiene (0.10)
12. *n*-Butane (0.40), -1-butene (0.60)
13. *n*-Butane (0.78), -1-butene (0.22)
14. *n*-Butane (0.84), -1-butene (0.16)
15. *n*-Butane (0.91), 1-butene (0.09)
16. *n*-Butane (0.74), isobutone (0.26)
17. *n*-Butane (0.86), isobutylene (0.14)
18. *n*-Butane (0.25), acetylene (0.75)
19. Ethylene (0.62), acetylene (0.38)
20. Methane (0.33), hydrogen (0.33), butadiene (0.17), isobutylene (0.17)

correlates directly with ΔT as determined in the Luminometer. The identity of the combustible fuel is immaterial; all data fall on the same curve. Mixtures containing a diluent or high percentage of hydrogen may deviate, but with this possible exception, Luminometer readings may be taken to represent a measure of mass burning rate at a constant level of radiant energy release. The same curve, or one slightly displaced from it, would probably also represent liquid mixtures in general.

Figures 3 to 6 indicate that the component of lower Luminometer number in a mixture exerts proportionally greater influence than the component of higher Luminometer number. Thus, a mixture will not have a Luminometer number as high as would be predicted by assuming each component to be contributing its proportionate share toward the Luminometer number of the mixture. The more luminous material exerts the greater influence on either a mole or mass basis. The effect may be accentuated if the comparison is made on a mole basis and the molecular weights of the two substances are highly different, as in Figure 3.

Combining this conclusion with the information from Figure 7, it appears that two combustibles burned separately will produce less luminosity than if burned together at the same mass flow rate. Conversely, for a fixed rate of radiant energy transmission, a smaller total mass flow rate must be used if the two combustibles are burned as a mixture than if they are burned separately.

Addition of hydrogen or nitrogen, or a material of low luminosity such as ethylene or *n*-butane, to a highly luminous substance such as benzene, Tetralin, acetylene, or butadiene, results in a mixture of decreased luminosity—i.e., higher Luminometer number. The effects of nitrogen, hydrogen, and ethylene on benzene; of hydrogen and ethylene on Tetralin; of hydrogen, nitrogen, and *n*-butane on acetylene; and of hydrogen on butadiene clearly indicate higher Luminometer numbers with decreasing concentration of the luminous compound.

In other studies of smoke formation, dilution with nitrogen has also been reported to reduce smoking tendency in diffusion flames (*2*). It has been generally postulated that carbon formation proceeds from initial dehydrogenation steps, so the effect of nitrogen dilution has been attributed (*1*) to its aiding the recombination of hydrogen atoms in the flame, thus removing them from further dehydrogenation reactions. The fact that hydrogen and especially ethylene cause an even greater decrease in flame luminosity is perhaps surprising. The increase in flame temperature may burn some of the carbon, but probably the cause is much more complex than this and involves the specific mechanisms of dehydrogenation and subsequent reaction.

From the viewpoint of comparing the luminosity of the products of an endothermic reaction with that of the starting fuel, it is evident that dehydrogenation or aromatization reactions will lead to a mixture of products of increased luminosity. In the cracking of a saturated hydrocarbon, however, the decreased luminosity of lower molecular weight products in general may more than compensate for the increase in luminosity caused by the appearance of unsaturated compounds.

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