Relation of Luminometer Number to Molecular Structure and Smoke Point

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THE control of smoke, carbon deposits (coke), and radiant heat transfer from the combustion zone to the walls of the combustor (flame radiation) is important in gas-turbine combustor design. Although some control of these factors has been accomplished through proper engine design, considerable emphasis has also been placed on controlling fuel quality (*8*). A summary of tests which have been used for controlling jet fuel quality, the maximum specification, and the year the test was introduced appear in Table I. Of these, smoke point and naphthalene content were adopted mainly to control flame radiance. However, these tests have not proved to be adequate.

Recently, Pratt and Whitney Aircraft Division of United Aircraft Corp. developed a new instrument for measuring combustion quality (*9*). Under the auspices of the Coordinating Research Council (CRC) it has evolved into a new test method, the CRC luminometer (*2*), which may supplant all present combustion control tests. Fuel ratings obtained with the luminometer correlate with liner temperatures (*9, 15*) and total flame radiant energy (*17*) from gas turbine combustors. Since the luminometer embodies some novel features, it seemed desirable to evaluate the combustion quality of a variety of hydrocarbons with it to see if any new relationships between molecular structure and combustion quality could be found which would help to explain carbon formation in flames.

THE CRC LUMINOMETER

The CRC luminometer is a modified smoke point lamp in which the combustion quality of a fuel is evaluated by determining the heat released on burning at a fixed level of radiant energy. This compares with the Standard IP smoke lamp (*1*) in which combustion quality is evaluated on the basis of smoke point, which is the height of the tallest flame that can be produced without smoking.

In the luminometer, the test fuel is burned in a wick-type lamp similar to the Standard IP smoke lamp. An optical filter and photocell circuit are provided which indicate flame luminosity and the intensity of radiant energy released by burning fuel. The filter limits the radiant energy measured to a wave length range of 4800 to 7000 A. with the peak transmittance at 5200 A. A dual thermocouple circuit measures the temperature rise across the flame and provides a measure of the heat released. Both thermocouples in this circuit are rigidly mounted in the instrument. As a result, the distance between flame and thermocouple which responds to flame temperature varies with height of flame. A schematic diagram of the luminometer is shown in the preceding article (p. 627).

Table I. Evolution of Combustion Quality Control Tests for Jet Fuels

Test Method	Specification	Year Adopted
Aromatic content, vol. %	25 max.	1946
Aromatic boiling over 400° F., vol. %	5 max.	1950
Smoke point, mm. (for kerosines)	25 min.	1954
Smoke-volatility index (for JP-4) (smoke point + 0.42 vol. % boiling under 400° F.)	52 min.	1954
Naphthalenes, vol. %	3 max.	1957
16-hour lamp burning test	. . .	1957

The instrument has been evaluated by the CRC for reproducibility and repeatability of fuel ratings (*6*) and the standard method of operation has been published by the ASTM as a proposed test method (*2*).

LUMINOMETER NUMBER

The measure of combustion quality obtained with the luminometer is called the luminometer number (LN). The LN of a test fuel is determined by comparing the temperature rise of the test fuel and two standard reference fuels at a standard level of radiant energy. One of the reference fuels is Tetralin, which burns with a luminous flame typical of fuels of poor burning quality. It gives a relatively small temperature rise at the standard radiant energy level; it has arbitrarily been given an LN of 0. The other reference fuel is iso-octane; it burns with a relatively nonluminous flame, typical of fuels of good burning quality, and gives a relatively large temperature rise at the standard radiant energy level. It has been given an LN of 100. The standard level of radiant energy at which all fuels are evaluated has been defined as the smoke point of Tetralin.

LN is calculated from the difference in temperature rise between the test fuel and the temperature rise for Tetralin divided by the difference in temperature rise between iso-octane and Tetralin as follows;

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

$$\Delta T = \text{temperature rise}$$

Because of the arbitrary choice of reference fuels, LN's may be greater than 100 or less than 0. A high LN is equivalent to a high smoke point and a low LN to a low smoke point.

DATA ON MATERIALS USED

LN's have been obtained for 83 hydrocarbons including 31 paraffins, 22 naphthenes, 10 olefins, and 20 aromatics (Table I). The actual and literature value of refractive index and/or estimated purity expressed in mole per cent based on freezing point measurements are included. The majority were at least 98% pure, and no materials less than 95% pure were used. In all cases, impurities were of the same hydrocarbon type and were generally isomers of the major constituent. Although the hydrocarbons included in this study represent those types which would most likely be present in JP-4 and kerosine-type jet fuels, the majority fall in the lower half of the JP-4 boiling range. This is due solely to the fact that samples of pure, high boiling hydrocarbons are generally unavailable. However, the general conclusions relating LN to hydrocarbon type and molecular structure should be applicable to higher boiling materials.

PREVIOUS STUDIES

Previous studies with hydrocarbons on the relationship between molecular structure and combustion quality or smoking tendency of diffusion flames have been conducted with wick-type lamps or open cup burners. A wick-type lamp was first used by Kewley and Jackson (*12*) and later by Minchin (*14*) to evaluate the smoking tendency of lamp kerosine. They showed that smoking tendency increased in the series paraffins, napththenes, aromatics and varied with boiling point. A modification of this lamp was adopted by the Institute of Petroleum Technologists in 1933, (*11*, *18*), as a standard test for the smoking tendency of kerosine and is used in current U. S. military fuel specifications (*5*). However, only materials with smoke points of 50 mm. or less could be evaluated in this lamp.

Clarke, Hunter, and Garner (*4*) used an open cup burner in which flame height was varied by changing the burning area. Flame heights as high as 450 mm. could be measured and 25 hydrocarbons were evaluated. Schalla and McDonald (*16*) studied 38 gaseous and liquid hydrocarbons, mostly C_6 or lighter, by burning them on either a wick or a jet. Smoking tendency was evaluated as the maximum quality of material which burned smoke-free per unit time. More recently, Hunt (*10*) evaluated 108 pure hydrocarbons on a modified wick-type lamp in which maximum flame heights of about 150 mm. were attainable. Of the modifications, the latter is probably the best, since it is simpler to use than the open cup type and has the greatest range of wick-type lamps.

All of these investigators found similar relations between smoking tendency and molecular structure. In general, normal paraffins showed the least smoking tendency, followed in order by mono-, di-, and trimethyl paraffins. Naphthenes and normal olefins had about the same smoking tendency as trimethyl paraffins. Branched olefins and naphthenes, as well as addition of double bonds to the latter, increased smoking tendency. Aromatics had the greatest smoking tendency, and varying the character of the side chains had little effect, except in blends.

RESULTS AND DISCUSSION

The smoking tendencies of hydrocarbons evaluated in this study, expressed as LN, are presented in Table II. Their relative ranking with regard to their combustion quality is identical with that established previously on the basis of smoke point. Indeed, even fine differences in smoking tendency due to minor changes in molecular structure within a particular hydrocarbon type are for the most part the same. This is demonstrated in Figure 1, where LN is compared with smoke point as obtained by Hunt with the Indiana smoke point lamp (*10*). These data were used for comparison, since they were the most extensively available and offered the largest number of direct comparisons. The plot includes all hydrocarbons which were evaluated by both methods. With the possible exception of olefins, the samples were of comparable purity as based on refractive index. As shown, the relation between LN and Indiana smoke point is linear between 40 and 130 LN; a fairly diverse group of hydrocarbons is covered in this range. Above 130 LN, where the hydrocarbons are primarily normal paraffins and below 40 LN, where they are aromatics, there are deviations from linearity. This is due to the fact that the luminometer differentiates among aromatics and normal paraffins, while the Indiana smoke point lamp does not.

Paraffins. The LN's of normal and branched paraffins are shown in Figure 2. The highest LN's are exhibited by normal paraffins, and they decrease with increasing number of carbons. The rate of decrease is about 16 LN's per carbon between *n*-hexane and *n*-decane, and about 5 LN's per carbon between *n*-decane and *n*-hexadecane. No reason has been established for this variation, but it apparently cannot be attributed to changing viscosity and its effect on capillarity, since studies carried out by others (*3*) show that varying the fuel reservoir temperature over a range of 165° F. has little or no effect on LN.

Figure 3 also shows that while LN's of branched paraffins appear to be fairly constant in the C_6 to C_9 range, they probably decrease as molecular weight increases above this level. Thus 5-methylundecane is 24 LN's lower than 4-methyloctane and 2,4,8-trimethylnonane is 15 LN's lower than 2,3,4-trimethylpentane. Data also show how increased branching decreases LN. Among dimethyl and trimethyl isomers, those which contain the 2,2-dimethyl grouping show the lowest LN's. This observation was also made by Hunt.

Data on normal paraffins show that the luminometer has a much greater range of utility than other available wick-type lamps, since it does not depend on maintaining tall, stable flames. And other workers (*13*) have demonstrated that the luminometer can be adapted for evaluating very clean burning C_2 to C_4 gaseous hydrocarbons either alone or in mixtures with gases or limited amounts of normally liquid or solid material. Apparently, only methane and ethane burn so cleanly that they cannot be evaluated in the luminometer.

Naphthenes. Figure 3 shows how the LN's of cyclohexanes are affected by changes in molecular structure. Addition of a methyl group decreases LN by about 30 numbers; but increasing the length of the side chain further has no effect on LN over the range studied. Increased branching of the molecule, either in the side chain or by adding methyl groups in the ring, reduces LN by about 10 to 20 numbers. The greastest reductions, however, are obtained when the molecule is given increased aromatic character. Thus, cyclohexene is 59 LN's lower than cyclohexane and the Decalins are 25 numbers lower than the highly branched *tert*-butylcyclohexane. As noted by Hunt, fused ring Decalins have the poorest combustion quality among the naphthenes. Indeed, Decalins are some 15 numbers lower than the higher molecular weight, unfused cyclohexylcyclohexane.

As shown in Table II, cyclopentanes are 10 to 14 LN's lower than comparable cyclohexanes. There is evidence that increasing the normal paraffin character of the molecule

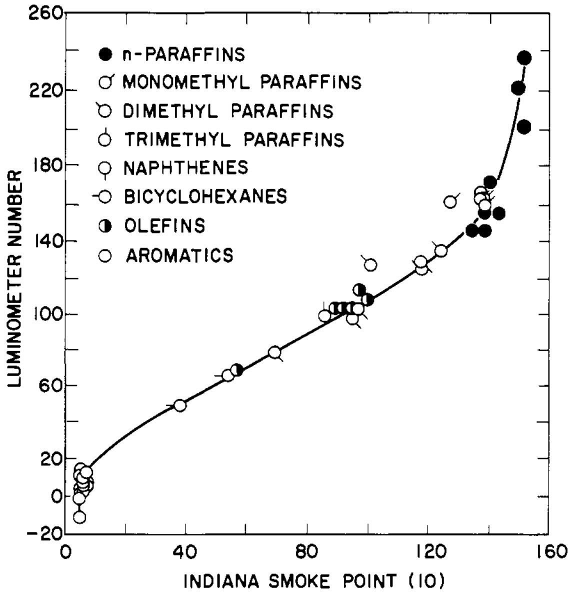

Figure 1. The CRC luminometer shows differences in combustion quality among both normal paraffins and aromatics not evident with a more conventional wick-type smoke lamp

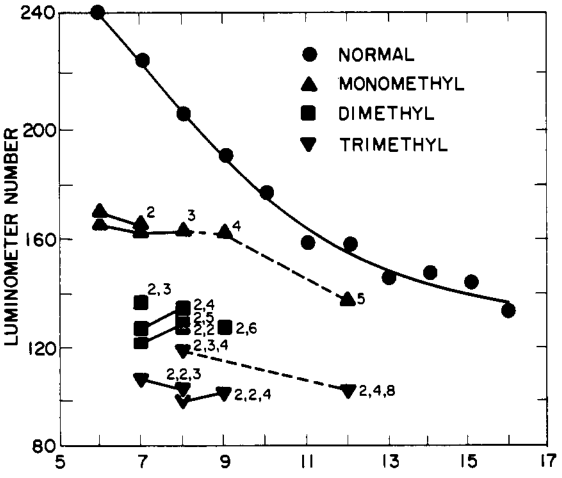

Figure 2. Among paraffins, LN decreases with increased branching and increased molecular weight

increases LN, since 2-cyclopentylheptane is 15 numbers higher than 2-cyclopentylbutane.

Olefins. As shown in Figure 4, the LN's of normal olefins are fairly constant across the molecular weight range studied. Branching and/or cyclizing decreases LN to a lesser extent than shown by paraffins and naphthenes.

Aromatics. Prior to the luminometer, all smoke point lamps showed pure aromatics to have about the same smoking tendency, although Hunt showed that significant differences exist which can be related to molecular structure when aromatics are evaluated as blends in a high smoke point base stock. The luminometer, however, is sufficiently sensitive to differentiate among unblended aromatics, as shown in Table II. And these data correlate fairly well with Hunt's blended smoke point data as shown in Figure 5.

Actually, an examination of Hunt's data (*10*) will show that the blended smoke points are more sensitive to changes in molecular structure of aromatics than are the LN's of the unblended aromatics. However, the luminometer yields the general trends. Thus, LN decreases from benzene to toluene and then tends to increase as the length of the normal paraffin side chain is increased. As with the other hydrocarbon types, increasing either the number of methyl groups on the ring or branching in the side chain, decreases LN. 1-Methylnapththalene, with a fused ring structure, gives the lowest LN of the compounds measured, −14.

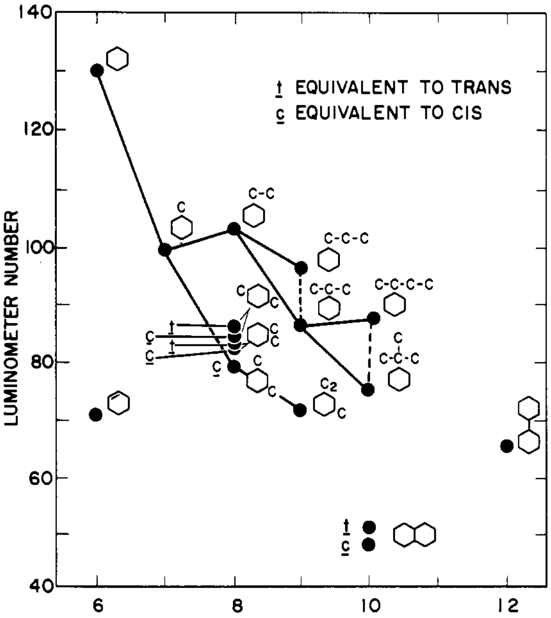

Figure 3. Among cyclohexanes, LN decreases with increased branching

A limited amount of LN data on blends of aromatics in kerosine-type turbo fuel were obtained to demonstrate that the relative ratings obtained in the luminometer are essentially correct. Thus, 1-methylnaphthalene, triethylbenzene, isopropylbenzene, and benzene have LN's of −14, 5, 9, and 11, respectively, when rated pure. They show the same order and relative smoking tendency when blended up to 5 volume % in a 50.3 LN base stock, as shown in Figure 6.

ACKNOWLEDGMENT

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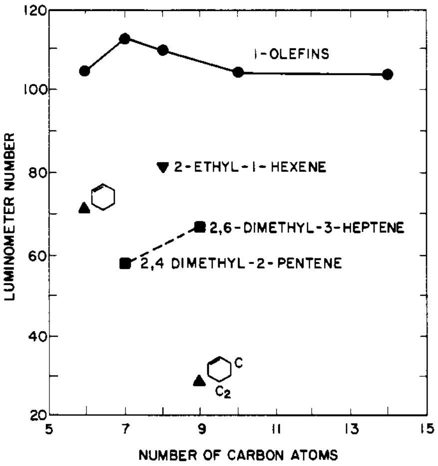

Figure 4. Among olefins, LN decreases with increased branching and/or cyclization

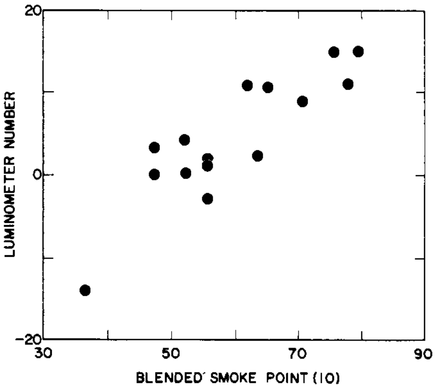

Figure 5. LN's of unblended aromatics show fair correlation with blended smoke points as obtained by Hunt (*10*)

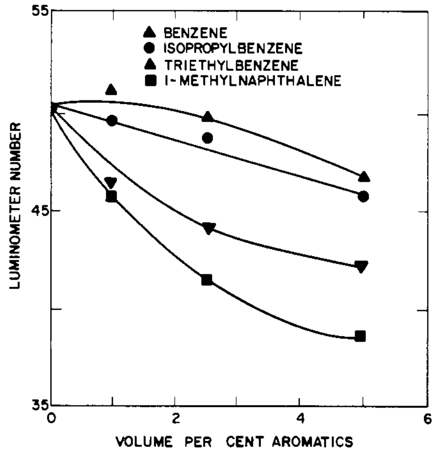

Figure 6. Blended aromatics show the same order and relative smoking tendency as unblended

Table II. Luminometer Numbers of Pure Paraffinic, Naphthenic, Olefinic, and Aromatic Hydrocarbons

Material	Luminometer No.	Refractive Index, n^{20}_D		Estd. Purity, Mole %
		Actual	Lit. (7)	
Paraffins				
n-Hexane	240	1.3750	1.3750	99+
n-Heptane	224	1.3880	1.3877	99+
n-Octane	205	1.3980	1.3976	99+
n-Nonane	190	1.4055	1.4056	99+
n-Decane	175	1.4124	1.4114	99+
n-Undecane	159	1.4174	1.4173	98+
n-Dodecane	158	1.4217	1.4216	98+
n-Tridecane	148	1.4256	1.4250^a	99.4
n-Tetradecane	148	1.4287	1.4289	96.9
n-Pentadecane	145	...	...	99.9+
n-Hexadecane	135	1.4347	1.4344	98.6
2-Methylpentane	169	1.3720	1.3715	99+
3-Methylpentane	165	1.3764	1.3766	99
2-Methylhexane	165	1.3849	1.3849	99.6
3-Methylhexane	162	1.3887	1.3887	98+
3-Methylheptane	163	1.3984	1.3985	98+
4-Methyloctane	162	1.4058	1.4061	98
5-Methylundecane	138	1.4219	...	98+
2,2-Dimethylpentane	122	1.3821	1.3822	99.3
2,3-Dimethylpentane	136	1.3916	1.3921	98
2,4-Dimethylpentane	127	...	...	99+
2,2-Dimethylhexane	128	1.3937	1.3931	98.6
2,4-Dimethylhexane	134	...	...	99+
2,5-Dimethylhexane	129	...	...	95
2,6-Dimethylheptane	127	1.4003	1.4008	98+
2,2,3-Trimethylbutane	108	...	...	99.8
2,2,3-Trimethylpentane	104	1.4029	1.4028	99.3
2,2,4-Trimethylpentane	100^a	1.3916	1.3914	99+
2,3,4-Trimethylpentane	120	1.4043	1.4043	99.4
2,2,4-Trimethylhexane	103	1.4033	1.4031	98+
2,4,8-Trimethylnonane	105	1.4180	...	98+
Naphthenes				
Ethylcyclopentane	91	1.4197	1.4196	97
n-Propylcyclopentane	87	1.4260	1.4266	98
Isopropylcyclopentane	74	1.4260	1.4260	99
2-Cyclopentylbutane	75	1.4360	1.4361	99
2-Cyclopentylheptane	90	1.4450	...	98
cis-*trans*-*cis*-1,2,4-Trimethylcyclopentane	62	1.4115	...	95
Cyclohexane	130	1.4258	1.4262	99.9+
Methylcyclohexane	100	1.4231	1.4230	99
Ethylcyclohexane	104	1.4331	1.4332	98
n-Propylcyclohexane	97	1.4370	1.4370	98
Isopropylcyclohexane	87	1.4409	1.4408	99.8
sec-Butylcyclohexane	89	1.4467	1.4485	99
tert-Butylcyclohexane	76	1.4469	1.4463	98+
Naphthenes				
trans-1,2-Dimethylcyclohexane	84	1.4271	1.4271	98
trans-1,4-Dimethylcyclohexane	87	...	...	99.6
cis-1,2-Dimethylcyclohexane	83	1.4360	1.4361	98
cis-1,3-Dimethylcyclohexane	80	1.4230	1.4310	98+
cis-1,4-Dimethylcyclohexane	85	...	1.4299	99.8
1,1,3-Trimethylcyclohexane	72	1.4293	1.4237^b	98
cis-Decalin	49	1.4810	1.4811	98+
trans-Decalin	52	1.4692	1.4697	98+
Cyclohexylcyclohexane	67	1.4800	1.4795	98
Olefins				
1-Hexene	105	1.3877	1.3880	98+
1-Heptene	113	1.3998	1.3991	98
1-Octene	110	1.4087	1.4090	98+
1-Decene	105	1.4214	1.4220	98+
1-Tetradecene	105	1.4363	1.4365	95+
2,4-Dimethyl-2-pentene	58	1.4036	1.403^c	98
2,6-Dimethyl-3-heptene	67	1.4120	1.4123	98
2-Ethyl-1-hexene	82	1.4157	1.4207	95–98
Cyclohexene	71	1.4467	1.4467	98
3,5,5-Trimethyl-1-cyclohexene	29	1.4383	1.4434	98+
Aromatics				
Benzene	11	...	...	99.9+
Toluene	3	...	...	99.6
Ethylbenzene	2	...	...	99.7
n-Propylbenzene	11	1.4918	1.4919	99
Isopropylbenzene	9	1.4910	1.4912	98+
n-Butylbenzene	15	...	...	99.8
sec-Butylbenzene	15	1.4900	1.4880^a	98
tert-Butylbenzene	11	1.4927	1.4905^a	99
1,2-Dimethylbenzene	0	...	...	99.5
1,3-Dimethylbenzene	1	...	...	99.4
1,4-Dimethylbenzene	−2	...	...	99.6
1,2,4-Trimethylbenzene	−5	...	...	99.3
1,3,5-Trimethylbenzene	−3	...	...	99.7
1,3-Diethylbenzene	4	1.4953	1.4955	99.4
1,4-Diethylbenzene	4	1.4947	1.4952	98
Mixed triethylbenzenes	5	1.5008	...	...
1,4-Diisopropylbenzene	10	1.4900	1.4912	98
Cyclohexylbenzene	6	1.5250	1.5254	95–98
Tetralin	0^d	1.5410	1.5438	...
1-Methylnaphthalene	−14	1.6156	1.6149^a	95+

^{a} At 25° C. ^{b} At 15° C. ^{c} At 19° C. ^{d} By definition.

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