Net Heat of Combustion and Other Properties of Kerosine and Related Fuels

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THE WORK described was undertaken to provide accurate information on fuels boiling in the kerosine range, including net heat of combustion, aniline point, API gravity, hydrogen, carbon, and sulfur content, and composition in terms of hydrocarbon types. Specifications were previously established as MIL-F-25576A (USAF) for Rocket Engine Fuels, grade RP-1, but few commercial products meet them. The results of the present work provide a basis for possible modification of the above specifications and also information of interest in connection with estimating net heat of combustion of a hydrocarbon fuel from more easily measured properties. Previous work (*4, 14, 15, 20*) has shown that for a given class of fuels, net heat of combustion can be reported to a fair degree of approximation by a linear function of any one of the following fuel properties: aniline point, API gravity, product of aniline point and API gravity, and per cent hydrogen.

In general, with a linear equation of the type described above, agreement between observed and calculated values of net heat of combustion is best when the product of aniline point and API gravity is taken as the independent variable. However, even with this variable the difference between observed and calculated values may be considerably greater than the experimental error of measurement, and in many cases the calculated value is not sufficiently accurate for some applications of the data. This type of linear equation has the further disadvantage that different values of the intercept and slope are found for different classes of hydrocarbon fuels. These findings, together with the fact that the equations are purely empirical in character, suggest that such equations are of doubtful value. If they are used, it should be recognized that the calculated values of heat of combustion are only estimates, and that each such equation applies only to a restricted class of fuels, and even for this restricted class may be in error by 0.5% or more for individual fuels.

Because of the generally unsatisfactory character of such empirical relations, recent data on aviation gasolines (*4*) were correlated also with the composition of these fuels in terms of hydrocarbon types. The resulting equation, giving net heat of combustion per unit weight as a function of percentages by weight of paraffins, olefins, aromatics, and naphthenes, is semirational in character and represents the data on aviation gasolines more accurately than any of the purely empirical linear equations of the type referred to above.

The data obtained in the present work, resulting from measurements on 110 petroleum distillates (kerosines), were correlated with the product of aniline point and API gravity and also with composition in terms of percentage by weight and by volume of paraffins, olefins, naphthenes, and aromatics. The heat of combustion of these fuels may be represented as a linear function (Equation 1) of the aniline-gravity product, with a standard deviation of 0.12% and a maximum deviation of 0.43%. For the fuels used in this correlation the values of ($A \times G$) range from 4414° to 8969° F. × API, the aniline points from 124° to 173° F., and the gravities from 36° to 55° API. Equations were also derived to represent the net heat of combustion as a function of the composition (both weight and volume per cent) in terms of hydrocarbon type (Equations 2 and 3). However, the standard deviations are considerably larger than calculated for Equation 1.

Data are also presented for alkylates boiling in the kerosine range (350° to 450° F.) and for several special fuels developed for Wright Air Development Center as possible alternates for RP-1 fuels. No correlations have been developed for these classes of fuels, since their chemical composition is different from the petroleum-distillate kerosines, and the number of samples is not large enough to be statistically significant.

FUELS INVESTIGATED

Samples for this investigation were requested by the Wright Air Development Center from 88 refineries, virtually all in the United States. A total of 250 samples was received from 80 refineries from April 1956 to December 1958: straight-run or blended petroleum-distillate kerosines, alkylates boiling in the kerosine range, and a few special formulations of interest to the Wright Air Development Center. Information as to the source of the crude indicated that the fuels were derived from crude oils from widely distributed oil-producing regions of the United States or from blends of such crudes. In some cases the blends included components from Venezuela and the Netherlands West Indies.

We believe that these samples are representative of the production of such fuels in the United States during the period mentioned. No claim can be made, however, that the fuels tested constitute a statistically representative sample of a well-defined population. There was, for example, no control over the selection of the samples. This was left to the individual suppliers. Further, there appeared at that time to be no very definite specifications for kerosines, so that the properties of such fuels varied over a relatively wide range. In other words, the population of such fuels was not well defined. The requests for samples contained a set of specifications for the fuels, but few of the samples submitted conformed to all of the specified requirements.

Of the 250 fuels received, measurements were made on 110 straight-run or blended kerosines, 13 alkylates, and 16 special fuels supplied by WADC. With three exceptions all of the first 114 were investigated. These included 107 petroleum-distillate kerosines and 4 alkylates. Later, for practical reasons, a selection had to be made. The remaining samples, aside from the special WADC fuels, were chosen to meet specifications for RP-1 fuel as nearly as possible with regard to low aromatic content and to provide a large range of API gravity.

The results obtained and the relations between heat of combustion and other properties derived from these results can be regarded as strictly applicable only to the particular group of samples investigated. Because of possible changes in refinery practices, these relations may not apply to kerosines produced after the samples investigated were procured.

EXPERIMENTAL MEASUREMENTS

Net Heat of Combustion. Heats of combustion of the 139 fuel samples were measured with a bomb calorimeter. The calorimeter and accessory apparatus used in the measurements, and the methods of making precise bomb-calorimetric measurements on liquid hydrocarbon fuels, have been described (*13, 16*). The fuel samples for combustion in the bomb were enclosed in thin-walled glass bulbs of the type used in previous measurements on volatile fuels (*4, 14, 15, 20*). The bulbs were filled by means of a hypodermic needle (No. 27) and syringe (*4, 13*).

The calorimeter was calibrated by burning benzoic acid (NBS standard sample 39g) in the bomb. In this calibration the value 26433.8 absolute joules per gram mass (weight in vacuum) (*11, 12, 21*) was taken as the heat of combustion of this sample of benzoic acid under the standard conditions of the bomb process. Calibration experiments were repeated from time to time during the work, especially after repairs to the calorimeter. In a typical series of 7 calibration experiments the standard deviation of the mean result was 0.012% of the energy equivalent of the calorimeter.

Heats of combustion of the fuels were measured in terms of absolute joules per gram weight of fuel in air against brass weights. They were converted to British thermal units per pound in air, using the factor 1 abs. joule per gram = 0.429917 B.t.u./lb.

Two or more acceptable measurements were made on each sample except number 45, on which only one measurement was made. Measurements were rejected if there was evidence of incomplete combustion, such as the odor of unburned gas or the presence of unburned carbon upon opening the bomb, or other evidence of experimental failure. In general the results of duplicate experiments agreed within 0.01 to 0.03%, with a maximum difference of 0.07%. An estimated standard deviation of ±3.5 B.t.u./lb. (0.02%) for a single experimental measurement was calculated from the differences between duplicate measurements for the various fuels.

The results were obtained as the gross heat of combustion at constant volume [Q_v(gross)], the heat liberated when unit weight of the fuel is burned in a constant-volume bomb, the products of combustion being gaseous carbon dioxide and liquid water. A few of the fuels contained appreciable amounts of sulfur, which formed aqueous sulfuric acid in the combustion reactions. The results for such fuels were reduced to the basis that the product of combustion of the sulfur was gaseous sulfur dioxide. The measurements were made at 28° C. and adjusted to 25° C. by Rothberg and Jessup's procedure (*20*). Net heat of combustion at constant pressure [Q_p(net)] was usually calculated from Q_v(gross) using the following equation given by Jessup and Cragoe (*15*):

$$Q_p(\text{net})\ (\text{B.t.u./lb.}) = Q_v(\text{gross}) - 91.23\ (\%\text{H})$$

where Q_p is the heat liberated when unit weight of fuel is burned at a constant pressure of 1 atm. to form gaseous carbon dioxide, gaseous water, and gaseous sulfur dioxide. the hydrogen contents of samples 12, 67, and 121 were not determined, and for these samples net heats of combustion were calculated by means of empirical equation expressing Q_p(net) as a function of Q_v(gross). The error involved in this procedure is probably less than 0.2%.

The mean observed values of Q_p(net) (B.t.u./lb.) at 25° C. are given in Table I, with values of other properties obtained in this investigation.

The density values at 25° C. (grams per milliliter) can be combined with values of heat of combustion (B.t.u./lb.) to obtain values of the heat of combustion at 25° C., in B.t.u./gallon (volume referred to 60° F.). The measured densities at 25° C. (77° F.) can be reduced to 60° F. by means of ASTM-IP data (*2*).

Aniline Points, API Gravity, and Composition. Aniline points of the fuel samples were measured by ASTM Method D 611-55T (*3*), API gravities by ASTM Method D 287-55 (*3*), and sulfur contents by ASTM Method D 90-55T (*3*).

The analyses of the kerosines into hydrocarbon types were carried out in two steps: First, the whole kerosine was analyzed for saturate, olefins, and aromatic by silica gel chromatography; and, second, the saturate portion was separated from the kerosine and the paraffin-naphthene ratio was determined from the hydrogen-carbon ratio.

The analytical method for the determination of saturate, olefin, and aromatic in kerosine is by silica gel chromatography as described by Criddle and Le Tourneau (*5*). This is also designated as ASTM Method D 1319-56T (*3*).

The saturate portion was separated from the whole kerosine by means of silica gel and small fractions were taken. The refractive index was determined on each fraction and the material having the constant, relatively low refractive index was considered as the saturate portion.

Paraffin and naphthene can be determined by several different methods based upon refractive index, density, and other related properties. However, because of the paucity of data on hydrocarbons, particularly the naphthenes, in the kerosine range, it was decided to use a modification of the method of Hindin and Grosse (*9*) which is based on the relative hydrogen-carbon ratio of the various fractions. The hydrogen-carbon ratio was determined by means of the beta-ray adsorption technique devised by Jacobs, Lewis, and Piehl (*10*).

To estimate the weight percentages of paraffin and naphthene in the saturate portion from the hydrogen-carbon ratio it is necessary to make certain assumptions regarding molecular weight of the hydrocarbon classes concerned. In addition, the conversion of volume percentage to weight percentage required additional assumptions regarding the average densities of these materials.

The principal study of the individual hydrocarbons and classes of hydrocarbons forming a representative kerosine has been made by the American Petroleum Institute Project 6 (*19*). The petroleum sample selected for that work is intermediate in properties when compared with petroleum produced by a wide variety of fields. While the amounts of the various hydrocarbon classes may differ considerably with different petroleums, it is thought that the amounts of individual hydrocarbons composing a given class would be sufficiently uniform for satisfactory calculation of average properties. This view has been supported recently by Martin and Winters (*18*).

The analysis of this kerosine fraction by hydrocarbon type is given in Table II. Other observations on this material are:

The normal paraffins are *n*-undecane and *n*-dodecane.

The isoparaffins are made up of undecanes, dodecanes, and tridecanes. A wide variety of individual isoparaffins are present. However, the less highly branched compounds predominate with only small amounts of the gem compounds present.

The alkylcyclopentanes and alkylcyclohexanes are varied. However, the tendency is toward a number of short side chains rather than one long side chain. This class of naphthenes consists of 11- and 12-carbon molecules.

The formation on the dicycloparaffins is sparse. These would include 10- and 11-carbon molecules.

The mononuclear aromatics consist of 10- and 11-carbon molecules. As with the monocyclic naphthenes, the tendency is toward several short side chains rather than one long side chain.

The dinuclear aromatics consist of 10- and 11-carbon molecules. This class of compounds includes not only naphthalenes but tetrahydronaphthalenes and indanes as well.

From the above information and compilations of physical properties of hydrocarbons by Doss (*6*), Egloff (*7*), and Francis (*8*) and the work of API Projects 6 and 44 (*1*) the average values for density, molecular weight, and hydrogen-carbon ratio for these classes of compounds were calculated (Table II).

Because of the rather wide differences in density between the monocyclic and dicyclic naphthenes, the density of the total naphthene fraction was calculated from the experimental density of the saturate portion and the paraffin-naphthene ratio.

Since the amount of olefin is very small in every case, the density of triisobutylene (*22*) was used as the density of the olefin fraction.

The volume percentages of paraffin, naphthene, olefin, and aromatic are obtained by combining the analyses of the whole kerosine by means of silica gel chromatography with the paraffin-naphthene ratio determined for the saturate portion. In turn the weight percentages may be determined by the usual methods, using the previously calculated densities. The volume and weight percentage of the different components are given in Table I.

The success of the calculations depends on the statistical homogeneity of the various hydrocarbon classes in the various kerosine-like fuels. This homogeneity can be assumed for the petroleum-distillate kerosines, but not for the alkylates or of commercially pure hydrocarbons. In this last case it was necessary to consider each compound individually, when analyzing for hydrocarbon type, making use of available inspection data.

For the petroleum-distillate kerosines, the picture is complicated by the appearance of dicyclics such as decahydronaphthalene in the naphthene portion and by naphthalenes, indanes, and tetrahydronaphthalenes in the aromatic portion. In some cases the presence of these dicyclics in the naphthene range would tend to shift the determined paraffin-naphthene ratio in favor of the naphthenes. The error involved is believed to be in no case larger than 10%, in most cases about 2 to 3%. An estimate of the precision of the calculated compositions of all fuels is given at the end of Table I.

For the petroleum-distillate kerosines, the aromatic and paraffin contents of the saturate portion are related to the geographical source of the crude as shown in Figure 1. This figure shows the saturate portion of the great majority of kerosines to be in the range of 30 to 50% paraffin. At the extremes, the Michigan kerosine is almost completely paraffinic, while the California kerosines cover a range extending to nearly 100% naphthene. The distribution with respect to aromatic content is probably less meaningful than might be supposed, because of the various dearomatizing procedures used, particularly by the West Coast refineries.

CORRELATION OF HEATS OF COMBUSTION WITH OTHER PROPERTIES

Experimental values of net heat of combustion of all fuels are shown plotted against aniline-gravity product ($A \times G$), aniline point, API gravity, and weight per cent hydrogen content in Figures 2 to 5.

The experimental data on net heats of combustion [Q_p(net)] of 110 petroleum-distillate fuels have been correlated with the aniline-gravity product ($A \times G$) by means of the empirical equation.

$$Q_p(\text{net}) = 17{,}909 + 0.10976\,(A \times G) \qquad (1)$$

This equation was derived by the method of least squares from the observed values of Q_p(net) and ($A \times G$) given in Table I. This equation is represented graphically by the line shown in Figure 2.

The standard deviation of an individual experimental value of Q_p(net) from Equation 1 was found to be 22 B.t.u/lb. and the maximum deviation was +80 B.t.u./lb. The estimate of standard deviation was found, as usual, as

$$\sigma = \left(\sum_{i=1}^{N} \Delta_i^2 / (N-2) \right)^{1/2}$$

where $\Delta = Q_p$(net) experimental $- Q_p$(net) calculated, and N is the total number of samples in the correlation. These deviations (Δ) are shown graphically in Figure 6. The value of the estimated standard deviation given above (σ = 22 B.t.u./lb.) is not far different from that found in previous studies (*4, 14, 15, 20*) of JP-4, JP-5, AN-F-58, and AN-F-28 fuels and of aviation gasoline. From the maximum and standard deviations it may be seen that the heat of combustion calculated from the aniline-gravity product is, at best, only a fair substitute for the experimentally determined value in the case of natural kerosine-like fuels. In particular, the magnitudes of the deviations found for fuels not included in the correlation may be large, and indicate that this equation should not be used for alkylates or other types of fuels which are fundamentally different in composition from the natural kerosine-like fuels.

(Continued on page 114)

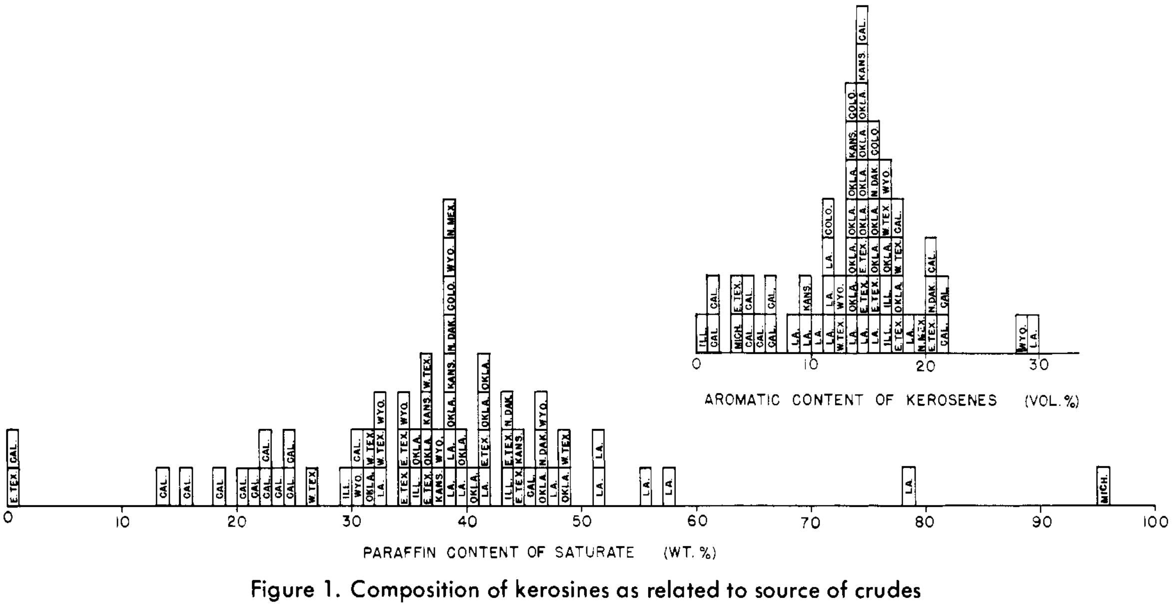


Figure 1. Composition of kerosines as related to source of crudes

States refer to source of crude

Table I. Physical Properties, Heat of Combustion,

NBS Sample No.	Aniline Point, A, ° F.	Gravity, G, ° API	$A \times G$, ° F. × ° API	Net Heat of Combustion, Q_p(Net), B.t.u./Lb.	Elemental Composition, Wt. %			Density at 25° C., G./Ml.
					Carbon	Hydrogen	Sulfur	
1	159.27	44.21	7,041	18,640	86.01	13.96	0.03	0.7972
2	145.27	43.81	6,364	18,611	86.08	13.88	0.04	0.7997
3	148.17	41.09	6,088	18,575	86.33	13.62	0.05	0.8125
4	152.67	40.57	6,194	18,574	86.26	13.70	0.04	0.8103
5	150.60	41.30	6,220	18,557	86.29	13.67	0.04	0.8116
6	150.42	43.82	6,591	18,639	85.90	13.98	0.12	0.7997
7	135.90	39.05	5,307	18,461	86.78	13.19	0.03	0.8225
8	136.47	39.36	5,371	18,441	85.77	13.27	0.96	0.8210
9	151.86	42.72	6,487	18,621	86.08	13.86	0.06	0.8048
10	157.62	43.17	6.804	18,639	85.95	14.01	0.04	0.8027
11	153.90	42.76	6,581	18,662	86.02	13.98	0.00	0.8046
12	162.00	43.46	7,041	18,700			0.00	0.8014
13	156.78	43.06	6,751	18,679	85.87	14.12	0.01	0.8032
14	163.44	43.90	7,175	18,720	85.70	14.30	0.00	0.7994
15	150.04	43.37	6,507	18,606	86.16	13.81	0.03	0.8018
16	150.19	44.54	6,689	18,646	86.18	13.78	0.04	0.7959
17	150.55	42.16	6,347	18,610	86.10	13.78	0.12	0.8044
18	156.56	43.80	6,857	18,679	85.80	14.17	0.03	0.7998
19	148.93	43.50	6,478	18,624	86.02	13.93	0.05	0.8012
20	150.40	43.03	6,472	18,605	86.13	13.82	0.05	0.8033
21	148.93	42.53	6,334	18,589	86.24	13.69	0.07	0.8057
22	146.66	42.55	6,240	18,590	86.14	13.76	0.10	0.8056
23	145.76	45.43	6,622	18,614	85.91	14.04	0.04	0.7923
24	153.26	45.28	6,940	18,658	85.90	14.06	0.04	0.7933
25	150.62	42.19	6,355	18,609	86.12	13.79	0.09	0.8073
26	152.42	44.22	6,740	18,627	86.00	13.94	0.06	0.7978
27	153.01	45.74	6,999	18,662	85.79	14.14	0.07	0.7909
28	157.53	45.47	7,163	18,711	85.58	14.30	0.12	0.7921
29	165.63	47.05	7,793	18,781	85.38	14.61	0.01	0.7850
30	164.19	44.53	7,311	18,724	85.61	14.38	0.01	0.7964
31	151.70	55.09	8,357	18,783	84.94	14.89	0.17	0.7502
32	144.91	45.29	6,563	18,635	85.91	14.01	0.08	0.7929
33	150.69	43.22	6,513	18,635	86.09	13.85	0.06	0.8025
34	149.52	43.70	6,534	18,625	86.03	13.93	0.04	0.8003
35	148.62	41.98	6,239	18,588	86.23	13,74	0.03	0.8084
36	152.67	43.80	6,687	18,655	85.96	13.98	0.06	0.7998
37	142.45	42.30	6,026	18,578	86.29	13.69	0.02	0.8068
38	151.32	43.00	6,507	18,624	86.05	13.89	0.06	0.8035
39	147.18	41.30	6,079	18,575	86.28	13.63	0.09	0.8116
40	156.00	43.55	6,794	18,663	85.87	14.06	0.07	0.8009
41	148.98	44.12	6,573	18,655	85.96	13.99	0.05	0.7982
42	166.93	45.90	7,662	18,782	85.73	14.26	0.01	0.7901
43	141.96	41.70	5,920	18,546	86.40	13.55	0.05	0.8097
44	135.48	43.23	5,857	18,550	86.31	13.61	0.08	0.8024
45	133.88	38.27	5,124	18,479	86.74	13.16	0.10	0.8262
46	124.34	47.32	5,884	18,623	86.49	13.44	0.07	0.7841
47	128.66	40.10	5,159	18,465	86.80	13.07	0.13	0.8174
48	157.84	42.70	6,740	18,670	85.97	14.03	0.00	0.8049
49	147.90	41.80	6,182	18,566	86.35	13.60	0.05	0.8092
51	145.74	43.42	6,328	18,608	86.13	13.81	0.06	0.8016
52	149.10	43.54	6,494	18,624	86.19	13.73	0.08	0.8010
53	160.00	43.76	7,002	18,691	85.76	14.24	0.00	0.8000
54	149.16	43.50	6,488	18,618	86.05	13.84	0.11	0.8015
55	146.22	41.65	6,090	18,580	86.28	13.65	0.07	0.8098
56	127.06	37.82	4,805	18,445	86.91	13.07	0.02	0.8285
57	148.20	43.75	6.484	18.628	85.97	13.91	0.12	0.8000
58	144.61	41.32	5,975	18,563	86.37	13.59	0.04	0.8115
59	145.15	43.75	6,350	18,619	86.15	13.84	0.01	0.8000
60	144.43	41.35	5,972	18,500	86.24	13.73	0.03	0.8113
61	144.52	42.57	6,152	18,582	86.21	13.75	0.04	0.8055
62	129.40	35.70	4,620	18,410	86.71	12.95	0.34	0.8392
63	136.60	38.79	5,299	18,472	86.64	13.26	0.10	0.8237
64	145.54	43.19	6,286	18,606	86.07	13.84	0.09	0.8026
65	151.39	39.90	6,040	18,523	86.14	13.40	0.46	0.8184
66	161.65	49.59	8,016	18,766	85.45	14.53	0.02	0.7736
67	160.39	51.44	8,250	18,808			0.01	0.7656
68	141.35	41.17	5,819	18,561	86.27	13.61	0.12	0.8121
69	125.69	36.97	4,647	18,388	86.67	13.06	0.27	0.8327
70	145.85	43.78	6,385	18,621	86.23	13.64	0.13	0.7999
71	139.37	41.41	5,771	18,548	86.42	13.53	0.05	0.8111
72	189.88	51.87	9,849	18,915	84.84	15.15	0.01	0.7638
73	174.76	51.32	8,969	18,884	85.05	14.94	0.01	0.7662
74	142.72	43.10	6,151	18,621	86.20	13.79	0.01	0.8030
75	145.00	43.10	6,250	18,603	86.15	13.77	0.08	0.8030
76	149.86	42.65	6,392	18,584	87.07	12.89	0.04	0.8051

and Analyses of Fuels Investigated

Hydrocarbon Type Composition										
Per Cent by Volume					Per Cent by Weight					Type of Fuel
Aromatic	Olefin	Saturate	Paraffin	Naphthene	Aromatic	Olefin	Saturate	Paraffin	Naphthene	
12.5	1.0	86.5	44.1	42.4	13.9	1.0	85.1	41.4	43.7	K
16.3	1.0	82.7	38.2	44.5	17.9	1.0	81.1	35.8	45.3	K
15.9	1.0	83.1	26.2	56.9	17.3	0.9	81.8	24.2	57.6	K
15.6	1.1	83.3	28.1	55.2	17.0	1.0	82.0	25.9	56.1	K
15.7	0.7	83.6	29.3	54.3	17.1	0.7	82.2	27.1	55.1	K
13.7	1.0	85.3	29.3	56.0	15.0	0.9	84.1	27.2	56.9	K
21.8	0.9	77.3	19.9	57.4	23.6	0.8	75.6	18.3	57.3	K
23.9	0.9	75.2	24.4	50.8	25.8	0.8	73.4	22.5	50.9	K
14.1	1.1	84.8	32.7	52.1	15.5	1.0	83.5	30.5	53.0	K
11.6	1.1	87.3	33.1	54.2	12.8	1.0	86.2	30.9	55.3	K
6.7	0.9	92.4	18.8	73.6	7.3	0.8	91.9	17.5	74.4	K
2.5	1.2	96.3	21.9	74.4	2.7	1.1	96.2	20.5	75.7	K
5.4	0.7	93.9	22.3	71.6	5.9	0.7	93.4	20.7	72.7	K
1.2	0.7	98.1	24.4	73.7	1.3	0.7	98.0	22.8	75.2	K
14.8	0.7	84.5	41.3	43.2	16.3	0.7	83.0	38.8	44.2	K
13.6	1.0	85.4	35.3	50.1	15.0	1.0	84.0	33.0	51.0	K
14.2	1.3	84.5	33.0	51.5	15.6	1.2	83.2	30.7	52.5	K
5.1	0.8	94.1	24.8	69.3	5.6	0.8	93.6	23.2	70.4	K
12.8	1.0	86.2	37.8	48.4	14.1	1.0	84.9	35.4	49.5	K
14.8	0.9	84.3	37.6	46.7	16.3	0.9	82.8	35.1	47.7	K
15.2	0.8	84.0	34.8	49.2	16.7	0.8	82.5	32.4	50.1	K
15.3	1.0	83.7	34.0	49.7	16.8	0.9	82.3	31.7	50.6	K
15.6	1.1	83.3	49.7	33.6	17.4	1.1	81.5	47.0	34.5	K
12.2	1.0	86.8	46.4	40.4	13.6	1.0	85.4	43.8	41.6	K
12.5	0.8	86.7	32.6	54.1	13.6	0.8	85.6	30.0	55.6	K
12.6	0.7	86.7	47.7	39.0	13.9	0.7	85.4	44.6	40.8	K
12.4	0.9	86.7	50.6	36.1	13.7	0.9	85.4	47.6	37.8	K
7.3	0.9	91.8	45.8	46.0	8.1	0.9	91.0	43.3	47.7	K
0.9	0.5	98.6	43.8	54.8	1.0	0.5	98.5	41.7	56.8	K
2.2	1.1	96.7	29.1	67.6	2.4	1.0	96.6	27.3	69.3	K
3.9	0.9	95.2	91.4	3.8	4.6	0.9	94.5	90.4	4.1	K
13.1	1.0	85.9	41.8	44.1	14.5	1.0	84.5	39.5	45.0	K
14.1	0.9	85.0	34.9	50.1	15.5	0.9	83.6	32.5	51.1	K
13.5	1.1	85.4	39.3	46.1	14.9	1.0	84.1	36.9	47.2	K
13.0	1.3	85.7	32.1	53.6	14.3	1.2	84.5	29.9	54.6	K
10.5	0.7	88.8	42.2	46.6	11.6	0.7	87.7	39.5	48.2	K
13.8	0.7	85.5	36.3	49.2	15.0	0.6	84.4	33.5	50.9	K
12.8	1.1	86.1	36.6	49.5	14.1	1.0	84.9	32.6	52.3	K
16.1	0.7	83.2	25.7	57.5	17.6	0.7	81.7	23.8	57.9	K
9.6	0.8	89.6	32.6	57.0	10.6	0.8	88.6	30.5	58.1	K
12.5	1.2	86.3	37.8	48.5	13.8	1.1	85.1	35.5	49.6	K
1.6	0.9	97.5	35.6	61.9	1.8	0.9	97.3	33.6	63.7	K
16.8	0.9	82.3	36.5	45.8	18.5	0.8	80.7	34.1	46.6	K
19.9	0.5	79.6	41.6	38.0	21.9	0.5	77.6	39.0	38.6	K
21.6	0.5	77.9	13.3	64.6	23.2	0.5	76.3	12.1	64.2	K
13.7	0.7	85.6	27.4	58.2	15.2	0.7	84.1	25.7	58.4	K
20.7	0.8	78.5	19.7	58.8	22.4	0.8	76.8	18.1	58.7	K
6.0	0.7	93.3	13.8	79.5	6.6	0.7	92.7	12.8	79.9	K
16.5	0.7	82.8	38.7	44.1	18.1	0.7	81.2	36.1	45.1	K
15.0	1.1	83.9	40.9	43.0	16.6	1.0	82.4	38.3	44.1	K
16.1	1.6	82.3	41.3	41.0	17.8	1.5	80.7	38.7	42.0	K
4.1	0.9	95.0	22.8	72.2	4.5	0.9	94.6	21.3	73.3	K
16.1	2.1	81.8	39.3	42.5	17.8	2.0	80.2	36.7	43.5	K
15.3	1.1	83.6	32.5	51.1	16.7	1.0	82.3	30.2	52.1	K
21.2	0.8	78.0	0	78.0	22.6	0.7	76.7	0	76.7	K
14.3	1.0	84.7	39.6	45.1	15.8	1.0	83.2	37.2	46.0	K
16.2	0.7	83.1	29.0	54.1	17.7	0.7	81.6	26.8	54.8	K
15.1	0.7	84.2	38.2	46.0	16.7	0.7	82.6	35.8	46.8	K
19.1	1.0	79.9	33.2	46.7	20.9	0.9	78.2	30.8	47.4	K
13.9	0.9	85.2	31.4	53.8	14.7	0.9	84.4	29.4	55.0	K
22.2	0.7	77.1	0	77.1	23.5	0.6	75.9	0	75.9	K
19.0	0.5	80.5	14.0	66.5	20.5	0.5	79.0	12.8	66.2	K
16.4	1.0	82.6	35.7	46.9	18.0	1.0	81.0	33.3	47.7	K
20.5	1.1	78.4	32.5	45.9	22.3	1.0	76.7	30.0	46.7	K
9.3	0.8	89.9	71.8	18.1	10.6	0.8	88.6	69.5	19.1	K
										K
16.8	0.9	82.3	32.1	50.2	18.4	0.8	80.8	29.9	50.9	K
20.7	0.9	78.4	0	78.4	22.0	0.8	77.2	0	77.2	K
18.9	0.7	80.4	45.7	34.7	20.8	0.7	78.5	42.8	35.7	K
20.2	1.2	78.6	32.1	46.5	22.0	1.1	76.9	29.8	47.1	K
1.0	1.7	97.3	81.5	15.8	1.2	1.7	97.1	79.6	17.5	A
1.4	1.4	97.2	74.6	22.6	1.6	1.4	97.0	72.7	24.3	A
14.2	0.7	85.1	32.0	53.1	15.6	0.7	83.7	29.8	53.9	K
15.5	1.2	83.3	37.7	45.6	17.1	1.1	81.8	35.3	46.5	K
24.8	1.0	74.2	30.5	43.7	27.0	0.8	72.2	28.2	44.0	K

(*Continued*)

Table I. Physical Properties, Heat of Combustion,

NBS Sample No.	Aniline Point, A, ° F.	Gravity, G, ° API	$A \times G$, ° F. × ° API	Net Heat of Combustion, Q_p(Net), B.t.u./Lb.	Elemental Composition, Wt. %			Density at 25° C., G./Ml.
					Carbon	Hydrogen	Sulfur	
77	145.72	45.20	6,587	18,620	86.03	13.87	0.10	0.7933
78	147.97	43.83	6,486	18,617	86.07	13,89	0.04	0.7997
79	153.09	45.70	6,996	18,696	85.79	14.20	0.01	0.7911
80	147.51	45.02	6,641	18,658	85.96	14.04	0.00	0.7941
81	146.61	43.62	6,395	18,610	86.07	13.73	0.20	0.8006
82	149.85	44.90	6,728	18,647	85.92	14.02	0.06	0.7947
83	148.84	44.31	6,595	18,660	85.90	14.04	0.06	0.7974
84	148.66	42.96	6,386	18,593	86.07	13.81	0.12	0.8085
85	148.93	42.64	6,350	18,604	86.08	13.82	0.10	0.8100
86	149.13	42.64	6,359	18,609	85.98	13.83	0.19	0.8052
87	129.33	41.82	5,409	18,486	86.56	13.39	0.05	0.8091
88	146.05	43.03	6,285	18,590	86.13	13.82	0.05	0.8033
89	151.65	43.25	6,559	18,621	86.00	13.87	0.13	0.8023
90	144.61	41.36	5,981	18,581	86.25	13.70	0.05	0.8113
91	163.69	44.20	7,235	18,725	85.65	14.34	0.01	0.7979
92	139.77	47.40	6,625	18,640	85.85	14.01	0.14	0.7834
93	146.43	45.90	6,721	18,638	85.86	13.96	0.18	0.7906
94	146.77	46.83	6,873	18,686	85.92	13.85	0.23	0.7863
95	140.47	48.05	6,750	18,668	85.68	14.11	0.21	0.7804
96	119.07	39.97	4,759	18,511	86.57	13.40	0.03	0.8180
97	158.16	45.38	7,177	18,703	85.59	14.29	0.12	0.7929
98	138.09	42.53	5,873	18,547	86.12	13.60	0.28	0.8056
99	152.58	43.21	6,593	18,619	86.04	13.92	0.04	0.8026
100	154.38	50.55	7,804	18,795	85.2[a]	14.8	0.01	0.7695
101	173.46	50.62	8,781	18,861	84.7	14.9	0.08	0.7692
102	158.95	44.68	7,102	18,716	85.9	14.3	0.05	0.7957
103	135.67	40.03	5,431	18,477	86.0	13.5	0.34	0.8180
105	146.07	42.06	6,144	18,566	85.9	13.8	0.05	0.8080
106	152.36	44.88	6,838	18,652	86.0	14.1	0.02	0.7948
107	157.77	46.40	7,321	18,685	85.4	14.4	0.04	0.7878
108	149.34	43.37	6,477	18,618	86.1	13.9	0.04	0.8018
109	131.70	39.94	5,260	18,484	86.0	13.4	0.12	0.8163
111	116.76	37.80	4,414	18,370	87.0	13.0	0.13	0.8242
112	158.94	42.09	6,690	18,666	85.8	13.9	0.02	0.8078
113	159.84	44.18	7,062	18,709	85.8	14.2	0.02	0.7981
114	159.47	44.20	7,049	18,732	85.9	14.2	0.02	0.7980
121	155.32	44.71	6,944	18,674	85.80	14.11	0.09	0.7956
122	148.12	43.62	6,461	18,600	85.85	14.01	0.14	0.8006
124	157.66	43.14	6,801	18,691	85.72	14.27	0.01	0.8028
129	197.56	48.95	9,670	18,897	85.34	14.65	0.01	0.7765
135	175.89	51.45	9,050	18,896	85.12	14.87	0.01	0.7656
178	186.71	51.56	9,627	18,908	85.06	14.93	0.01	0.7652
181	201.20	44.78	9,010	18,781	85.2	14.7	0.03	0.7952
185	184.55	54.95	10,141	18,954	84.64	15.35	0.01	0.7508
186	198.28	45.25	8,972	18,780	84.88	15.13	0.03	0.7931
187	197.56	47.07	9,299	18,822	85.2	14.9	0.03	0.7848
193	184.2	54.9	10,113	18,946	84.64	15.35	0.01	0.7510
197	186.3	54.7	10,191	18,952	84.80	15.19	0.01	0.7519
142	90.81	27.50	2,497	18,300	87.10	12.90	0.00	0.8831
145	155.89	41.67	6,496	18,586	86.07	13.93	0.00	0.8098
146	−1.61	27.78	−45	17,902	89.67	10.29	0.04	0.8814
147	161.89	33.30	5,391	18,586	87.16	12.82	0.02	0.8516
149	105.17	17.55	1,846	18,158	87.1	12.8	0.01	0.9428
151	115.61	17.45	2,017	18,184	87.8	12.5	0.01	0.9431
152	105.31	26.90	2,833	18,318	87.6	12.5	0.00	0.8863
154	156.65	41.45	6,493	18,641	86.49	13.50	0.01	0.8109
155	92.43	27.50	2,542	18,300	86.86	13.13	0.01	0.8830
158	171.35	40.07	6,865	18,690	86.28	13.71	0.01	0.8175
160	F	11.77		17,212	91.56	8.23	0.21	0.9807
161	<−24	14.20		17,433	90.9	9.3	0.01	0.9642
162	113.90	27.43	3,124	18,396	86.86	13.13	0.01	0.8834
167	108.21	26.90	2,911	18,280	87.0	13.1	0.01	0.8863
168	107.31	27.42	2,942	18,311	87.5	12.7	0.01	0.8834
169	147.73	29.00	4,284	18,464	86.23	13.76	0.01	0.8746

[a] Percentages of carbon and hydrogen on samples 100–114, 149, 151, 152, 161, 167, and 168 were determined by combustion analysis by R.A. Paulson, Analytical Chemistry Section.

F, freezes at −0.04° F.

K, petroleum distillate kerosine. A, alkylate. WADC, special materials and technically pure hydrocarbons submitted by Wright Air Development Center, Dayton, Ohio. NBS No. 142 and 155 are mixed Decalins, NBS No. 160 is technical grade Tetralin, and NBS No. 169 is monoisopropylbicyclohexyl. Remainder are highly naphthenic kerosine cuts from which the aromatic has been removed.

Estimated precision of hydrocarbon-type analysis. The precision of values given by the silica gel method is (2): aromatic ±2.0 vol. %, and Analyses of Fuels Investigated *(Continued)*

Hydrocarbon Type Composition										
Per Cent by Volume					Per Cent by Weight					Type of Fuel
Aromatic	Olefin	Saturate	Paraffin	Naphthene	Aromatic	Olefin	Saturate	Paraffin	Naphthene	
18.4	0.9	80.7	53.9	26.8	20.5	0.9	78.6	50.9	27.7	K
15.4	0.7	83.9	41.9	42.0	17.0	0.7	82.3	39.3	43.0	K
8.6	0.9	90.5	42.4	48.1	9.6	0.9	89.5	40.0	49.5	A
12.1	1.1	86.8	41.1	45.7	13.4	1.0	85.6	38.8	46.8	A
12.0	0.5	87.5	36.1	51.4	13.2	0.5	86.3	33.8	52.5	K
13.3	0.9	85.8	44.4	41.4	14.8	0.9	84.3	41.9	42.4	K
10.4	0.9	88.7	34.9	53.8	11.5	0.9	87.6	32.9	54.7	K
14.8	1.2	84.0	35.1	48.9	16.3	1.1	82.6	32.8	49.8	K
14.6	1.0	84.4	35.0	49.4	16.1	1.0	82.9	32.7	50.2	K
14.9	0.8	84.3	36.9	47.4	16.4	0.8	82.8	34.4	48.4	K
20.6	1.0	78.4	32.1	46.3	22.6	0.9	76.5	29.8	46.7	K
14.0	1.0	85.0	35.9	49.1	15.4	1.0	83.6	33.5	50.1	K
12.8	1.4	85.8	36.6	49.2	14.1	1.3	84.6	34.3	50.3	K
14.3	0.7	85.0	32.4	52.6	15.7	0.7	83.6	30.2	53.4	K
2.1	1.0	96.9	27.7	69.2	2.3	1.0	96.7	26.0	70.7	K
17.6	0.7	81.7	65.5	16.2	19.8	0.7	79.5	62.5	17.0	K
16.8	0.9	82.3	56.5	25.8	18.8	0.9	80.3	53.7	26.6	K
15.9	1.1	83.0	58.8	24.2	17.9	1.1	81.0	56.1	24.9	K
15.9	0.7	83.4	62.6	20.8	18.0	0.7	81.3	60.0	21.3	K
11.6	0.8	87.6	0	87.6	12.5	0.7	86.8	0	86.8	K
7.8	1.2	91.0	44.1	46.9	8.8	1.1	90.1	41.6	48.5	K
17.2	0.9	81.9	33.2	48.7	18.9	0.8	80.3	30.9	49.4	K
12.0	1.0	87.0	38.2	48.8	13.2	1.0	85.8	35.8	50.0	K
3.1	1.1	95.8	61.0	34.8	3.5	1.1	95.4	59.1	36.3	K
1.8	1.1	97.1	70.8	26.3	2.1	1.1	96.8	68.7	28.1	K
6.2	0.9	92.9	33.8	59.1	6.9	0.9	92.2	31.7	60.5	K
17.4	0.9	81.7	22.1	59.6	18.9	0.8	80.3	20.4	59.9	K
14.7	0.7	84.6	30.6	54.0	16.1	0.7	83.2	28.5	54.7	K
10.5	0.7	88.8	45.9	42.9	11.7	0.7	87.6	43.4	44.2	K
9.6	0.8	89.6	54.7	34.9	10.8	0.8	88.4	52.1	36.3	K
13.7	0.8	85.5	36.6	48.9	15.1	0.8	84.1	34.2	49.9	K
17.7	0.9	81.4	17.8	63.6	19.2	0.8	80.0	16.4	63.6	K
26.4	1.1	72.5	14.9	57.6	28.3	1.0	70.7	13.6	57.1	K
7.7	0.8	91.5	2.0	89.5	8.4	0.8	90.8	1.8	89.0	K
3.6	0.6	95.8	17.9	77.9	4.0	0.6	95.4	16.7	78.7	K
3.2	0.7	96.1	20.6	75.5	3.5	0.7	95.8	19.3	76.5	K
12.2	1.2	86.6	26.8	59.8	13.5	1.1	85.4	26.1	59.3	K
14.6	1.4	84.0	19.7	64.3	16.1	1.4	82.5	19.1	63.4	K
2.4	1.2	96.4	0	96.4	2.6	1.1	96.3	0	96.3	K
0	7.1	92.9	66.6	26.3	0	7.2	92.8	67.4	25.4	K
0	4.9	95.1	43.4	51.7	0	4.8	95.2	43.3	51.9	A
6.4	8.2	85.4	61.3	24.1	6.5	7.1	86.4	61.4	25.0	A
18.8	23.9	57.3	0	57.3	21.0	23.4	55.6	0	55.6	A
0	3.5	96.5	91.4	5.1	0	3.5	96.5	91.2	5.3	A
0	0	100.0	31.0	69.0	0	0	100.0	31.6	68.4	A
										A
0	3.3	96.7	96.7	0	0	3.3	96.7	96.7	0	A
0	3.9	96.1	95.7	0.4	0	4.1	95.9	95.5	0.4	A
3.3	1.0	95.7	0	95.7	4.0	1.0	95.0	0	95.0	WADC
14.2	1.1	84.7	20.7	64.0	15.6	1.0	83.4	20.0	63.4	WADC
80.4	1.0	18.6			82.0	0.9	17.1			WADC
3.5	5.2	91.3	0	91.3	3.6	4.7	91.7	0	91.7	WADC
0	0	100.0	0	100.0	0	0	100.0	0	100.0	WADC
0	3.9	96.1	0	96.1	0	3.8	96.2	0	96.2	WADC
4.1	0.8	95.1	0	95.1	4.1	0.7	95.2	0	95.2	WADC
12.2	0.9	86.9	0	86.9	13.6	0.9	85.5	0	85.5	WADC
0	1.0	99.0	0	99.0	0	1.0	99.0	0	99.0	WADC
4.0	5.1	90.9	0	90.9	4.3	4.7	91.0	0	91.0	WADC
99.3	0.7	0	0	0	99.4	0.6	0	0	0	WADC
99.0	1.0	0	0	0	99.1	0.9	0	0	0	WADC
3.7	0.5	95.8	0	95.8	4.4	0.6	95.0	0	95.0	WADC
3.2	1.3	95.5	0	95.5	3.2	1.1	95.7	0	95.7	WADC
3.5	0.9	95.6	0	95.6	3.5	0.8	95.7	0	95.7	WADC
0	2.8	97.2	0	97.2	0	2.8	97.2	0	97.2	WADC

olefin ±2.0 vol. %, and saturate ±1.5 vol. %. The H/C ratio is precise to ±0.2 %; hence the paraffin-naphthene ratio calculated from this value should be within ±2%. Because of uncertainties in the nature of the naphthene portion caused by the presence of dicyclics, it is probable that the paraffin-naphthene ratio is more accurate for highly paraffinic fuels than highly naphthenic fuels. From the composition of the saturate portion, the total paraffin and naphthene content of the kerosines should be within ±3%. The weight percentages should be of the same precision as the volume percentages.

Repeatability of ASTM methods by a single operator. API gravity (D287) ±0.2° API; aniline point (D611) ±0.3° F.; and sulfur (D90) ±0.001% (0.002 to 0.25 wt. %) and 0.5% of mean (greater than 25%).

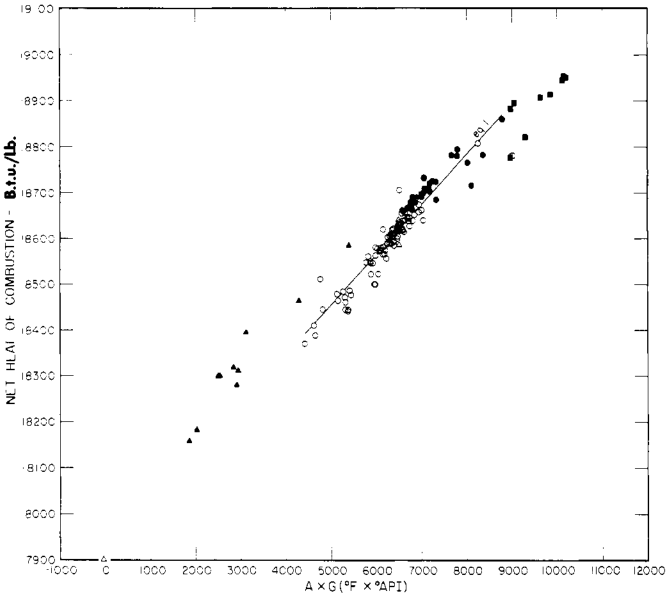


Figure 2. Net heat of combustion vs. aniline-gravity product of fuels

O Petroleum-distillate kerosine fuels
□ Alkylate fuels
△ Special WADC fuels
▲ ■ ● Fuels containing not more than 10% aromatics
—— Equation 1

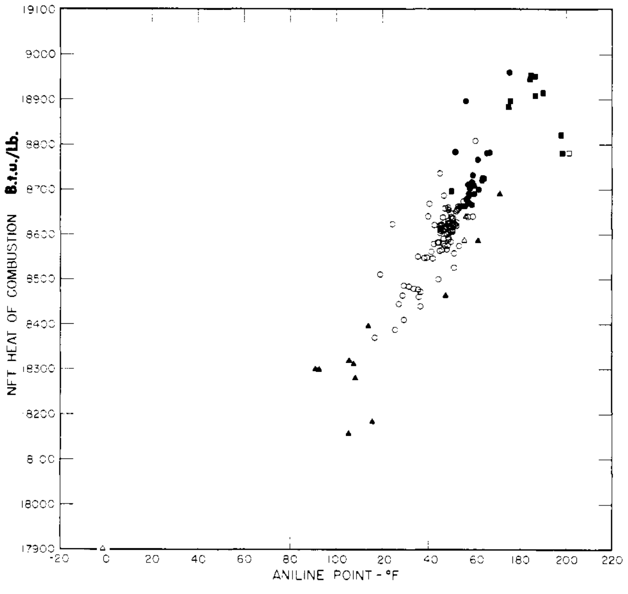
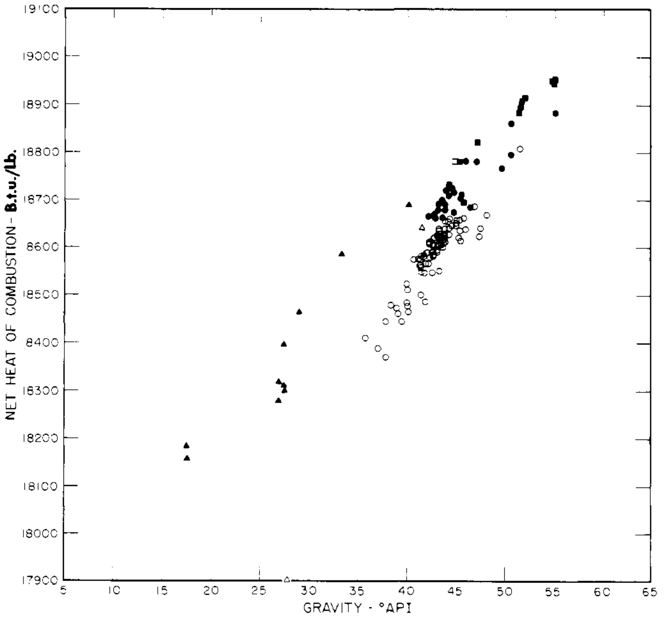


Figure 3. Net heat of combustion vs. aniline point of fuels
Symbols same as in Figure 2



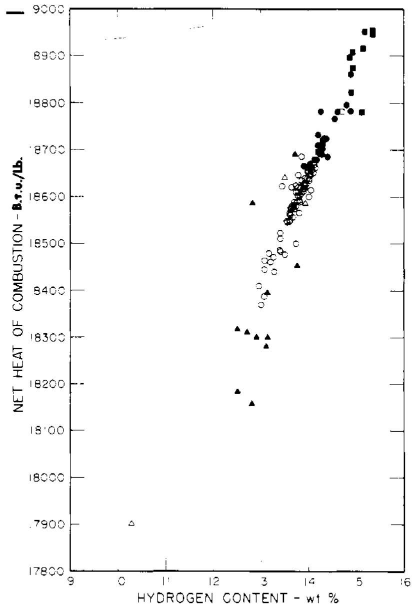


Figure 5. Net heat of combustion vs. hydrogen content (weight per cent)
Symbols same as in Figure 2

←
Figure 4. Net heat of combustion vs. API gravity of fuels
Symbols same as in Figure 2

Upon application of the specification for Type A Aviation Turbine Fuel [ASTM Method D 1665-59T (*3*)] to all samples measured, it was noted that neither the alkylates nor special fuels conformed. About 70% of the natural kerosine-like fuels conformed to this specification in all facets in which data were available.

The net heat of combustion calculated from three of the samples—NBS 31, 46, and 96—showed much greater deviations than the remainder of the kerosines. However, there was nothing in the manufacturer's data to indicate that these samples were different from the others.

The heats of combustion calculated for kerosines of low aromatic content tend to show a positive deviation, while kerosines of high aromatic content tend toward a negative deviation. While mixtures of pure paraffins and naphthenes in the kerosine range do not deviate greatly from ideal solutions, there are considerable deviations from ideality in the cases of both paraffins and aromatics, and naphthenes and aromatics (*17*). It is conceivable that these nonidealities, alone or when superimposed upon another component (aniline), would yield data which show a systematic trend of deviation as the aromatic content increases. The idea of adding a third term to the aniline-gravity equation to account for these deviations was rejected because there is no assurance that it would be generally applicable. Such a term would tend to lead to a false sense of security in the use of the equation.

Since the attempt to correlate the net heat of combustion with the analysis by hydrocarbon type was successful with the aviation gasolines (*4*), this method was also used with

Table II. Amounts and Properties of Hydrocarbon Types Occurring in the Kerosine Fraction

(B. p. 350° to 450° F.)

Hydrocarbon Type	Vol. % in Kerosine Fraction (*19*)	Density at 25° C., G./Ml.	Av. Mol. Wt.	H/C (by Weight)
Normal paraffins	23	0.7404	162.59	0.18252
Isoparaffins	15	0.7505	168.33	0.18202
Monocycloparaffins	33	...	161.30	0.16786
Dicycloparaffins	11	...	145.26	0.15188
Mononuclear aromatics	16	0.8603	...	...
Dinuclear aromatics	2	0.9913	...	...
Total paraffin	38	0.7443	164.83	0.18232
Total naphthene	44	[a]	157.29	0.16413
Total aromatic	18	0.8790	...	...
Total olefin	..	0.7575[b]	...	...

[a] Calculated from paraffin-naphthene ratio and experimentally determined density on saturate portion.

[b] (*2, 22*).

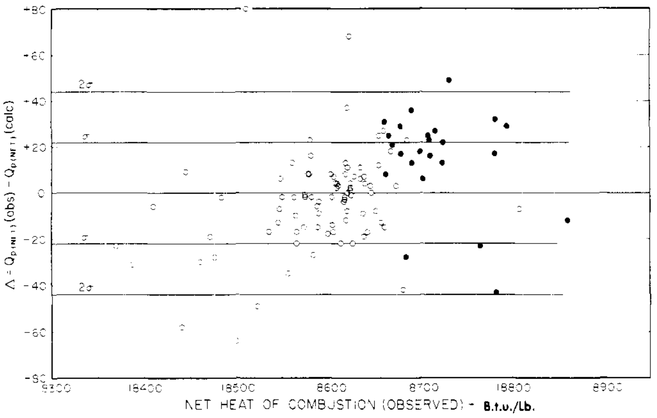


Figure 6. Deviation of calculated from observed heat of combustion vs. observed heat of combustion

○ Petroleum-distillate kerosine fuels

● Petroleum-distillate kerosine fuels containing less than 10% aromatics

the kerosines. The data for the same 110 natural kerosine-like fuels were fitted by the method of least squares to yield the equations

$$Q_p(\text{net}) = 18{,}935 - 2.419\,(N') - 14.663\,(Ar') \qquad (2)$$

where (N') is the volume per cent naphthene and (Ar') is the volume per cent aromatic, and

$$Q_p(\text{net}) = 18{,}934 - 2.316\,(N) - 13.666\,(Ar) \qquad (3)$$

where (N) is the weight per cent naphthene and (Ar) the weight per cent aromatic. The standard deviations were found to be 27 and 32 B.t.u./lb. and the maximum deviations +119 and −150 B.t.u./lb. for the volume per cent and weight per cent equations, respectively.

While four variables were considered in the fitting, only two appear in the equations. The four variables are not independent, because the sum of the percentages of the different hydrocarbon types must total 100. The olefin and paraffin percentages were combined because, owing to the relatively small quantities of olefin present, a positive coefficient was obtained when the olefins were considered as a separate variable. This is inconsistent with the mass of data obtained on pure paraffins and olefins, as the heat of combustion of a pure olefin is slightly less than that of the corresponding paraffin. This high positive value for the separate olefin coefficient is probably related to the fact that the olefin contents of the fuels studied are generally too low to permit an accurate determination of this coefficient. Therefore, the extrapolation to 100% olefin cannot be expected to yield an accurate result. A marked deviation of the olefin coefficient was also encountered with the aviation gasoline (*4*), although it was not so obvious, since the olefin coefficient was negative. Since the net heats of combustion per unit weight of the liquid olefins differ only slightly from those of corresponding paraffins, it was deemed more satisfactory to represent the net heat of combustion of fuels of low olefin content in Equations 2 and 3 in terms of only three variables: paraffins plus olefins, naphthenes, and aromatics.

Equations 2 and 3 do not provide as good a correlation as the corresponding equations for aviation gasolines. This is not surprising, for while there are four types of hydrocarbons in the gasoline range, there are no subtypes. In the kerosine range, on the other hand, naphthenes may include compounds of the alkylcyclohexane type, the bicyclohexyl type, and the decahydronaphthalene type, while aromatics may include alkylbenzenes, biphenyls, naphthalenes, and tetrahydronaphthalenes. There would also arise the question of the relative aromaticity of a compound such as *n*-hexylbenzene as compared with triethylbenzene. Because of such differences in structure, substances falling into a single category by the method of analysis used may have large differences in heat of combustion.

Therefore, four parameters are inadequate to describe a hydrocarbon mixture boiling in the kerosine range. Since it would take so many variables to describe these systems properly, the labor involved in performing an analysis of this type would be prohibitive.

In general, the heat of combustion may be estimated fairly well from the aniline-gravity product or the analysis by hydrocarbon type only if the fuels belong to a restricted, well-defined class. Even so, these correlations should only be considered a fair substitute for a well-determined experimental heat of combustion.

CONCLUSION

It appears that the best representation of the data of this investigation is given by Equation 1, which expresses the net heat of combustion of petroleum-distillate kerosines as a function of the aniline-gravity product. This equation was derived from the results of 110 of the petroleum-distillate kerosines investigated. It is not represented, however, as being applicable to alkylates or pure compounds boiling in the kerosine range.

The equations relating the net heat of combustion to composition by hydrocarbon type (Equations 2 and 3) show standard and maximum deviations from 25 to 60% greater than Equation 1. Thus, the superiority of the correlation of heat of combustion with composition found for aviation gasolines (*4*) is not found for the kerosines.

Equations 2 and 3 are subject to the further restriction that they can be applied with confidence only to fuels whose composition within the arbitrary hydrocarbon groups is essentially the same as that of the kerosine treated in API Project 6 on the Ponca City petroleum, as discussed above. If the compositions are very different, the percentages of hydrocarbon types given in Table I may be misleading. Further, among fuels with boiling points as high as those studied in this work, or higher, the diversity of hydrocarbons that may be present makes it difficult to describe the fuel adequately for correlation with heat of combustion by stating their composition in terms of only four different hydrocarbon types. On the other hand, further analysis of the fuel would be so difficult and time-consuming as to lessen the value of this method of estimating the net heat of combustion.

Table III. Equations Relating Net Heat of Combustion of Fuels to Other Properties

Equation No.	Equation	Std. Dev.	Max. Dev.
1	$Q_p(\text{net}) = 17909 + 0.10976 (A \times G)$	22	+80
2	$Q_p(\text{net}) = 18935 - 2.419 (N') - 14.663 (Ar')$	27	+119
3	$Q_p(\text{net}) = 18934 - 2.316 (N) - 13.666 (Ar)$	32	−150

[a] Equations represent 110 petroleum-distillate fuels considered in this work.

At the present time there is no reliable method of calculating an accurate value for the heat of combustion of a given petroleum fuel from a relation between heat of combustion and other properties. The best that can be obtained from such a relation is an estimated value of the heat of combustion. Some idea of the reliability of such an estimate is afforded by the fact that about 95% of the measured values differ from values calculated from a relation derived by the method of least squares by not more than twice the standard deviation. Thus, 95% of the experimental results obtained on petroleum-distillate fuels in this investigation differ from the corresponding values calculated by means of Equation 1 by not more than 46 B.t.u./lb., or about 0.25%. The other 5% of the calculated values are in error by greater amounts, ranging up to 80 B.t.u./lb., or 0.43%. Further, it is not safe to assume that any of the equations would represent the heats of combustion of another group of similar fuels as accurately as it represents the results obtained in this investigation.

It may also be anticipated that the equations may be less reliable in the event of changes in manufacturing procedures which may bring about a systematic change in the nature and relative amounts of the hydrocarbons present in the fuels. As an illustration of this possibility, the equations obtained for aviation gasolines in 1945 (*14, 15, 20*) differ from the equation derived in 1958 (*4*) for aviation gasolines meeting different specifications by 0.2 to 0.4% in the range of aniline-gravity product covered in both investigations.

It appears, therefore, that at the present time the only reliable method of obtaining an accurate value for the heat of combustion of a petroleum fuel is by means of an accurate experimental measurement. Equations such as those derived in this article should be used with extreme caution and only with a realization of their limitations. However, with the advent of the jet and the rocket age, the need for rapid methods of determining the absolute heat of combustion with high accuracy will become more pressing. While combustion calorimetry will remain the ultimate research tool, the pressure "to get the work out" in the control laboratory (whether at the refinery or the airport) has tended to place a low limit on the accuracy of this method as a routine procedure. It is essential that the search be continued for a rapid, accurate method of determining heats of combustion suitable for routine control use.

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