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Effect of Hydrocarbon Types on Solvency and Burning Characteristics of Petroleum Naphthas

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PETROLEUM naphthas are selected for specific applications largely on the basis of empirical tests that have been related to end-use properties—viz., various types of octane tests, etc. The relationship to actual hydrocarbon composition has been largely qualitative. This article provides a quantitive relationship between hydrocarbon types and boiling range on the contribution of each hydrocarbon type towards solvency or burning quality.

BACKGROUND

The solvent naphthas usually boil in the range of 100° to 400° F. Most have a boiling point spread of 50° to 150° F. They are virgin cuts which contain paraffins, naphthenes, and aromatics; olefins are generally absent or present only in trace quantities. Solvency is often measured by the kauri butanol (K B) test (*1*). High values indicate high solvency power, and low values indicate low solvency power. The contention always was that aromatics control solvency; not much is generally said about the role played by naphthenes and/or paraffins. Because of the lack of adequate and accurate analytical techniques, no attempts were made to correlate solvency, measured by some empirical test such as the K B value, as a function of hydrocarbon types. Published data which relate the K B value to other tests such as the aniline point, the mid-boiling point, or A.P.I. gravity (*3*), only predict solvency from other easily determined and standardized physical tests. From a processing standpoint, these correlations are of no great value, because they shed no light on schemes that should be used to convert a naphtha of a known composition to another in order to meet a certain specification. If, on the other hand, the individual effects of different hydrocarbons on solvency are known, processing schemes could be chosen to change the composition of a naphtha to meet a certain specification.

Kerosine and kerosine-type jet fuels are usually virgin naphthas which boil in the range of 300° to 550° F. Most have a boiling point spread of 150° to 250° F. The required high boiling quality of kerosines and jet fuels is measured by the smoke point. This test (*4*) is designed to evaluate a product in respect to its ability to burn without smoke. High values indicate good burning characteristics, and low values indicate poor burning characteristics. Here again, the contention always was that the burning quality of a naphtha, as measured by the smoke point, improves by decreasing the aromatics content, but not much is generally said about the role of naphthenes and/or paraffins. Hunt (*5*) measured the smoke point of hydrocarbon compounds of different structures and molecular weights. His measurements were generally made on pure aromatics, naphthenes, or paraffins. Some measurements were made on pure aromatics blended with *n*-dodecane. Hunt, however, did not make measurements on mixtures of aromatics, naphthenes, and paraffins to evaluate the effects of blending these three hydrocarbons on smoke point. Nelson (*6*) attempted to describe quantitatively the effect of aromatics, naphthenes, and paraffins on smoke point. His correlation was handicapped by the lack of accurate analytical techniques available at the time of its development. Therefore, it could not predict smoke points to the desired accuracy.

Attempts were made to find the contribution of each hydrocarbon to solvency and burning quality; the interaction effect, if any, that one type of hydrocarbon has on any other when two or more are combined; and the effect of naphtha boiling range on the contribution of each hydrocarbon type towards solvency or burning quality.

The recent advances in analytical techniques for the determination of aromatics, paraffins, and naphthenes were a great help in correlating the effects of hydrocarbon types on solvency and smoke point.

ANALYTICAL TECHNIQUES AND EQUIPMENT

On petroleum naphthas boiling below 400° F., paraffins, naphthenes, aromatics, and condensed naphthenes were determined in a mass spectrometer using a method similar to that described by Elliot, Lumpkin, and Thomas (*7*). For the stocks boiling above 400° F., extrapolated calibration data were used in the application of the method. This procedure is believed to be accurate because percolation of the same samples over silica gel gave substantially the same results depicted from the extrapolated method.

Analyses were made using a Consolidated Electrodynamics Model 21-103 mass spectrometer equipped with an all-glass inlet system operated at 572° F.

In this work the naphthenes and condensed naphthenes are reported as naphthenes to simplify calculations.

K B determinations were made by the ASTM method (*1*); this measurement is accurate to within ±0.2 unit. Smoke point determinations were made by the method of the British Institute of Petroleum (*5*); this measurement is accurate to within ±1 mm. The boiling ranges of the naphtha stocks were measured by the ASTM method (*2*).

EFFECTS ON SOLVENCY

Hydrocarbon Types. K B determinations were made on five sets of naphtha samples, all of the same boiling range. In each set, the naphthenes content was constant and the aromatics content was varied. Over-all, naphthenes ranged from 0 to 40%, aromatics from 2 to 25%, and paraffins from 35 to 98%.

The scheme followed in preparing the paraffins, aromatics, and naphthenes used in preparing these blends is shown in Figure 1. All hydrocarbon fractions were cut by distillation to a 310° to 390° F. ASTM boiling range, because it was considered to be representative of a normal boiling range spread of commercial hydrocarbon solvents.

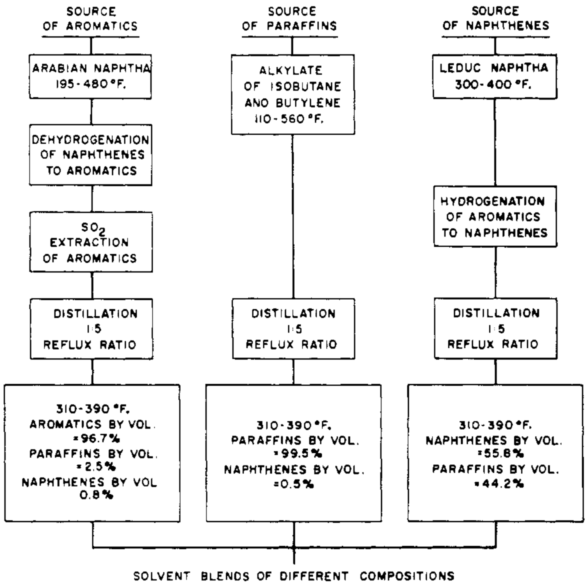

Figure 1. Scheme for preparing aromatics, naphthenes, and paraffins for solvency evaluation

Solvency, measured by the K B value, is not a function of aromatics alone (Figure 2). At any constant aromatics content, increasing the naphthenes increases solvency; increasing the paraffins decreases solvency.

The data seem to indicate that solvency is generally an additive property. This can be seen by cross-plotting and extrapolating the curves (Figure 2) to 0% paraffins, 0% naphthenes, and 0% aromatics. This results in K B value for each hydrocarbon type:

naphthenes	aromatics	paraffins
39.6	75.5	26.4

Such manipulation is not unorthodox. It is sound because the actual K B value of the paraffins alone was 26.4. This checks the value obtained by extrapolation and places more confidence in the values estimated for naphthenes and aromatics.

The K B value for any blend is then calculated from the equation

$$\text{K B} = A \times (\text{K B})_a + N \times (\text{K B})_n + P \times (\text{K B})_p \qquad (1)$$

where A, N, and P (volume fractions) and subscripts a, n, and p refer to aromatics, naphthenes, and paraffins, respectively. Substitution in Equation 1, produces substantially the same values as depicted in Figure 2 (Table I). The weight fractions can be also used for substitutions in Equation 1 if the K B values for the individual hydrocarbons are obtained from extrapolation of weight rather than volume data.

At low naphthenes, and low aromatics content, the calculated K B values are higher than the actual values. This could be explained by the fact that paraffins seem to decrease the solvency of aromatics slightly beyond that expected from a straight additive volumetric combination of the two, especially around the range of 0% naphthenes.

At high naphthenes and high aromatics content the calculated K B values are lower than the actual ones. This indicates that naphthenes seem to increase the solvency of aromatics slightly beyond that expected from a volumetric

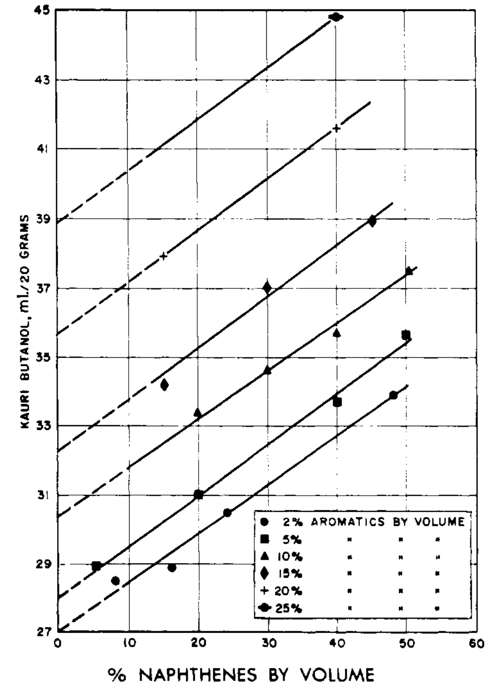

Figure 2. Solvency vs. naphthenes and aromatics content

ASTM boiling, 310° to 390° F.

Table I. Solvency of 310° to 390° F. Blends of Aromatics, Naphthenes, and Paraffins

% by Volume			Kauri Butanol Value, Ml./20 G.		
Naphthenes	Aromatics	Paraffins	Calcd.	Exptl.	Diff.
0	2	98	27.4	27.0	+ 0.4
0	5	95	28.9	28.0	+ 0.9
0	10	90	31.3	30.4	+ 0.9
0	15	85	33.8	32.3	+ 1.5
0	20	80	36.2	35.7	+ 0.5
0	25	75	38.7	38.9	−0.2
10	2	88	28.7	28.8	−0.1
10	5	85	30.2	29.6	+ 0.6
10	10	80	32.6	31.8	+ 0.8
10	15	75	35.1	33.8	+ 1.3
10	20	70	37.5	37.2	+ 0.3
10	25	65	40.0	40.1	−0.1
30	2	68	31.3	31.4	−0.1
30	5	65	32.8	32.5	+ 0.3
30	10	60	35.2	34.6	+ 0.6
30	15	55	37.7	36.7	+ 1.0
30	20	50	40.1	40.2	−0.1
30	25	45	42.6	43.4	−0.8
40	2	58	32.7	32.7	0.0
40	5	55	34.1	33.9	+ 0.2
40	10	50	36.6	36.0	+ 0.6
40	15	45	39.0	38.2	+ 0.2
40	20	40	41.5	41.6	−0.1
40	25	35	44.0	44.8	−0.8

Table II. Calculated Kauri Butanol Values of Hydrocarbon Types by Extrapolation Procedure

Boiling Range, ° F.	50% Boiling Point, ° F.	Slope of 20 to 80% ASTM Distillation Curve[a]	Kauri Butanol, Ml./20 G.		
			Paraffins	Aromatics	Naphthenes
300-385	334	0.617	26.4	70.0	39.6
315-450	378	0.80	24.7	63.5	37.0
345-520	427	1.16	24.0	56.9	36.0
290-550	428	2.30	23.8	71.0	35.7

[a] Slope = (vapor temperature, ° F. for 80% overhead − vapor temperature, ° F. for 20% overhead)/60.

combination of the two, especially in the region of 30 to 40% naphthenes and 20 to 25% aromatics.

The last two observations are not very firm, but they bring out an interesting phenomenon; there seems to be some interaction between the hydrocarbon components contributing to solvency.

These interaction effects cannot be determined from the data available now, because only a limited area of hydrocarbons composition was studied—e.g., aromatics 0 to 25%, naphthenes 0 to 45%. In future investigations, however, a quantitative determination of these effects would constitute a real contribution.

Boiling Range. Solvency is, in general, an additive property for the 310° to 390° F. specially prepared naphtha, so further work was done to see if this phenomenon applies to other boiling range stocks.

K B determinations were made on naphthas of different origins, hydrocarbon types distribution, and boiling ranges: 300° to 385° F. cut from a Leduc crude, 315° to 450° and 345° to 520° F. cuts from an Arabian crude, and a 290° to 550° F. cut from a Tia Juana crude. To make several samples from each stock the hydrocarbons distribution was changed by hydrogenating the aromatics in the fresh feed to naphthenes. Sometimes, however, the fresh feed containing high aromatics was blended with a completely hydrogenated stock to make samples of intermediate aromatics concentration. Figure 3 shows a plot of the K B values at different aromatics content for the different stocks used. Because of insufficient data, it was not possible to cross plot and extrapolate to 0% paraffins, naphthenes, and 0% aromatics to determine the K B value of each hydrocarbon type. However, by assuming that the ratio of K B for naphthenes to paraffins 39.6/26.4 does not change with change of boiling range, and solvency is an additive property, the K B values for each of the naphthenes and paraffins in each stock can be determined by extrapolating the curves shown in Figure 3. From K B values at 0% aromatics, and again assuming solvency to be an additive property, the K B of aromatics in each stock can be calculated. The K B for the aromatics remained reasonably constant (±1 K B) with change of composition for each stock. Therefore, the assumption that solvency is an additive property was true. K B values for each hydrocarbon type (Table II) are plotted as a function of the 50% boiling point in Figure 4. K B values for the synthetic blend are also shown and seem to correlate nicely with the values of the other stocks studied.

The K B values shown in Table II were substituted in Equation 1, using weight fractions to predict solvency values from a knowledge of the composition. In general, this method predicted the K B values of the samples tested within ±1.5%. The calculated *vs.* the actual values with the per cent deviations are shown in Table III.

The calculated K B values for the individual hydrocarbons indicated that, except for the wide boiling range (290° to 550° F.) Tia Juana naphtha, solvency decreased with increase of the 50% boiling point. The K B of the aromatic portion of the Tia Juana naphtha was 71. From elevation of the 50% boiling point, this value was expected to be around 57. The difference could be explained by the higher ratio of low boiling (high K B) to high boiling (low K B) aromatics in the 290° to 550° F. as compared to that in the 345° to 520° F. stock. This is proved from the detailed anaylsis of the samples tested. Table IV shows the breakdown of each hydrocarbon type by molecular weight. If C_6H_6 to C_9H_{12} single rings represent the low boiling aromatics, and $C_{10}H_{14}$ to $C_{14}H_{22}$ plus the naphthalene and indans represent the high boiling aromatics, the ratio of low boilings to high boilings, at any total aromatics level, is higher for the wide boiling (290° to 550° F.) than for the narrower boiling (345° to 520° F.) (Table IV and Figure 5). This ratio is higher for the stocks with low 50% boiling points. The last observation confirms that solvency of any specific hydrocarbon type increases with decrease of 50% boiling point.

From the K B values shown in Table II, solvency values can be predicted for other naphthas having 50% boiling point between 330° and 430° F. by interpolation between the numbers shown in Table II and plotted in Figure 4. The interpolation probably will not accurately predict the K B value of stocks having a slope of the distillation curve outside the range of 0.6 to 1.2, because the data show that

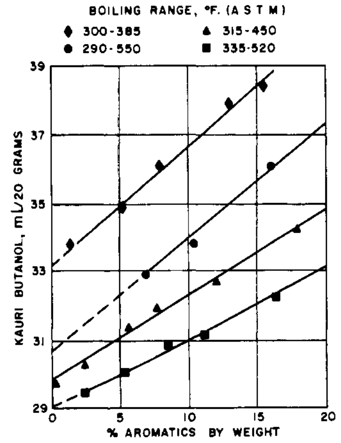

Figure 3. Kauri butanol values for naphtha stocks as a function of aromatics content

Table III. Summary of Analytical Results, Kauri Butanol and Smoke Point Measurements

Comparison of Actual and Calculated Measurements

Stock Boiling Range, ° F.	50% Mid-Boiling Point	50% Mid-Boiling Point – (20) (Slope)[a]	Sample No.	Aromatics, Wt. %	Naphthenes, Wt. %	Paraffins, Wt. %	Actual Kauri Butanol, Ml./20 G.	Calcd.[b] Kauri Butanol, Ml./20 G.	Difference, Calcd. – Actual	% Dev.	Actual Smoke Point, Mm.	Calcd.[c] Smoke Point, Mm.	Difference, Calcd. – Actual	% Dev.
300 to 385	334	322	A_1	15.4	41.5	43.1	38.45	38.61	+ 0.16	+ 0.52	25	24	−1	−4
			A_2	13.0	44.1	42.9	37.94	37.85	−0.09	−0.37	26	29	+ 3	+12
			A_3	7.9	50.1	42.0	36.13	36.46	+ 0.33	+ 0.74	31	31	0	0
			A_4	5.3	52.9	41.8	34.95	35.60	+ 0.65	+ 1.50	34	37	+ 3	+12
			A_5	1.4	57.4	41.2	33.81	34.46	+ 0.65	+ 1.40	40	40	0	0
										Av. ±0.9				±7
315 to 450	378	362	B_1	18.0	20.8	61.2	34.23	34.30	+ 0.07	−0.20	26	26	0	0
			B_2	12.1	28.5	59.4	32.78	32.90	+ 0.12	+ 0.37	30	30	0	0
			B_3	7.7	32.8	59.5	31.91	31.73	−0.18	−0.56	35	40	+ 5	14.3
			B_4	5.8	36.2	58.0	31.34	31.40	+ 0.06	+ 0.19	37	37	0	0
			B_5	2.6	40.2	57.2	30.26	30.65	+ 0.39	+ 1.29	40	40	0	0
										Av. ±0.5				±3.5
345 to 520	427	382	C_1	16.4	24.6	59.0	32.27	32.40	+ 0.13	+ 0.40	23	20	−3	13.1
			C_2	11.3	30.0	58.7	31.13	31.32	+ 0.19	+ 0.61	26	26	0	0
			C_3	8.6	33.0	58.4	30.88	30.79	−0.09	−0.29	30	30	0	0
			C_4	5.4	35.6	59.0	30.00	30.05	+ 0.05	+ 0.17	36	36	0	0
			C_5	2.5	39.2	58.3	29.48	29.52	+ 0.04	+ 0.14	40	40	0	0
										Av. ±0.3				±3.3
										−0.36	19	21	2	10.5
290 to 550	428	404	D_1	16.1	38.5	45.4	36.13	36.0	−0.13	...	21	21	0	0
			D_2	13.5	42.2	44.3	...	...	...	+ 0.56	23	23	0	4.3
			D_3	10.4	45.5	44.1	33.81	34.0	+ 0.19	+ 0.03	26	26	0	0
			D_4	6.9	50.0	43.1	32.99	33.0	+ 0.01	...	34	34	0	0
			D_5	2.1	54.1	43.8	...	...	...	Av. ±0.2				±2.9

[a] Slope of 20 to 80% ASTM distillation curve = (vapor temperature, ° F., for 80% overhead − vapor temperature, ° F., for 20% overhead)/60.

[b] Calculated from Equation 1. K.B. values for each hydrocarbon type in different stocks, Table II.

[c] Calculated from Equation 3. Values of S for each hydrocarbon type in different stocks, Table V.

when the slope of the distillation curve is high—i.e., 290° to 550° F. stock—the ratio of the low boiling (high K B) to high boiling aromatics (low K B) could be higher than that of s stock—e.g., 345° to 520° F.—of the same 50% boiling point, but of lower distillation curve slope. This difference in ratios could make the K B differ substantially for any hydrocarbon type from one stock to another when these have the same 50% boiling point, but vary widely in slope of distillation curve—e.g., 2.30 for 290° to 550° F. stock *vs.* 1.16 for 345° to 520° F. stock.

The K B values calculated for the 300° to 385° F. naphtha used in the boiling range study are in good agreement with those calculated for the specially prepared blend (310° to 390° F.). The latter was used in the study of effect of hydrocarbon types on solvency. The two cuts were from a widely varying origin.

Interaction effects of one hydrocarbon on another in regard to solvency are not discussed here. To summarize, solvency is, in general, an additive property, regardless of the boiling range. In some naphthas, solvency can be predicted from a knowledge of the composition and boiling range.

EFFECT ON BURNING CHARACTERISTICS

Hydrocarbon Types. To evaluate this effect, smoke point measurements were made on the four naphtha stocks used in the solvency evaluation. As previously indicated, Nelson (*6*) reported that the smoke point of a naphtha can be predicted from the following formula:

$$\text{Smoke point: } = 48\,P + 32\,N + 20\,A \qquad (2)$$

in which P, N, and A are the fractions of paraffins, naphthenes, and aromatics. The nature of Nelson's equation postulates that the smoke point is an additive property. This is mathematically demonstrated by the following equation:

$$\text{Smoke point} = S_p \times P + S_n \times N + S_a \times A \qquad (3)$$

in which P, N, and A (weight per cent fractions) and subscripts p, n, and a refer to paraffins, naphthenes, and aromatics. S values represent the contribution of each hydrocarbon type to the smoke point. Equation 2, when applied to these data, did not predict the smoke point with any accuracy. Although Nelson did not specify whether, P, N, or S were weight or volume fractions, deviations of as high as 50% were noted on either basis. Example: naphtha sample A_4 (315° to 450° F.). The S values obtained by Nelson did not predict the data presented here, because the hydrocarbon type analysis available at the time Equation 2 was developed was not accurate and since then has been considerably improved (7); and Nelson did not take into account the effect of boiling range on the contribution of each hydrocarbon to the smoke point. The latter is important.

The values of S were determined here by assuming the linear relationship expressed in Equation 3, and solving for the values of S from equations using the analytical data shown in Table III. For example, using samples B_1, B_4, and B_5 for the 315° to 450° F. stock for which the composition and smoke point of blend is shown in Table III, a series of three linear equations can be written and solved.

$$26 = S_p \times 61.2 + S_n \times 20.8 + S_a \times 18.0$$
$$37 = S_p \times 58.0 + S_n \times 36.2 + S_a \times 5.8$$
$$40 = S_p \times 57.2 + S_n \times 40.2 + S_a \times 2.6$$

As a result $S_p = 2.7$, $S_a = -4.83$, $S_n = -2.54$. Values of these constants (Table V) were obtained for other stocks using the same method.

The values of S are constant for any particular stock over the range of compositions studied. S_p is always positive; S_a and S_n are always negative. This indicates that the addition of aromatics or naphthenes to a paraffins stock

Table IV. Ratio of Low Boiling to High Boiling Aromatics in Stocks Treated

	300° to 385°					315° to 450°					345° to 520° F.					290° to 550° F.				
Stock boiling range	A_1	A_2	A_3	A_4	A_5	B_1	B_2	B_3	B_4	B_5	C_1	C_2	C_3	C_4	C_5	D_1	D_2	D_3	D_4	D_5
% Single Ring Aromatics by Volume																				
C_6H_6	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	...
C_7H_8	0.2	0.2	0.0	0.0	0.1	0.4	0.2	0.1	0.1	0.1	0.3	0.3	0.2	0.2	0.0	0.5	0.4	0.4	0.2	...
C_8H_{10}	1.9	1.4	0.4	0.0	0.1	1.5	1.0	1.5	0.3	0.0	1.5	1.0	0.8	0.4	0.1	2.1	1.8	1.2	0.8	...
C_9H_{12}	6.6	5.6	3.6	2.4	0.4	4.1	2.8	1.6	1.2	0.5	2.2	1.7	1.2	1.0	0.5	3.6	3.0	2.2	1.4	...
Total low boiling Arom. (*A*)	8.8	7.2	4.0	2.4	0.6	6.0	4.0	3.2	1.6	0.6	4.0	3.0	2.2	1.6	0.6	6.3	5.3	3.8	2.4	...
$C_{10}H_{14}$	4.2	3.7	2.6	2.1	0.4	4.9	3.3	2.2	1.6	0.7	3.4	2.2	1.7	1.1	0.5	2.5	2.1	1.7	1.2	...
$C_{11}H_{16}$	0.9	0.7	0.4	0.2	0.1	2.7	1.8	1.3	1.0	0.5	2.7	1.8	1.4	0.8	0.4	1.5	1.3	1.0	0.8	...
$C_{12}H_{18}$	...	...	...	...	...	1.2	0.8	0.5	0.5	0.2	1.6	1.0	0.8	0.5	0.2	0.9	0.8	0.7	0.5	...
$C_{13}H_{20}$	...	...	...	...	...	0.4	0.3	0.3	0.2	0.1	1.0	0.7	0.6	0.3	0.2	0.8	0.6	0.6	0.4	...
$C_{14}H_{22}$	...	...	...	...	...	0.1	0.1	0.1	0.1	0.1	0.7	0.5	0.4	0.2	0.2	0.6	0.6	0.5	0.4	...
% Double Ring Aromatics (Naphthalene) by Volume																				
$C_{10}H_8$	0.1	0.1	0.1	0.1	0.1	0.4	0.2	0.1	0.1	1.0	0.7	0.4	0.3	0.1	0.1	1.4	0.9	0.4	0.2	...
Indans, C_9H_{10}, %	0.4	0.3	0.2	0.1	0.1	0.7	0.5	0.3	0.2	1.0	0.9	0.7	0.4	0.3	0.1	0.9	0.9	0.8	0.5	...
Total high boiling arom. (*B*)	5.6	4.8	3.3	2.5	0.7	10.4	7.0	4.8	3.7	8.1	10.6	7.3	5.6	3.3	1.7	8.6	7.2	6.2	4.1	...
	1.55	1.58	1.21	0.96	0.86	0.58	0.57	0.67	0.43	0.35	0.40	0.41	0.39	0.48	0.35	0.73	0.73	0.61	0.58	...
A/B	14.3	12.0	7.3	4.9	1.3	16.4	11.0	7.0	5.3	2.4	14.6	10.3	7.8	4.9	2.3	14.9	12.5	9.5	6.3	...
Total high aromatics	15.4	13.0	7.9	5.3	1.4	18.0	12.1	7.7	5.8	2.6	16.4	11.3	8.6	5.4	2.5	16.1	13.5	10.4	6.9	2.1
Vol. %	30.5	32.5	37.9	40.3	44.8	15.8	21.6	25.0	28.1	30.9	16.8	21.4	23.8	26.6	29.3	27.3	29.5	32.1	34.5	...
Wt. %	31.0	33.0	38.7	41.1	45.8	16.4	22.4	25.9	29.2	32.1	17.3	22.1	24.6	27.6	60.6	27.8	30.0	33.0	35.2	...
Naphthenes																				
Vol. %	9.5	10.0	10.3	10.6	10.4	3.9	5.4	6.1	6.2	7.2	6.5	7.0	7.5	7.1	7.8	9.7	11.0	12.2	13.4	...
Wt. %	10.5	11.1	11.4	11.8	11.6	4.0	6.1	6.9	7.0	8.1	7.3	7.9	8.4	8.0	8.8	10.0	12.2	12.5	14.8	...
Condensed naphthenes																				
Wt. %	41.5	44.1	50.1	52.9	57.4	20.8	28.5	32.8	36.2	40.2	24.6	30.0	33.0	35.6	39.2	38.5	42.2	45.5	50.0	54.1
Paraffins																				
Vol. %	45.7	45.5	44.5	44.2	43.5	63.9	62.0	61.9	60.4	59.5	61.7	61.3	60.9	61.4	60.6	48.0	47.0	46.3	45.7	...
Wt. %	43.1	42.9	42.0	41.8	41.2	61.2	59.4	59.5	58.0	57.2	59.0	58.7	58.4	59.0	58.3	45.4	44.3	44.1	43.1	43.8

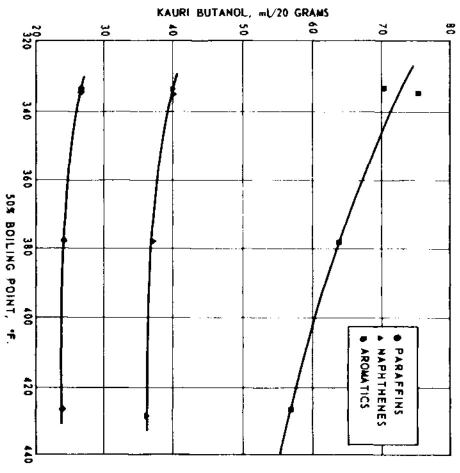

Figure 4. Calculated kauri butanol values of hydrocarbons as a function of boiling range

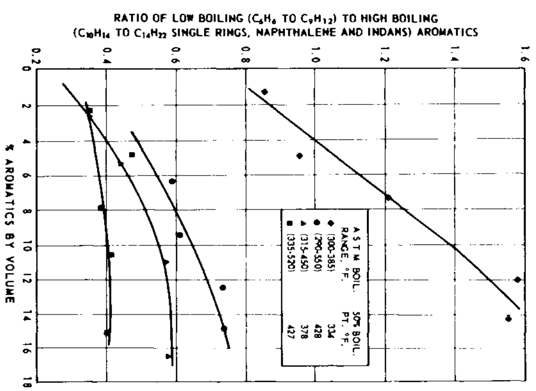

Figure 5. Ratio of low boiling (C_6H_{12} to C_9H_{12}) to high boiling ($C_{10}H_{14}$ to $C_{14}H_{22}$ single rings, naphthalene and indane aromatics at different aromatic contents

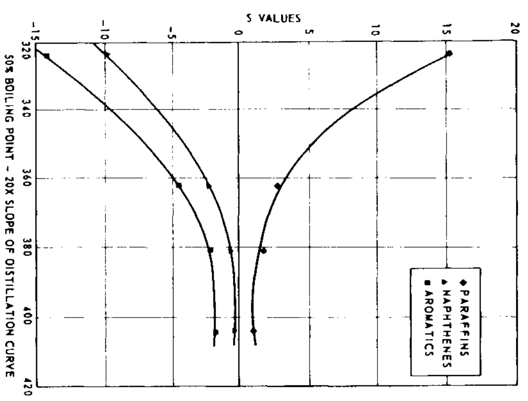

Figure 6. Calculated values of S as a function of boiling range

Table V. Calculated S Values of Hydrocarbon Types from Smoke Point Measurements of Naphtha Stocks

Boiling Range, ° F.	50% Boiling Point, ° F.	Slope of 20-80% ASTM Dist. Curve	50% B.P. −20 Slope	S_p	$-S_a$	$-S_n$	$-S_a/S_p$	S_a/S_n
300–385	334	0.617	322	15.1	14.3	9.8	0.947	1.46
315–430	378	0.80	362	2.7	4.83	2.54	1.785	1.90
290–550	428	2.30	382	1.93	2.11	0.85	1.092	2.48
345–520	427	1.16	404	0.99	1.95	0.33	1.98	5.92

decreases its smoke point and therefore degrades its burning characteristics. Equation 3 can then be rewritten by assigning negative values to S_n and S_a. In this new form, the equation can better express the degrading effect on burning characteristics due to naphthenes and aromatics.

$$\text{Smoke point} = S_p \times P - S_n \times N - S_a \times A \qquad (4)$$

The S values shown above for each stock were substituted in Equation 3. Smoke points for the samples tested were predicted to within ±13%. The calculated *vs.* the actual values with the per cent deviations are shown in Table III.

Boiling Range. This effect could be well explained by comparing the values of S for each hydrocarbon in the different stocks tested. In general, S_p decreased and S_a/S_p grew increasingly negative with increase of 50% boiling point. This indicates that the elevation of the boiling range would generally lower the smoke point of a naphtha for any hydrocarbon type distribution. This observation did not, however, apply to the high slope wide boiling Tia Juana naphtha (290° to 550° F.). In this stock, S_a/S_p was lower than expected—i.e., the aromatics were not degrading the burning characteristics of paraffins as much as would be expected from elevation of 50% boiling point alone. This could be explained by the higher ratio of low boiling (high smoke point) to high boiling (low smoke point) aromatics in the (290° to 550° F.) stock as compared to the (345° to 520° F.) naphtha. Figures supporting this conclusion have already been explained under the solvency evaluation study. They could be seen from Table IV and Figure 5, also.

If an attempt is made to correct the 50% boiling point by considering the change of S_p and S_a/S_p as a function of the 50% boiling point-20x slope, for all stocks, S_p decreases and S_a/S_p becomes increasingly negative with increase of the corrected 50% boiling point. This correction was chosen to place all the stocks tested on a more or less equal slope for the distillation curve. A plot of S values *vs.* the corrected 50% boiling point is shown in Figure 6. The smoke point of any naphtha having a 50% boiling point from 330° to 430° F. and a 20 to 80% ASTM Distillation slope from 0.6 to 2.3 can be predicted by the use of Equation 3 and the necessary interpolation from Figure 6. These correlations were obtained on stocks that varied in smoke point from 19 to 40 mm. Outside this range, there are no assurances that this method of calculation will hold. Another restriction is that in the samples tested here, whenever the aromatic content decreased, the naphthenes content increased and the paraffins content did not change or decreased slightly, because the hydrogenation reaction converted the aromatics to naphthenes. If samples are produced by some other means than converting the aromatics to naphthenes, there are no assurances that the correlations shown above will hold.

The correlations developed here show more than anything else the extent to which aromatics affect the smoke point of paraffins as compared to naphthenes. It is clear from the S values in Table V that the aromatics contribute to a larger extent than naphthenes towards the degradation of naphtha burning characteristics. This, of course, is evidenced by the fact that S_a/S_n is always greater than 1. S_a/S_n increases in general with increase of boiling range. This means that aromatics have a stronger adverse effect on burning quality in the higher boiling stocks. This directionally agrees with experience in jet fuels that certain aromatics fractions—those boiling above 400° F.— are prone to cause excessive carbon deposits in combustion chambers. Lower boiling aromatics do not appear to be particularly harmful.

CONCLUSIONS

Solvency of naphthas measured by the kauri butanol value is, in general, an additive property. Each hydrocarbon type (paraffins, naphthenes, and aromatics) is contributing a part proportional to its solvency power and per cent by volume or weight.

At low naphthenes (0 to 10%) and low aromatics content (0 to 15%), paraffins seem to decrease the solvency of aromatics slightly beyond that expected from a straight volumetric combination of the two. At high naphthenes (30 to 40%) and high aromatics content (20 to 25%) naphthenes seem to increase the solvency of aromatics slightly beyond that expected from a straight volumetric combination of the two.

Solvency of hydrocarbons decreases with increase of the 50% boiling point.

K B values of naphthas which boili in the range of 300° to 520° F. and have a boiling spread of no more than 175° F. can be predicted from composition data (per cent paraffins, naphthenes, and aromatics) and 50% boiling point. Average deviations of calculated from actual values were ±1.5.

The burning quality of kerosine measured by the smoke point improves by decreasing the aromatics content.

At any aromatics content, increasing the naphthenes degrades the burning characteristics of kerosine.

Aromatics tend to have a larger effect on degrading the smoke point of paraffins as the boiling range is elevated.

Aromatics always have a larger effect than naphthenes on degrading the burning characteristics of kerosine. This effect is magnified in the higher boiling ranges.

The smoke point of naphthas which boil in the range of 290° to 550° F. and have a smoke point of 19 to plus 40, can be predicted from composition data, and boiling range. Average deviations of calculated from actual values were ±13%.

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