Composition of Catalytically Cracked Gasolines

J. R. BATES AND F. W. ROSE, JR.

Houdry Laboratories of the Catalytic Development Company, Marcus Hook, Penna.

S. S. KURTZ, JR., AND I. W. MILLS

Sun Oil Company, Marcus Hook, Penna.

BELOW 160° F. (70° C.) there are in gasoline few naphthenic compounds and no aromatics. Up to this boiling point, gasolines are composed mainly of paraffins with the corresponding olefins. The octane number in this range is primarily dependent upon the relative amounts of the isomeric paraffins present, straight-chain compounds showing a greater tendency to knock than corresponding branched-chain compounds. The paraffins in this portion of a gasoline are butanes, pentanes, and hexanes. Accordingly, careful analyses have been made of these compounds as they occur in the gasoline produced from catalytically cracking various petroleum fractions by the Houdry process.

The separation of butanes and pentanes was carried out on a Podbielniak heligrid-packed column of the automatic type.

The analyses by this method of eight samples of gasoline for butanes, butenes, and pentanes are shown in Table I. These samples were produced by cracking two stocks of widely different boiling ranges on different catalysts under varying conditions. The catalysts were of the same general class. The fraction containing four-carbon hydrocarbons was divided into an "isobutane cut" and a "normal butane cut". Both these cuts were analyzed for isobutene and normal butenes. Isobutene was determined by treatment with 64 per cent sulfuric acid. Bromine water was used to determine the total butenes or the normal butenes after the absorption of isobutene.

Considering the accuracy of the analytical methods and the variation in preparation of the samples, the constancy of the composition of the butane and pentane fractions at the various gasolines is of interest. The last four samples were prepared from a light gas oil and show a lower olefin content (pentenes are included in the residue, C_6+) that is probably due to the conditions of operation which favored polymerization and condensation reactions. The ratios of iso to total for the various hydrocarbons are shown in the last three lines of Table I. A high percentage of isoparaffins occurs in every sample, with an average of 85 per cent for the butanes and 89 per cent for the pentanes.

Since the data on the lower hydrocarbons proved of such interest, the much more difficult problem of separating the various hexane isomers was undertaken. Two samples of

Since the advent of commercial catalytic cracking of petroleum to produce gasoline there has been much speculation concerning the reason for the high octane number of this material as a motor fuel in comparison with fuels produced by thermal cracking, and those produced from the virgin crude by simple distillation. The work presented here shows that this high octane is due to the presence of a large excess of isoparaffins over normal paraffins in the lower boiling portions of the gasoline and to a high content of aromatic compounds in the higher boiling fractions. These relations are not affected by the olefin content of the gasoline which may vary over a wide range with varying conditions of cracking.

catalytic gasoline were used, both prepared by the Houdry process but from different charging materials cracked under different conditions. The two analyses were carried out in different laboratories by similar methods. Analyses of a typical thermal gasoline and of natural gasoline from the East Texas field were carried out at the same time as the second catalytic gasoline to obtain strictly comparable results on these different materials. Such products (400–410° F. end point) will have A. S. T. M. octane numbers of 55–60 in the case of the East Texas natural gasoline, 65–70 by thermal cracking, and 78–80 by catalytic cracking.

The hexane concentrates (105–165° F. or 41–74° C.) from these samples were prepared by distillation in a large still (either No. 1 or No. 3, Table II). The olefins and aromatics were removed from the C_6 fractions of the cracked naphthas by controlled acid treating (95 per cent sulfuric), neutralization, washing, and redistillation to remove any polymer. Freedom from olefins and aromatics was determined by a modification (unpublished) of the bromide-bromate method (5, 10), which has been carefully checked with pure compounds, and by specific dispersion. Since these tests showed that the C_6 fraction from straight-run

TABLE I. ANALYSES OF THE MORE VOLATILE COMPONENTS OF CATALYTICALLY CRACKED GASOLINES

Component	A	B	C	D	E	F	G	H	Av.
n-Butane	2.3	1.1	1.6	1.9	3.1	2.8	2.0	1.2	...
Isobutane	10.9	8.9	8.9	9.7	11.0	11.7	11.9	14.1	...
n-Butene	5.9	7.4	6.5	5.0	2.6	1.3	1.8	2.3	...
Isobutene	1.7	2.6	1.6	1.4	0.4	1.0	0.8	0.6	...
n-Pentane	1.3	1.3	1.8	1.5	1.6	0.8	1.1	1.5	...
Isopentane	10.3	8.6	8.4	11.6	12.6	12.8	12.9	11.9	...
Total pentenes	7.3	9.1	6.0	5.4	a	a	a	a	...
C_6+	60.3	61.0	65.2	63.5	68.7	69.6	69.5	68.4	...
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	...
Isobutane/ total butanes	0.83	0.89	0.84	0.83	0.78	0.80	0.86	0.92	0.85
Isobutene/ total butenes	0.22	0.26	0.20	0.22	0.13	0.43	0.30	0.19	0.24
Isopentane/ total pentanes	0.89	0.87	0.83	0.89	0.89	0.94	0.92	0.89	0.89

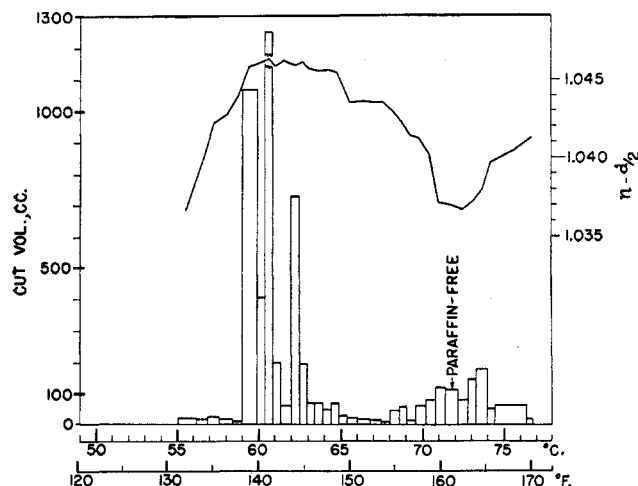a The normal and isopentane fractions contain 10–20% pentenes.

FIGURE 1. DISTRIBUTION OF HEXANE ISOMERS IN CATALYTI-
CALLY CRACKED GASOLINE (SAMPLE 1)

East Texas naphtha was olefin- and aromatic-free, it was not acid-treated.

To establish the reliability of the method of determining the relative proportions of the hexane isomers, a catalytically cracked sample (No. 1) was analyzed in detail (method A). A second catalytically cracked sample (No. 2), the thermally cracked sample, and the East Texas straight-run sample were then analyzed by a less detailed procedure (method B), which proved adequate.

Method A

The paraffin-naphthene mixture of sample 1 was distilled (still 4, Table II) to obtain the cuts shown in Figure 1. Density, refractive index, and specific dispersion were determined on all cuts. Consideration of these physical properties and the boiling points indicated that 2-methylpentane and 3-methylpentane were the predominant compounds present. Octane data on the first large cut indicated the presence of 2,3-dimethylbutane. To establish with further certainty the proportion of these compounds and of normal hexane, three composites were made and redistilled (still 5, Table II) with the results shown in Figure 2. The charge for run 1 was the first large cut (138.2–140° F., 59–60° C.). The bottoms of run 1, plus the cuts from 140–143.6° F. (60–62° C.), was the charge for run 2. The bottoms of this run and the cuts from 143.6–150.8° F. (62–66° C.) was the charge for run 3.

The refractivity intercept of the cuts obtained on redistillation show that practically no naphthene is present. The

high refractive index in run 1 shows 2,3-dimethylbutane; and the high refractive index in run 3 shows the presence of 3-methylpentane.

In Figure 1 there is no peak where normal hexane should occur. The paraffin in the bottoms from redistillation 3 and all the paraffin in the cuts boiling between 150.8° and 161.6° F. (66° and 72° C.) was calculated as n-hexane. The paraffin-naphthene split was made on the basis of refractivity intercept.
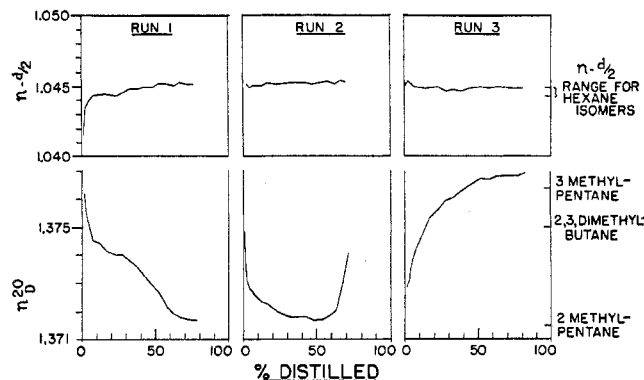

FIGURE 2. PROPERTIES OF CUTS OBTAINED ON REFRACTIONATION
OF HEXANE ISOMERS (SAMPLE 2)

The quantity of each isoparaffin was calculated on the basis of both the density and refractive index. These calculations check each other. The composition so calculated is given in Table III.

Method B

The split between the paraffin isomers can be made more simply, though with less precision, by careful interpretation of the first distillation of the olefin- and aromatic-free hexane concentrate. This eliminates redistillation.

The olefin- and aromatic-free hexane concentrate from the second sample of catalytically cracked gasoline was distilled in still 2 (Table II). The distillate was collected in 50-ml. fractions whose density, refractive index, specific dispersion, and boiling point were determined. Aniline points of various key fractions and octane numbers of blends of several fractions were determined. These properties provide an adequate check on the use of the boiling point curve for analysis. The calculation of the percentage of a compound is based on the premise that the break in the distillation curve of a binary mixture occurs midway between the boiling points, and that there is no tendency for deviation from ideal vapor-pressure relations. In mixtures containing no olefins or aromatics and little naphthene, vapor pressure relations should be nearly normal. This is permissible only if the fractionation is adequate. Ideally, the breaks in the distillation curve should be sharper than in the present data. Minor constituents showing no plateau must be calculated by some combination of physical properties. For example, in Figure 3 (upper graph) the percentage of 2,3-dimethylbutane plus

TABLE II. CHARACTERISTICS OF STILLS

Still No.	1	2	3	4	5
Size of helices for packing, in.	$^3/_{16}$	$^3/_{32}$	$^3/_{16}$	$^3/_{16}$	$^3/_{32}$
Height of column, ft.	8	9	22	10	4
Diam. of column, in.	1.6	1	2	$1^1/_4$	$^1/_2$
Capacity of still pot	37 liters	2.5 liters	34 gal.	2 gal.	200 ml.
Type of head	Rossini and Glasgow (13)	Rossini and Glasgow (13)	Total reflux, variable take-off	Total reflux, variable take-off	Total reflux, variable take-off
No. theoretical plates	25–30	100[a]	58	36	32
Av. reflux ratio	15:1	60:1	15:1	20:1	Total; intermittent take-off, 1 ml. (10 min.)

[a] Value by design. Actual tests indicate less than 50% of this value, probably due to improper packing.

TABLE III. DISTRIBUTION OF HEXANES IN GASOLINES

Type of Gasoline	Method of Analysis	2,2-Di-methyl-butane	2,3-Di-methyl-butane	2-Methyl-pentane	3-Methyl-pentane	n-Hexane[a]	Total % Isohexanes
Catalytically cracked (sample 1)	A	< 3	13	48	27	9 (±2)	91
Catalytically cracked (sample 2)	B	Trace[b]	11[c]	55[d]	28	6 (±3)	94
Thermally cracked	B	Trace[b]	< 3[c]	18[d]	16	63 (±5)	37
East Texas straight-run	B	Trace[b]	< 1[c]	<32[d]	16	51 (±5)	49

[a] The figures in parenthesis represent the authors' estimates of uncertainty.
[b] No 2,2-dimethylbutane was detected; only a trace is possible.
[c] As calculated by octane number.
[d] Percentage obtained by deduction of value for 2,3-dimethylbutane from total for 2,3-dimethylbutane and 2-methylpentane obtained from boiling point curve.

TABLE IV. OCCURRENCE OF ISOHEXANES IN GASOLINES

Source of Material	Ratio of Normal to Isohexanes[a]	Reference
Catalytically cracked gasoline (Houdry)	1:10 (±3)	This rept.
Thermally cracked gasoline	1:0.6 (±0.1)	This rept.
East Texas straight-run gasoline	1:1 (±0.1)	This rept.
Turner Valley, Alberta, straight-run gasoline	1:1	(22)
	1:1.3	(3)
Mid-continent straight-run gasoline	1:0.6	(1, 2, 12)
Thermally cracked naphtha	1:0.5	(17)
Thermal polymer gasoline	1:2	(17)
Plant-stabilized naphtha	1:0.8	(17)
Yates gasoline	1:2	(19)

[a] The figures in parentheses represent the authors' estimates of uncertainty.

2-methylpentane is 66 per cent (of the total hexanes) and the percentage of 3-methylpentane is 27 per cent. A split may be made between 2,3-dimethylbutane and 2-methylpentane by means of octane number (assuming that all of the former compound is present in the more volatile portion of the material assigned to these two compounds, and that the octane numbers of blends are linearly proportional to the values for the pure compounds). The amount of n-hexane is 6 per cent, based on the material occurring between 150.8° F. (66° C.) and 158.5° F. (70.3° C.), but corrected for naphthenic content by refractivity intercept (21). The octane number (66.5) of the blend (Figure 3) containing the n-hexane range agrees reasonably well with this figure. The analysis on this basis is summarized in Table III and is in good agreement with the more detailed analysis. Calculation of the composition of sample 1 from the distillation curve (method B) also gave good checks. These data justify use of the shorter method for comparison of other samples.

Figure 3 also shows the distillation curves for the olefin- and aromatic-free C_6 fraction of thermally cracked gasoline and of straight-run East Texas gasoline. Table III gives the isomer distribution for these samples. The outstanding fact established by the data in Table III is that the sum of the percentages of the isohexanes is above 90 per cent in the case of the catalytically cracked samples and is less than 50 per cent in the case of these thermal and straight-run samples.

Comparison of the data on the hexane isomers obtained in this investigation with data previously published is given in Table IV. The present data on East Texas straight-run is of the same order of magnitude as the data on hexanes published by A. P. I. Project No. 6 from mid-continent straight-run gasoline (12) and by Donald (3) and Watson and Spinks (22) on Turner Valley, Alberta, straight-run gasoline.

Comparison of the figures on thermally cracked gasoline with those for thermally cracked naphtha show a correspondence well within the accuracy of the experimental method.

Table III provides further confirmation of the high ratio of iso to normal paraffins in catalytically cracked gasoline. An earlier determination of the distribution of hexane isomers by this laboratory (11) was based on a much less complete

and a conservatively interpreted analysis and is not to be compared in accuracy with the present work.

To establish the fact that this type of distribution of paraffin isomers is not peculiar to the hexane and lower fractions, the C_7 fraction corresponding to sample 1 in Table III was refractionated. The number of isomers in this boiling range makes the separation more difficult, but the split shown in Table V was definitely established. Approximately 89 per cent of this fraction consists of isomers of moderate branching, and 6 per cent of more highly branched isomers. This allows only about 5 per cent for n-heptane. The boiling point of this fraction would allow the inclusion of any 2,2,4-trimethylpentane which might be present. These data are approximate but confirm the conclusions drawn from the analysis of the hexanes. Comparison of the percentage of normal isomer in the C_4, C_5, C_6, and C_7 cuts shows that the amount of normal isomer becomes less as the molecular weight and number of possible isomers increases. However, the accuracy of the present data does not justify a quantitative interpretation capable of extrapolation. As shown in subsequent discussion, this trend is also predicted by theoretical calculations.

TABLE V. DISTRIBUTION OF HYDROCARBONS IN 76–101° C. BOILING RANGE OF CATALYTICALLY CRACKED GASOLINE

Compounds[a]	Boiling Range, ° C.	% of Total Heptanes
2,2-Dimethylpentane 2,4-Dimethylpentane 3,3-Dimethylpentane 2,2,3-Trimethylbutane	76–88	6
2,3-Dimethylpentane 2-Methylhexane 3-Methylhexane 3-Ethylpentane	88–95	89
n-Heptane 2,2,4-Trimethylpentane	95–101	5 (max.)

[a] Compounds occurring in boiling ranges listed; no attempt was made to identify individual isomers.

Equilibrium Distribution of Hydrocarbon Isomers

The distribution of various isomeric butanes, butenes, and pentanes in the products of catalytic cracking is compared in Table VI with the distribution found in the products of a typical thermal operation, with that calculated from free-energy data of Rossini, Prosen, and Pitzer (14, 15), and with that determined by others (6, 16).

TABLE VI. EQUILIBRIUM DISTRIBUTION OF BUTANES, BUTENES, AND PENTANES COMPARED TO THAT OBTAINED BY CATALYTIC AND THERMAL CRACKING

Ratios	Equilibrium at 700° K. (800° F.) Calcd.	Exptl. (6, 16)	In Gasoline Catalytic	Thermal
Isobutane/total butane	0.38	0.33	0.85	0.15–0.25
Isobutene/total butene	0.32	0.45	0.24	0.35–0.45
Isopentane/iso- + n-pentane	0.70	..	0.89	....
Neopentane/n-pentane	0.20	..	0[a]	....

[a] No neopentane has been found in samples of catalytic gasoline.
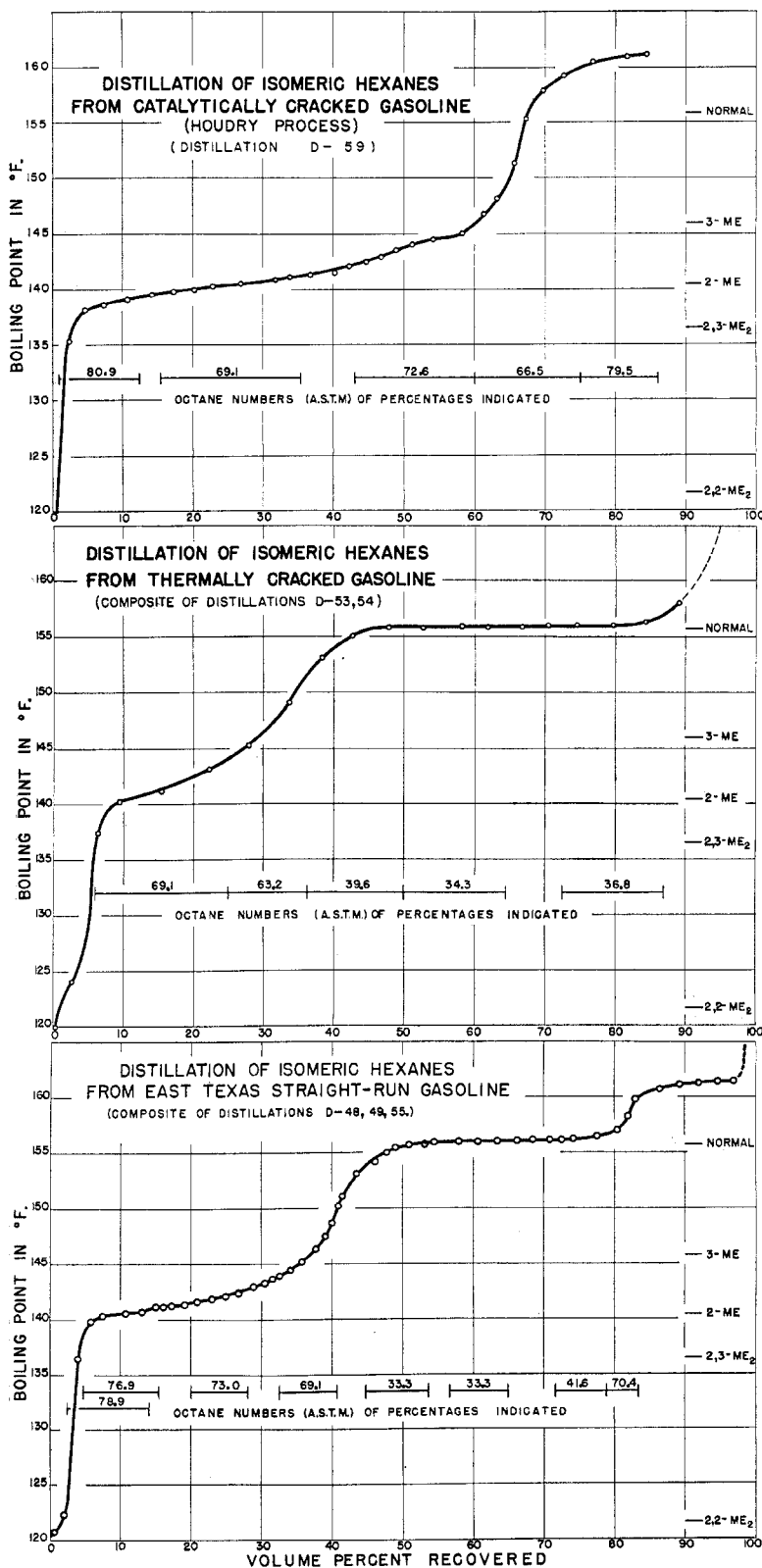
FIGURE 3. DISTILLATION OF HEXANE ISOMERS FROM VARIOUS GASOLINES

Table VII shows the isomer distribution at equilibrium for the hexanes at various temperatures, and also the comparison with catalytic gasoline and with the thermal and straight-run samples already described. A calculated distribution for the actual temperature of the catalytic cracking process (800° F. or 427° C.) is also included. The equilibrium between the isomers was again calculated from the data of Rossini, Prosen, and Pitzer.

The isoparaffins in catalytically cracked gasoline are present in amounts greater than would be expected from equilibrium calculations. This is true in the butanes, pentanes, and hexanes. In fact, the relative amounts of total isoparaffins among the hexanes is greater than would be predicted for any but very low temperatures, where the symmetrical 2,2-dimethylbutane should begin to predominate. Actually the latter compound was the only isomer whose presence could not be detected in catalytically cracked gasoline, although for equilibrium at the temperature of cracking it should have been present to the extent of about 20 per cent. The methylpentanes were found to constitute the major part of the hexanes. The ratio of 2-methyl- to 3-methylpentane is not far from the predicted equilibrium ratio (1.8 as compared with a theoretical 1.9). This ratio also holds fairly well for the methylpentanes in straight-run gasoline (2.0) although here, and in the thermal gasoline, the n-hexane has risen to over 50 per cent of the total hexanes, greater than the equilibrium value at any temperatures attainable in normal thermal cracking processes.

The ratio of isobutene to total butenes is lower in catalytically cracked gasoline than in thermally cracked, and is lower than at equilibrium (0.24 as compared with 0.32–0.45). This may be due to the well known fact that the isobutene is much more easily polymerized catalytically than is the normal butene. The ratio of isobutene to total butenes in thermal gasoline agrees with the equilibrium values. Values ranging from 0.35 to 0.45 were obtained, compared to 0.32 and 0.45 for the calculated and experimental ratios.

The explanation for the lack of agreement between the relative amounts of the isomers present and those predicted at equilibrium is simply that the products of these cracking processes to yield gasoline are not in equilibrium. The energy state attained in the processes is by no means the lowest possible for the particular quantities of carbon and hydrogen involved. Even if an equilibrium ratio of two or more isomers were attained or were present in the reactants, it would not necessarily remain constant but could reasonably deviate from this ratio with the production of nonequilibrium ratios. If the lowest possible energy state corresponding to the amounts of carbon and hydrogen at the particular temperature and pressure were attained, no such deviation would be possible.

TABLE VII. EQUILIBRIUM AND ACTUAL COMPOSITION OF HEXANE CUT OF GASOLINES

Paraffins from C₆ Cut	Theoretical Equilibrium, Mole % 25° C.	327° C.	427° C.	727° C.	Catalytic Gasoline Prepared at 427° C. (800° F.), Vol. %	Thermal Gasoline, Vol. %	East Texas Gasoline, Vol. %
n-Hexane	2	18	23	31	9	63	51
2-Methylpentane	8	28	30	27	48	18	32
3-Methylpentane	3	15	16	21	27	16	16
2,3-Dimethylbutane	6	10	10	9	13	3	1
2,2-Dimethylbutane	81	29	21	12	3	..	..
Total isoparaffins	98	81	77	69	91	37	49

TABLE VIII. COMPOSITION OF GASOLINES

Charge	Cracking (on Commercial Scale)	Sample Designation	Composition of Butane-Free Gasoline 50–347° F. (10–175° C.) Paraffins	Naphthenes	Olefins	Aromatics	50–437° F. (10–225° C.) Paraffins	Naphthenes	Olefins	Aromatics
Heavy naphtha from Coastal crude	Catalytic	A	43	24	5	28	39	29	4	28
Gas oil[a], 31 A. P. I. gravity	Catalytic	B	56	19	9	16	47	21	8	24
Gas oil[a], 29 A. P. I. gravity	Thermal	C	53	14	30	3	..	..	..	..
Heavy cracking stock from coastal crude	Catalytic	D	39	19	29	13	34	24	24	18

[a] Approximately 50-50 mixture of mid-continent grade and gulf coast grade gas oils, 10–90 per cent; catalytic 450–700° F.; thermal 430–650° F.

Analyses of Complete Gasolines

The components of gasoline, catalytic and thermal, above 160° F., where compounds other than paraffins play an important role, are compared by carrying out analyses of these gasolines throughout their boiling range.

Typical analyses of gasolines, produced by catalytic cracking from heavy naphtha (A), gas oil (B), and heavy charge stock (D) are shown in Table VIII and in Figure 4. A gasoline prepared by thermal cracking of gas oil (C) is also included. These gasolines were all produced on full-scale commercial units. Analyses were made by cuts, indicated on Figure 4. In this work the best features of several previously published methods of analysis were used (3, 4, 5, 7, 8, 9, 10, 18, 20, 21). Cross checks between two methods were obtained whenever possible. The aromatic and olefin figures are accurate within ±1 per cent. The split between paraffins and naphthenes is reproducible within ±1 per cent, but the absolute accuracy is considerably less, perhaps even ±5 per cent. These analytical methods will be described in detail elsewhere.

Table VIII and Figure 4 also show that the ratio of aromatics to olefins is much higher in catalytic gasoline than in thermal gasoline, whether the comparison is made on the basis of similar charging stocks (samples B and C) or on the basis of cracking to equal olefin content (samples C and D). When charging heavy naphtha or gas oil, the olefin and aromatic content is higher than when charging a heavy cracking stock. (By "heavy cracking stock" is meant a topped crude from which asphalt and similar high-boiling material have been removed by flash distillation.)

The low aromatic content of the 158–212° F. (70–100° C.) cut indicates little benzene in any of these samples. In cracking heavy naphtha, the highest percentage of aromatics (55 per cent) occurs in the xylene cut (257–302° F., 125–150° C.). In cracking heavy stocks, the percentage of aromatics increases steadily throughout this boiling range.
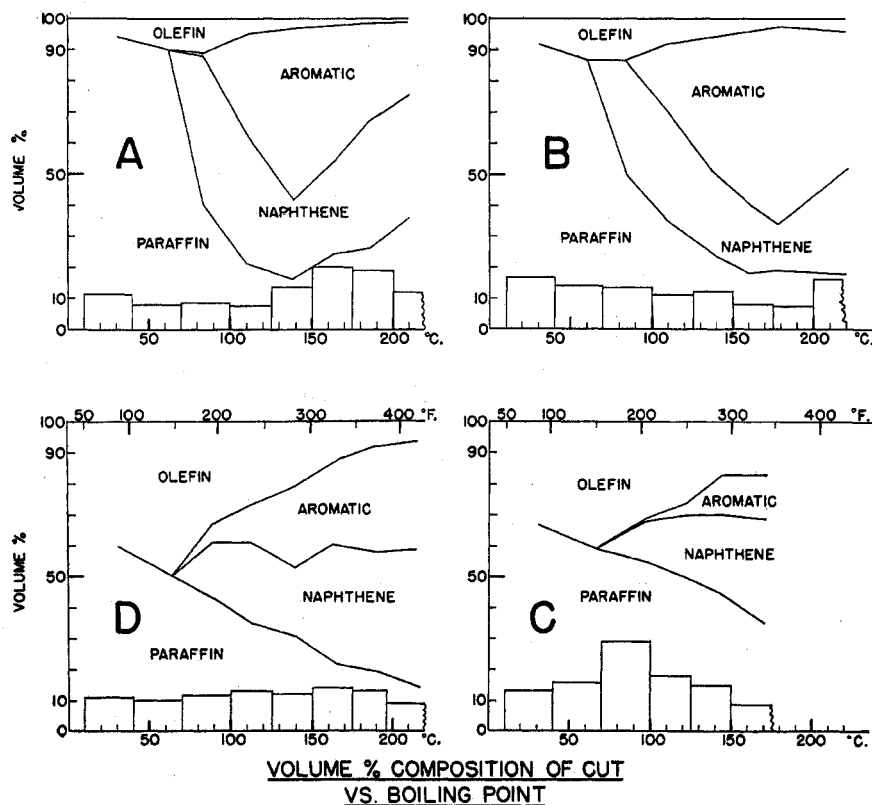

VOLUME % COMPOSITION OF CUT VS. BOILING POINT

FIGURE 4. COMPOSITION OF GASOLINES

A. Catalytic gasoline from heavy naphtha
B. Catalytic gasoline from gas oil
C. Thermal gasoline from gas oil
D. Catalytic gasoline from heavy cracking stock

Conclusions

The results show that the catalytic gasolines investigated owe their high octane numbers to a substantial absence of the normal paraffins rather than to a high concentration of the highly branched paraffins. The presence of high concentrations of aromatics in the heavier portions of the gasoline is also important from an octane standpoint.

The high ratio of isomeric to normal paraffins indicates that the thermodynamic equilibrium between the various isomeric forms has not been reached in catalytic cracking.

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Foaming Properties of Wine

Method and Preliminary Results

MAYNARD A. AMERINE, LOUIS P. MARTINI, AND WILLIAM DE MATTEI

University of California, Davis, Calif.

THE foaming properties of wines, the substances which cause the foam, and the stability of the foam are subjects which have received little study, although several cursory observations on foaming in wines have been made (1, 8, 9, 16, 17, 20, 23).

In contrast to beer (14, 26), foaming is generally undesirable in wines, especially in carbonated or naturally sparkling wines which have 3 to 6 atmospheres of pressure. (For a possible exception see Garino-Canina, 9). Sparkling wines contain from 11 to 14 per cent alcohol, and their sugar content varies from 0.20 to 10 per cent. It is undesirable to have either head retention or a very high foam capacity in these wines, since it makes them difficult to pour (especially if they are not thoroughly chilled), may cause undue loss of liquid from the bottle or glass, and is not customary. Head formation is greatly influenced by the gas content in beers (14), and this is undoubtedly a factor in the excess foaming of young sparkling wines that have been prepared by bottle fermentation and have been disgorged too soon and without much loss of gas. Champagnes which have aged in the bottle on the lees for a longer period (three to five years), as is customary for the better quality French champagnes, have only a small head formation. Direct or indirect losses in carbon dioxide during aging are partially responsible. Also, substances affecting the foaminess may be derived from the yeast cells during the long aging on the lees. In naturally sparkling wines (wines made by fermentation in closed containers), the bubbles are small and with proper aging and the usual disgorging the pressure is sufficiently reduced so that the foam capacity is diminished and there is, in addition, little head stability. Tarantola (24) showed that fermentation at low temperatures (5° C. or 41° F.) gives a greater foam stability in sparkling wines than is obtained in those which are fermented at ordinary temperatures (12-16° C., 53.6-60.8° F.). Sparkling wines fermented in large tanks by the Charmat process have reduced foam retention compared to wines fermented in the bottle (15). The use of different races of wine yeast also has an influence on the amount of foam in sparkling wines (6).

Marescalchi (16) made some observations on the foaming of Italian wines. He found foaminess to be greater if the wine were bottled for 15 to 30 days, compared to samples taken from the barrel. Increasing the alcohol content reduced persistence in foaming, especially in wines high in acid. Citric and phosphoric acids were found to increase foaming while malic, tannic, lactic, hydrochloric, and sulfuric caused little change. Succinic acid decreased foaming. Dilution with water was observed to increase the persistence of foaming. Ethyl acetate, ethyl sulfate, and glycerol were found to reduce foaming. Only qualitative data were reported in this study.

A knowledge of the factors influencing foaming, particularly bubble formation, would be especially desirable for carbonated wines in which there is frequently a tendency for the dissolved gas to be lost too soon owing to large bubble size and with