Composition of the Gas Oil Portions of Some California Jet Fuels

A. C. NIXON and R. E. THORPE
Shell Development Co., Emeryville, Calif.

ALTHOUGH jet fuels are currently manufactured predominantly from straight-run stocks, a broader view requires consideration of the possibility that components could be drawn from cracked materials as well. However, cracked fuels are generally less stable with respect to storage and high temperature stability than straight-run (*1, 2, 4*) so that an investigation of the influence of cracked components on these properties became necessary.

Since the higher boiling constituents of jet fuels are mainly responsible for instability, chief emphasis was placed on determining the composition and properties of the light gas oil fractions—those portions of the fuels boiling above about 350° F. This article reports the results of that portion of the work aimed at isolating and identifying the components responsible for instability.

EXPERIMENTAL

Three typical gas oils suitable for providing blending components for jet fuel manufacture were used (Shell Oil Co., Wilmington). The thermally cracked and straight run oils were chromatographed directly as indicated below. The more interesting catalytically cracked oil was first separated by distillation in a column with 10–15 theoretical plates. Appropriate overhead fractions from a 1000-gallon charge distilled at 3–7 mm. Hg and a 250-gallon charge at 2 mm. Hg were composited on an equivalent volumetric basis. The composited fractions are shown in Figure 1, with their ASTM boiling ranges as determined by analytical distillation. Because of the unusual degree of unsaturation characterizing the lower fractions of the overhead, the initial 2 volume % of the distillates with an ASTM boiling range of 340/430° F. and average boiling point of 400° F. was also studied separately. Component types were isolated from the distilled fractions by displacement chromatography on silica gel (Davison 923) using 2-propanol as the displacing agent. A 24-foot column consisting of four parallel 6-foot sections connected by capillary U-tubes and decreasing from 2.5 cm. diameter at the entrance to 0.5 cm. at the bottom was used at gel: oil ratios of about 10 to 1. The general scheme of separation is illustrated for catalytically cracked gas oil in Figure 1. The separated fractions were analyzed chemically and by ultraviolet and infrared spectroscopy, and in some cases by mass spectrometry. When needed, additional separation was accomplished by rechromatography on F-20 or H-41 alumina (Alcoa) or by gas-liquid chromatography. As the initial step in the isolation of the nitrogen base fraction, the bulk of the oxygen compounds and the nitrogen bases were first isolated from the 340/430° F. gas oil fraction by percolation through a synthetic magnesium silicate (Florisil) at low gel/oil ratio (about 0.85). The resin fraction was subsequently dissolved in benzene and extracted with either ethanolic HCl or dilute H_2SO_4 followed by extraction with dilute aqueous NaOH. There were thus obtained a nitrogen base fraction, a phenolic fraction, and a neutral fraction consisting of aromatic hydrocarbons and thiophenes plus polymeric material rich in both oxygen and nitrogen. These fractions were subsequently distilled in a micro whirling band column with 65 theoretical plates.

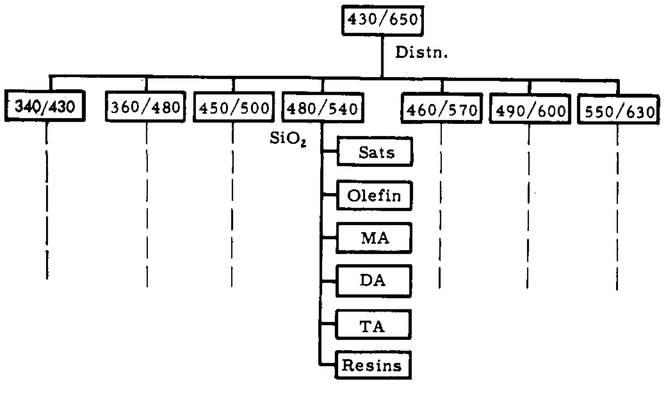

Figure 1. A California cat. cracked gas oil was separated by reduced pressure distillation and chromatography on silica gel

MA = monoaromatics, DA = diaromatics, TA = triaromatics

It was anticipated that anilines might affect the stabilities of gas oil fractions differently than pyridines and quinolines. To facilitate the separation of these families of bases, acetylation was employed. The total bases recovered from the 340/430° F fraction were treated with acetic anhydride to form amides from the anilines. The pyridines were subsequently extracted as salts. The acid amides were then hydrolyzed back to the aniline derivatives.

After the phenols and acids had been extracted with 20% aqueous NaOH, the pyrroles were isolated as their potassium salts by reaction with powdered KOH at about 140° to 175° C. The potassium pyrrolates were filtered and washed with isopentane. After hydrolysis of the salts, the pyrroles were extracted in benzene or ether and dried over sodium sulfate. A certain amount of tarry reaction product was always obtained. The pyrroles were concentrated by percolation through synthetic magnesium silicate followed by vacuum distillation. Data for the 480/540° F. fraction are presented as typical.

DISCUSSION

The main constituents of straight run, catalytically, and thermally cracked California gas oils are compared in Table I. The compositions of the cracked fuels differ markedly from that of the straight run, chiefly in the amounts of unsaturated and hetero compounds which constituted about 30% of the thermally and 14% of the catalytically cracked compared to only about 2% for the straight run gas oil. These differences are reflected in the storage characteristics of the three oils: after 3 weeks' storage at 70° C. under oxygen, the total gums were 82, 47, and 12 mg./deciliter, respectively.

The distribution of the major hydrocarbon classes with boiling range is shown in Figures 2 and 3 for the catalytically cracked gas oil fractions. The more unusual type components are described in detail.

Olefins and Diolefins. The olefins contents of the several gas oils are shown in Table I and Figure 2. In some of the olefin fractions, inflections or maxima occur in their ultraviolet absorption spectra in the vicinity of 2400 A. If thiophenes are absent, these are consistent with the presence of substituted cyclopentadienes. As shown in Figure 2 this species tends to concentrate in the low-boiling fractions, ranging from 0.2% in the 600° F. fraction to 1.4% in the 400° F. fraction of the catalytically cracked stock. In fractions free of triaromatics, the substituted cyclopentadienes appear to be roughly proportional to the maleic anhydride value. (Steric effects would prevent some of the substituted cyclopentadienes from reacting with maleic anhydride.) Cyclopentadienes are the most abundant conjugated polyolefin and occur in appreciable concentrations only in the cracked stocks. Very small concentrations of aliphatic dienes are probably present in all three gas oils.

The olefin contents determined by ultraviolet analysis using the absorptivity at 2150 A. agree reasonably well with values based on the bromine numbers of the individual chromatographed fractions. The absorptivity at 2150 A. is a linear function of bromine number until conjugated diolefins become appreciable, whereupon the former increases rapidly. This can be corrected by prior removal of the conjugated dienes with maleic anhydride.

Aromatic Olefins. Homologs of indene and styrene tend to be displaced from silica gel between mono- and diaromatics. However, the resolution is poor so that neither of the latter classes can be isolated in reasonable purity. The aromatic olefins can be concentrated by rechromatography on F20 alumina. They occur only in the cracked gas oils. Their exact concentration has not been determined for all fractions; the last column of Table I includes noncondensed polyaromatics—i.e., types such as $\Phi—\Phi$ or $\Phi—(CH_2)_n—\Phi$, as well as aromatic olefins.

Indenes were identified on the basis of refractive index and bromine number patterns (Figure 4), ultraviolet absorption and mass spectra and vapor phase chromatog-

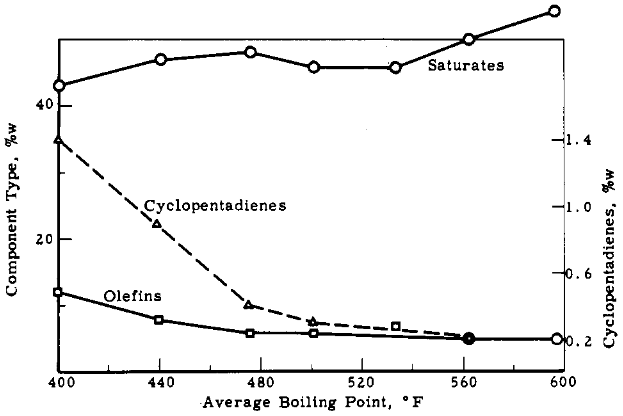

Figure 2. The unsaturation of cat. cracked gas oil decreased with increasing boiling point

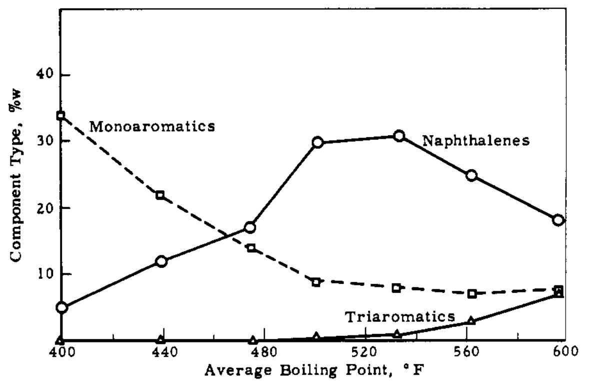

Figure 3. The monoaromatic content of the cat. cracked gas oil decreased with increasing boiling point

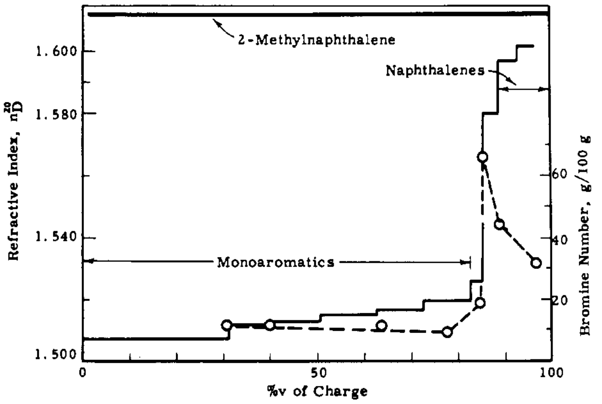

Figure 4. Aromatic olefins are indicated by a maximum in the bromine number between mono- and diaromatics

Solid line = refractive index

Dashed line = bromine number

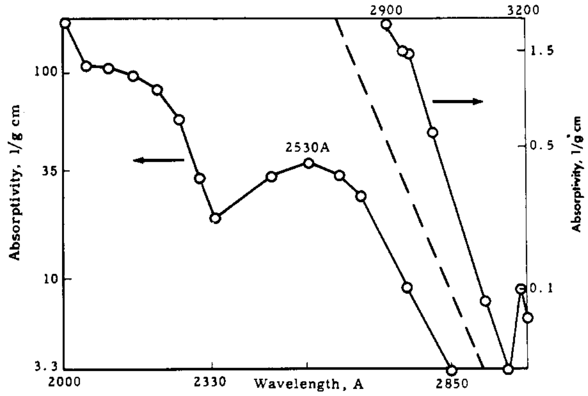

Figure 5. Ultraviolet absorption spectrum of the substituted indene concentrate from the 340/430° F. cat. cracked gas oil has a maximum at 2530 A.

Table I. Composition of Various Types of Gas Oils

				Type Components, %w					
Gas Oil	Range, °F.	Sats.	Olefins	MA	N	BT	TA	T	AO + NCPA
Cat. Cr.	430/650	52	6	10	17	3	2	0.2	7
Th. Cr.	406/542	43	19	15	6	2.5	<0.1	2.5	9
S. R.	330/580	78	<1	14.5	3	1	0.1	trace	1

MA = Monoaromatics N = Naphthalenes BT = Benzothiophenes TA = Triaromatics NCPA = Noncondensed Polyaromatics T = Thiophenes AO = Aromatic Olefins.

raphy. Their refractive indexes are intermediate to the values for monoaromatics and diaromatics. The bromine number, which had decreased from high values in the olefins to low values in the monoaromatics, increases sharply again as aromatic olefins are desorbed from the column (Figure 4). As shown in Figure 5 a substantial maximum in the ultraviolet absorption spectrum occurs at 2530 A. and traces of fine structure at 2870 (not shown) and 2950 A., suggest substituted indenes. The peak at 3185 arises from contamination by 5 weight % naphthalene including a little of its methyl homologs. Mass spectra indicate in one such fraction approximately 21 volume % C_nH_{2n-10}, corresponding to the empirical formula of indene homologs. Gas chromatography confirms the presence of indenes as a major component. Some styrenes are probably present also.

The indene-styrene content of the 340/430° F. catalytically cracked gas oil fraction is estimated to be 3 weight %, but the concentration decreases with increasing boiling point.

Hetero Compounds in Whole Gas Oils. Approximately 7% of the catalytically cracked gas oil consists of hetero compounds, of which 72% are sulfur compounds. Hetero compounds occur less extensively in the straight run (2%) and more extensively in the thermally cracked gas oil (9%). According to sulfur-type analysis about 95% of the sulfur in the catalytically cracked gas oil is thiophenic—predominantly mono- and dibenzothiophenes. The cracked stocks are more thiophenic than the straight run gas oils. Alkyl thiophenes occur in major proportions only in the thermally cracked stock, accounting for 2.5% of the gas oil.

The sulfur distribution, wt. %, in the three oils is:

	Gas Oil		
	Straight run	Cat. cracked	Thermally cracked
Total	0.39	0.78	0.98
Disulfide	0.007	0.0007	0.005
Mercaptan	0.002	0.0005	0.009
Sulfide	0.144	0.014	0.108
Thiophenic	0.24	0.76	0.86

Nitrogen Compounds. About 1% of the total catalytically cracked gas oil is accounted for by nitrogen compounds. About 40% are basic; pyrrolic compounds account for most of the remainder. (Carbazole, which accounts for more than 0.1 weight % of the gas oil, was identified by infrared and ultraviolet absorption. Certain fractions desorbed from silica gel on chromatography of the higher boiling fractions comprised as much as 35% carbazole which could be subsequently recrystallized. Indoles are the major pyrrolic component in the midboiling fractions. Infrared showed that pyrrolic compounds also occur in the thermally cracked and straight run products, but the relative proportions of indoles and pyrroles were not determined. The variation of basic nitrogen with boiling range is shown in Figure 6. This variation is contributed by members of the pyridine and aniline families. The presence of anilines may be peculiar to catalytically cracked stocks since the extensive researchers of Bailey in America and Wibaut in Holland do not indicate the occurrence of bases other than pyridines (and quinolines) in straight run or thermally cracked products (*3*).

Nitrogen Bases. When the ultraviolet absorption spectrum of the crude nitrogen bases isolated from the 340/430° F. catalytically cracked fraction is corrected for quinoline content, there remains a spectrum showing distinctly the dominant structural features of aniline homologs—i.e., maxima at about 2350 and 2900 A. The composition of each distilled nitrogen base fraction in order of increasing boiling point (Table II) was based on spectroscopic and chemical analysis:

Spectroscopically, in terms of the ultraviolet absorptivities at 2340 (for anilines) and 2650 A. (for pyridines) after correcting for quinoline as determined by the absorptivity at 3135 A.

Chemically, by acetylating the aniline homologs, and titrating the pyridines and quinolines with perchloric acid. Agreement between the two methods is satisfactory and indicates that tertiary anilines and saturated bases can be neglected.

As a consequence of the incremental spectroscopic analysis it is concluded that the nitrogen bases in the 340 to 430° F. catalytically cracked fraction are comprised of 35% pyridines, 25% quinolines, and 40% anilines. The distribution of nitrogen compounds, including pyrroles (Figure 7), is summarized:

	Weight %
Total nitrogen compounds	0.4
Nonbasic nitrogen compounds	0.1
Nitrogen bases	0.3
Pyridines	0.10
Quinolines	0.08
Anilines	0.12

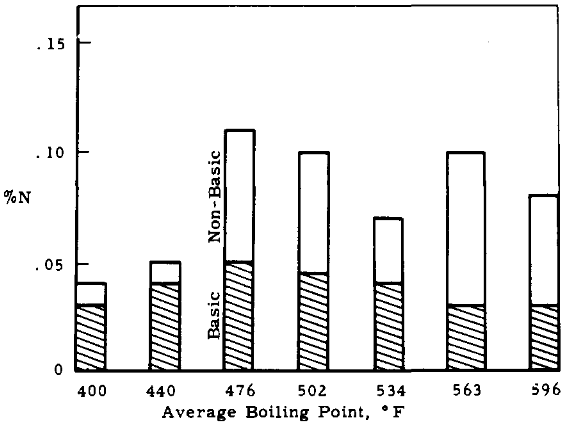

Figure 6. The basic nitrogen content of a cat. cracked gas oil is relatively constant with boiling point, the nonbasic nitrogen increased in the higher boiling fractions

Table II. Spectroscopic and Chemical Analyses for Nitrogen Base Types in 340/430° F. Catalytically Cracked Gas Oil

		Composition of Fraction, Weight %				
		Spectroscopic			Chemical	
Distillation Fraction	Vol., Ml.	Quinolines	Pyridines	Anilines	Quinolines-Pyridines	Anilines
1	0.65	0	92	8	91	9
2	1.59	0	76	24	69	31
3	5.35	3	54	43	46	54
4	5.22	28	25	47	47	53
5	5.20	50	10	40	63	37
6	0.90	57	<5	38	64	36

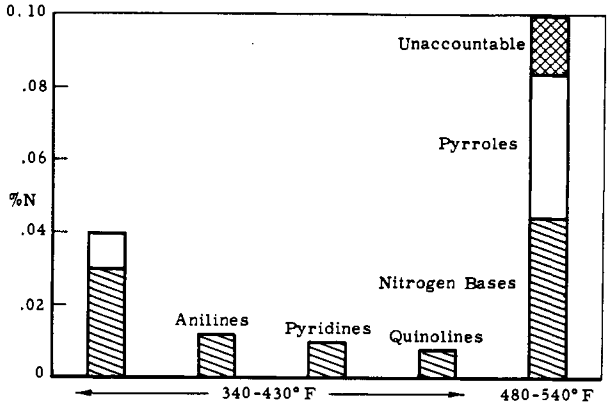

Figure 7. The nitrogen constitutents of cat. cracked gas oil fractions consist of anilines, pyridines, quinolines and pyrroles

A complete nitrogen aggregate was prepared by combining all overhead cuts. The properties are shown in Table III.

By acetylation 5.6 ml. of a pyridine-quinoline aggregate (40% quinolines, n_D^{20} = 1.5755) and 4.1 ml. of anilines (n_D^{20}= 1.5567) were obtained from 10.9 ml. of crude bases. On the basis of the refractive indices of quinoline ($1.6245^{24.9}$) and alkyl pyridines (1.505^{20}) a substantial portion of the pyridines are characterized by co-condensed naphthene rings, corresponding to 5,6,7,8-tetrahydroquinolines, or analogs with a five-membered saturated ring system (pyrindanes).

In Figure 8 the ultraviolet absorption spectrum of the anilines is compared with that of *m*-toluidine. Absorption maxima occur at 2400 and 2915 A. compared to 2350 and 2875 A. for the pure compound. This indicates the aniline aggregate is at least more highly substituted on the average than toluidine, a conclusion reinforced by the observed refractive index of 1.5567 and molecular weight of 130. The average aniline would appear to be somewhat more highly substituted than the xylidines.

Quinoline itself accounted for most of the quinolines present, as might be expected from its boiling point, 237.7° C. Very small amounts of substituted quinolines and possibly isoquinoline are also present.

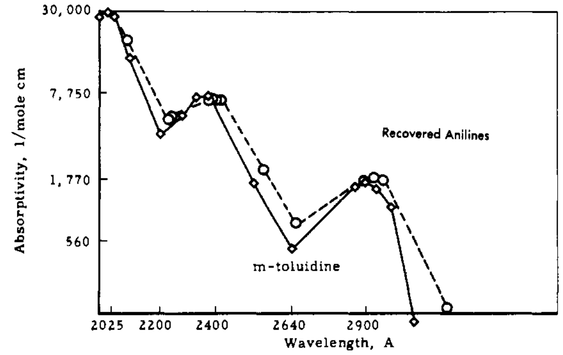

Figure 8. The ultraviolet absorption spectrum for anilines obtained from 340/430° F. cat. cracked gas oil resembles that of *m*-toluidine

Pyrroles. The properties of the pyrroles (includes pyrroles, indoles, and carbazoles) isolated from the 480/540° F. catalytically cracked gas oil fraction are shown in Table III. This fraction is a light yellow liquid boiling between 81° and 90° C. at 4 mm. Hg.

Infrared and ultraviolet spectra are shown in Figures 9 and 10. Infrared indicates intense NH structure at 2.87 and 2.89 μ (E = 5.6 liter/mole mm. compared to an average of 6.4 liter/mole mm. for indole and 2,5-dimethyl pyrrole). This absorptivity corresponds to a nitrogen content of about 8.1% compared to a value of 8.4% obtained by extrapolating the curve shown in Figure 11. The ultraviolet absorption spectrum is typical of indoles, with maxima at 2200, 2660, 2770, and 2880 A. The molar extinction coefficient at 2200 A. is 38,000 liters/mole cm. compared to a value of 25,600 for indole itself. The reason for this discrepancy has not been investigated further. However, the spectra show convincingly that the nitrogen atom itself is unsubstituted (infrared) and the pyrrolic compounds are chiefly indoles (ultraviolet).

Pyrroles constitute 0.5 weight % of the 480/540° F. gas oil fraction. This value agrees with a colorimetrically determined pyrrole content, using a modified Ehrlich reaction

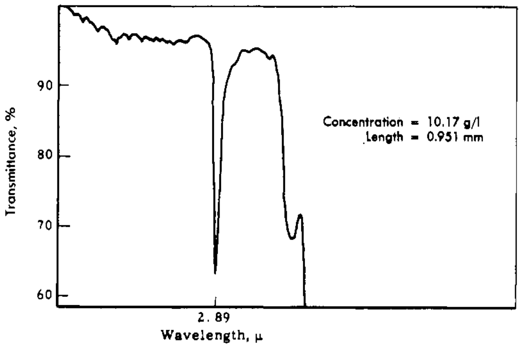

Figure 9. The infrared absorption spectrum for pyrroles obtained from 480/540° F. cat. cracked gas oil has a sharp H-N band at 2.89 μ

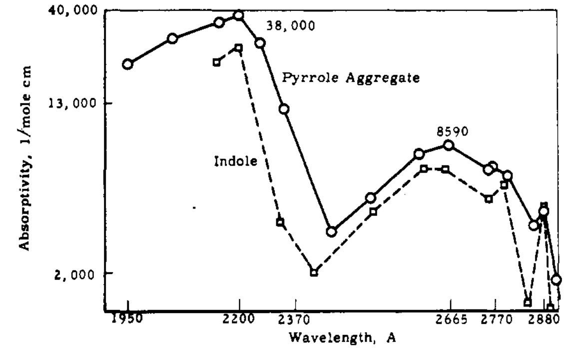

Figure 10. The ultraviolet absorption spectrum for pyrroles obtained from 480/540° F. gas oil resembles that of indole

Table III. Properties of Nitrogen and Oxygen Compound Fractions

Component	C.C. Gas Oil Fraction	Mol. Wt.	%N[a]	%O	Refractive Index, n_D^{20}
N-Bases	340/430	130	10.6 (10.8)	...	1.5612
Pyrroles	480/540	167	8.1 (8.4)	...	1.5927
Phenols	340/430	115	...	13.8 (13.9)	1.5362

[a] Numbers in parentheses represent theory.

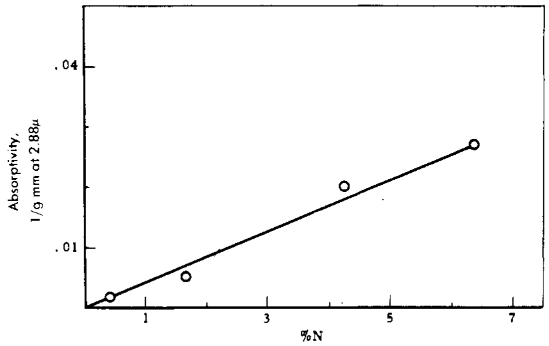

Figure 11. The infrared absorptivity for pyrrolic concentrates of various cat. cracked gas oil fractions increases with nitrogen content

with *p*-dimethylaminobenzaldehyde, which is believed to be sensitive to all pyrrolic constituents of aromaticity lower than carbazoles, a supposition supported by the results of the present investigation.

Thus the nitrogen picture is a fairly simple one with at least 80% of the nitrogen in this fraction accountable as nitrogen bases and pyrroles as shown in Figure 7 and tabulated below.

Distribution of Nitrogen in 480/540° F. Fraction

Basic	0.044
Pyrrolic	0.045
Unaccountable	0.016
Total	0.105

Agreement between the nitrogen content of the gas oil remaining after removal of pyrroles (0.045%) and the basic nitrogen content (0.044%) of the untreated gas oil is also excellent. It is therefore improbable that nitrogen basic to perchloric acid in this boiling range includes any appreciable quantities of basic pyrroles.

That all the pyrrolic constituents have unsubstituted nitrogen atoms can also be shown graphically by plotting $E_{2.88}$ *vs.* Kjeldahl nitrogen content for a number of pyrrolic concentrates from the various fractions. As shown in Figure 11 this curve is a straight line passing through the origin, thereby indicating that all the nitrogen is accounted for by N-H stretching frequencies.

Oxygen Compounds. We now have a fairly complete picture of the sulfur and nitrogen composition of the catalytically cracked gas oil but no systematic investigation has yet been made of the oxygen components. However, it is probable that cyclic oxygen systems similar to the sulfur and nitrogen systems are present at very low concentrations. The most abundant oxygen compounds found, however, were phenols. There is some evidence that these tend to be concentrated in the lower boiling catalytically cracked fractions. They occur to the extent of 0.26 weight % in the 340/430° F. fraction. Extraction with 20 volume % aqueous NaOH of the 340/430° F. hydrocarbon phase remaining after acid extraction to isolate the nitrogen bases gave practically quantitative yields of water-white phenols upon distillation. The crude phenolic aggregate possesses a molecular weight of 123, refractive index of 1.5325^{20}, and an oxygen content of 13.2 (theory for xylenol = 13.1). About 1% sulfur compounds were present in this product. The ultraviolet spectrum of the sulfur-free distilled phenols (properties shown in Table III) indicates phenols of high purity which contain about two alkyl substituents on the average. The purity of the phenols also suggests that the concentration of carboxylic acids must be quite low. The thermally cracked gas oil contained larger amounts of phenols than did the catalytically cracked whilst the straight run contained less.

LITERATURE CITED

(1) Apjohn, T., Nelson, F., *Petrol. Refiner* **27**, Part 2, 90 (1948).
(2) Johnson, C.R., Fink, D.F., Nixon, A.C., *Ind. Eng. Chem.* **46**, 2166 (1954).
(3) Lochte, H.G., Littman, E.R., "The Petroleum Acids and Bases," Chemical Publishing Co., New York, 1955.
(4) Schwartz, F., Ward, C.C., Smith, H., Soc. Automotive Engrs., preprint, November 3 (1953).

RECEIVED for review June 12, 1961. Accepted March 12, 1962. Division of Petroleum Chemistry, 130th Meeting, ACS, Atlantic City, N. J., September 1956.

CORRECTION

The article, "Vapor-Liquid Equilibria for the Ethane-Propane System," by D.E. Matschke and George Thodos [J. CHEM. ENG. DATA **7**, No. 2, 232 (1962)], should be changed as follows:

In Table I, last column, there should be no values under propane for the sixth item at 0° and the last item at 50° F.

In Table III, last column, there should be no values for the fourth and last items.

→

In revised Figure 3, corrected curves for propane at 0° and 50° F. are shown.