content of nitrogen. For those who wish to take the opposite view, asphalt may result from polymerization or condensation of the more reactive parts of the oil, and nitrogen would be expected to join these reactions.

Figure 2 depicts averages of the nitrogen-carbon residue ratio for oils produced from formations of different geologic ages. The number of oils entering into the averages for each period is given below the bar representing the ratio, so that greatest importance can be attached to those bars representing a large number of oils. It is apparent that oils from younger formations (Tertiary and Cretaceous) have higher ratios than those from the older formations, and oils from formations older than Triassic have a fairly constant value. This suggests that the ratio is significant in assessing the age of a petroleum.

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Neopentane and Cyclobutane in Western Venezuelan Crude Oils

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The presence of neopentane in crudes has been reported (*3*) and a quantitative method of analysis has been published (*4*). However, its presence is rarely reported in crude analyses and it is generally believed that the compound does not occur in most crudes. Cyclobutane has never been reported and probably does not occur naturally. A thorough investigation of straight-run refinery isopentane stream obtained from a western Venezuelan crude rich in naphthenes has shown that neopentane and/or cyclobutane are present in small amounts in certain crudes.

DETECTION AND QUANTITATIVE DETERMINATIONS

The routine gas chromatographic analysis of a virgin refinery isopentane stream derived from Bachaquero crude revealed two unidentified peaks in very low concentration. The chromatogram, presented in Figure 1, shows these two peaks, *A* and *B*, relative to the known constituents in the sample. This chromatogram was obtained with a standard Perkin-Elmer vapor fractometer. Resolution of the components was obtained using two columns in tandem. The columns consisted of 2 meters of tetraisobutylene on Celite followed by 2 meters of

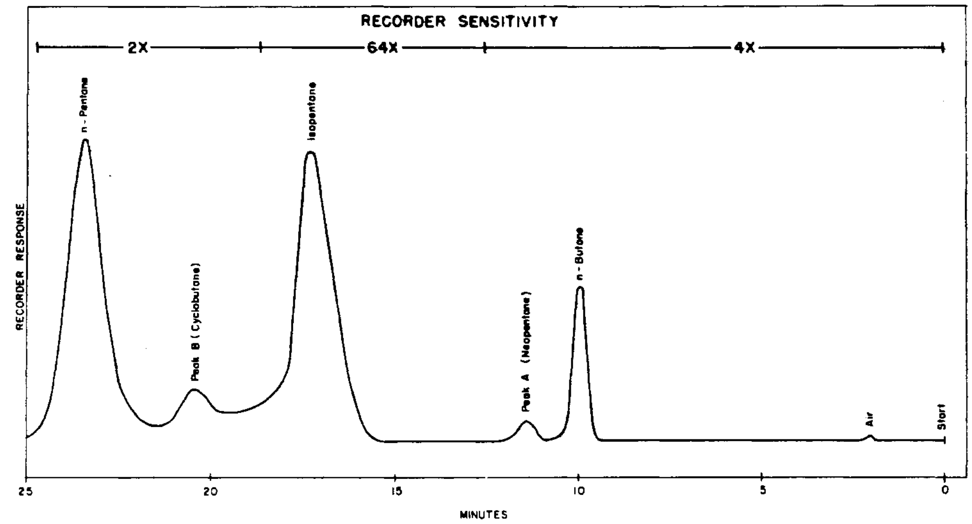

Figure 1. Gas chromatogram of refinery virgin isopentane using a two-stage column at 75° F.

diethylhexyl sebacate on Celite. Operating conditions are given in Table I. The composition of this sample, based on the relative area under each peak, is given in Table II.

Because of general nature of the stream neopentane was probably one of the unknown constituents. This was verified by determining the retention time of neopentane, under the same conditions as the sample, using a neopentane sample of at least 98% purity. The retention time observed for pure neopentane corresponded exactly with the first unknown peak (peak *A*).

Based on the boiling range of the sample, the other peak was probably cyclobutane, but this could not be verified in the same manner because pure samples of cyclobutane were unavailable. Cyclopentane was excluded because of boiling point considerations and because its retention time is much greater than that of *n*-pentane; the peak in question has a retention time shorter than that of *n*-pentane.

To obtain conclusive evidence that this peak is cyclobutane, the low boiling constituents of this stream were concentrated by high efficiency fractional distillation. Table III shows the boiling points and specific gravities of the various possible hydrocarbons between *n*-butane and cyclopentane.

Eight liters of sample were fractionated in a column of 80 theoretical plates at a reflux ratio of 20 to 1. That portion boiling up to 82° F., representing 4% of the sample, was collected and the bottoms discarded. Thus nearly all of the isopentane and all the *n*-pentane were removed from the sample. This 4% was refractionated in a column of 100 theoretical plates at a reflux ratio of 20 to 1. The first 50% was discarded, because this fraction was essentially pure *n*-butane with only trace quantities of neopentane as shown by gas chromatographic analysis.

The sample was concentrated by charging the bottoms from the second distillation, approximately 2% of the original sample, to a conventional Podbielniak low temperature distillation column segregating a fraction boiling between -2° and 45° F. at 400 mm. of mercury. This corresponds to a boiling range of approximately 35° to 75° F. at 760 mm. of mercury. The distillation curve, Figure 2, showed an ill-defined but still detectable plateau in the 50° F. region. Gas chromatographic analysis of this fraction, Figure 3, showed a large increase in the concentration of the peak suspected to be cyclobutane. This further substantiated the theory since cyclobutane has a boiling point close to but slightly higher than that of neopentane.

Table I. Operating Conditions for Gas Chromatographic Analysis

Chromatograph	Perkin-Elmer Model 154
Column dimensions	2 meters x ¼ inch
Column packings	2 meters of tetraisobutylene 35% by wt. on Celite 2 meters of diethylhexyl sebacate 35% by wt. on Celite
Carrier gas	Helium
Temperature	25° C.
Pressure:	25 p.s.i.g. flow rate, 66 ml./min.
Sample size	0.02 ml. liquid or 0.25 ml. gas
Recorder	L & N 0-10 mv. Type G Speedo-max recorder

Table II. Composition and Peak Retention Times of a Virgin Isopentane Stream

	R.T. Min.[a]	Mole %
n-Butane	9.9	1.21
Peak A	11.2	0.15
3-Methyl-1-butene	15.8	0.00
Isopentane	17.2	97.00
Peak B	20.5	0.17
n-Pentane	23.5	1.47
Cyclopentane	42.0	0.00

[a] Measured from moment of introduction to apex of component peak.

Table III. Physical Constants of Hydrocarbons from *N*-Butane to Cyclopentane (5)

	B.P., °F.	Sp. Grav., 60° F./60° F.
n-Butane	31.1	0.584
Neopentane	49.0	0.597
Cyclobutane	54.7	0.686
Isopentane	82.2	0.625
n-Pentane	96.9	0.631
Cyclopentane	120.7	0.751

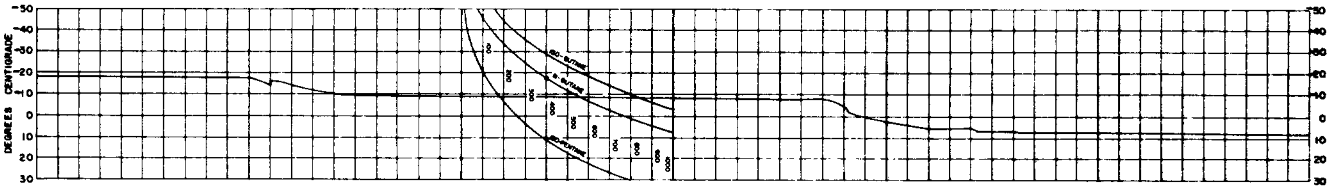

Figure 2. Distillation curve of fraction isolated by low temperature fractionation

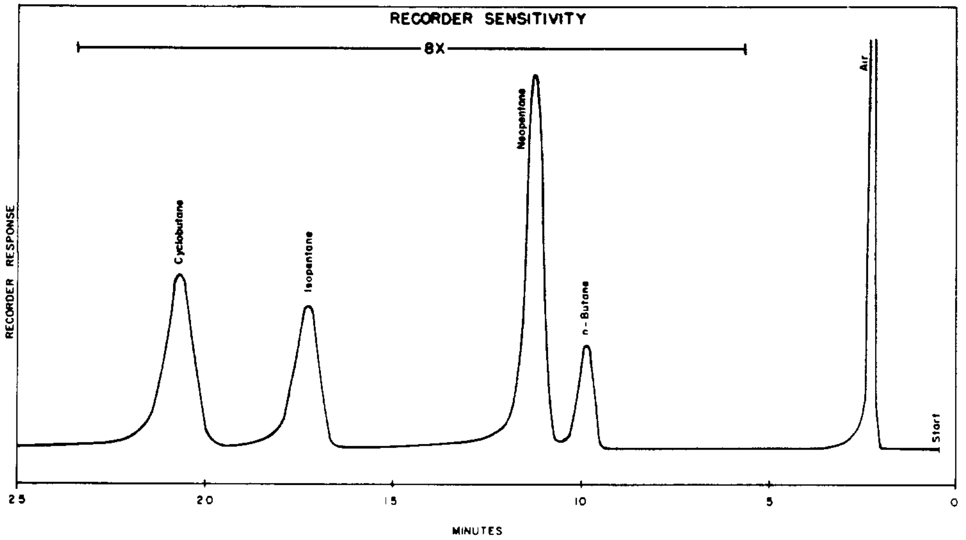

Figure 3. Gas chromatogram of fraction isolated by low temperature fractional distillation using a two-stage column at 75° F.

Final confirmation of the presence of cyclobutane was obtained with infrared spectrophotometry. A recording Beckman Model IR-2 infrared spectrophotometer was used in this part of the investigation. The conditions under which the various spectra were obtained are given in Table IV. Pure samples of the three known components, *n*-butane, neopentane, and isopentane, were scanned through the region in which cyclobutane would show maximum absorption and the other components would exhibit minimum absorption. The region 10.5 to 11.5 microns was selected based on spectra obtained through the API Research Project 44 (*1*, *2*). These are shown in Figure 4 with the spectrum of the concentrated portion of the sample.

Table IV. Operating Conditions for Infrared Identification of Cyclobutane

Wave length range, 10.5 to 11.5 microns; slit width, 0.429 mm., glass shutter; gain, 10.

Component	Operating Pressure (10 - Cm. Cell), Mm.
n-Butane	25
Neopentane	100
Isopentane	50
Cyclobutane	75[a]
Sample[b]	250

[a] Approximate pressure of cyclobutane in total sample.
[b] Sample containing all four components as shown in Figure 4.

The infrared spectrum of the sample showed high absorption at 10.9 and 11.0 microns. The peak observed at 10.9 microns is due to neopentane while the peak at 11.0 microns can only be attributed to cyclobutane. The complete spectrum of cyclobutane is shown in Figure 5.

Alpha-olefins also absorb in the region of 11.0 microns. Thus, isobutene, 1-butene, 3 methyl-1-butene, 1-pentene, or 2 methyl-1-butene could account for the absorbance observed at 11.0 microns. All but 3-methyl-1-butene can be excluded based on boiling points, since the two butene isomers have boiling points lower than that of *n*-butane, while the pentene isomers have boiling points higher than isopentane. 3-Methyl-1-butene, however, boils at 68.1° F. at 760 mm. of mercury. To eliminate this compound as a possibility, a synthetic mixture of pure isopentane, *n*-pentane and 3-methyl-1-butene was prepared and analyzed under the same conditions as the sample. The retention times observed were 15.8 minutes for 3-methyl-1-butene, 17.2 minutes for isopentane, and 23.5 minutes for *n*-pentane. Since the peak in question has a retention time of 20.5 minutes, it was concluded that it was due to cyclobutane.

A portion of the gas obtained from the low temperature fractionation was liquified and a micro specific gravity was determined. The liquid had a specific gravity of 0.633 at 60° F./60° F. compared to a calculated value of 0.630 at 60° F./60° F. If the unknown component had not been a cycloalkane, a specific gravity of 0.604 at 60° F./60° F. would have been observed.

RESULTS

Analysis of several other western Venezuelan crudes has shown that all contain neopentane in low concentration. However, it was found that Bachaquero is unique in that it also contains cyclobutane.

The concentration of neopentane indicated by these analyses corresponds to 0.003% of the crude by volume and is approximately the same for all western Venezuelan crudes. The concentration of cyclobutane corresponds to 0.001% of the crude by volume and is unique to Bachaquero crude.

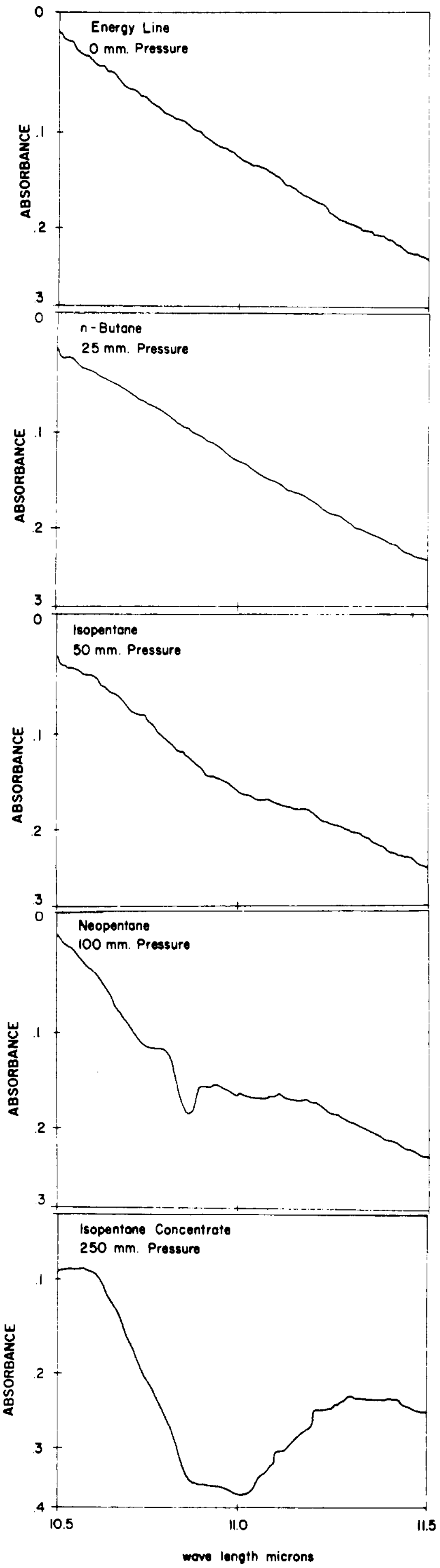

Figure 4. Spectra of pure hydrocarbons and concentrated fraction from refinery isopentane

All curves at indicated pressure in 10 cm. cell

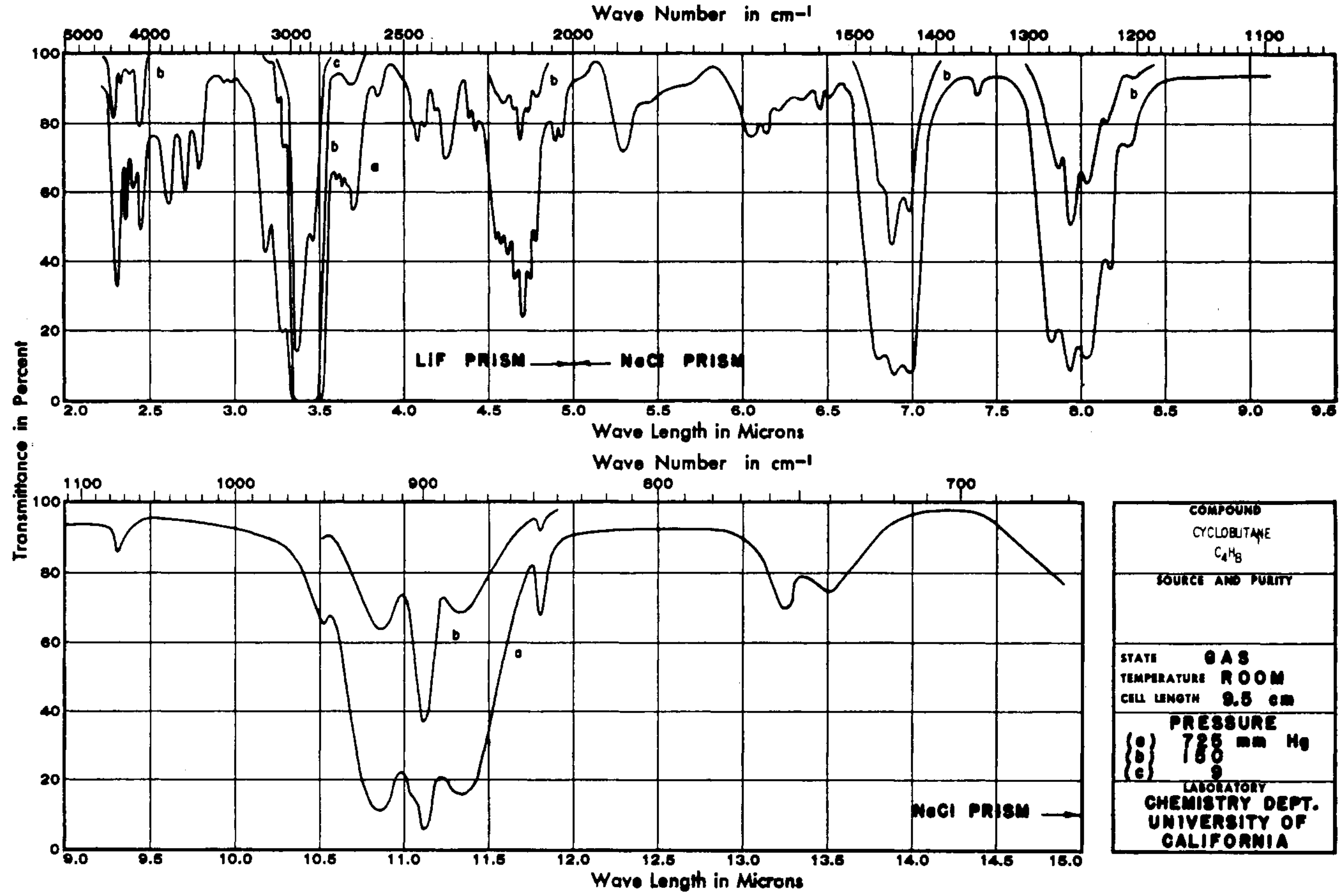

Figure 5. Infrared spectrum of cyclobutane

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Source and Some General Properties of Humic Acids from Lignitic Materials

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The lignite beds of North Dakota, South Dakota, and Montana contain numerous deposits of a poorly consolidated material, locally called leonardite, which is somewhat richer in oxygen and alkali-soluble, acid-insoluble components than is the average lignite. Although leonardite has some commercial value as an ingredient of drilling muds and as a soil conditioner, more important uses might be found for the recovered alkali-soluble portion as ion exchangers (*4, 17*) and as a source of chemicals (*9, 12*) and industrial carbon. Further, leonardite probably represents a naturally oxidized lignite (*18*) and might well be a logical starting point for an examination into the chemical nature of fossil fuels, since the products of coal oxidation, usually referred to as "humic acids," represent in the minds of many investigators (*1-3, 5, 6*, p. 404; *10-12, 15, 19, 21, 24*) minor degradation of the macromolecule to give material in part amenable to characterization by classical procedures. There is also strong evidence to support the theory that natural humic acids, which in general closely resemble the artificial product, are the precursors of some, if not all, coals (*7, 13, 14, 16, 22, 23*).