The Chemistry of Petroleum Hydrocarbons
Vol. 1 — Brooks, Kurtz, Boord, Schmerling
1954

in any crude oil with certainty. In all gasolines investigated, the abundance of 2,3-dimethylbutane is two or more times greater than that of 2,2-dimethylbutane.

Cyclopentanes and cyclohexanes are the only types of cycloparaffins found in gasoline fractions. Cycloheptane, found in Ponca gasoline in a very small amount (Table 1), is the only known exception. Of the cyclopentanes, cyclopentane itself is present in every crude oil, but in a very small amount, whereas alkylcyclopentanes are, in general, quite abundant. By contrast, alkylcyclohexanes and cyclohexane are quite abundant in crude oils. The alkylparaffins with two methyl groups at the same ring-carbon atom (in general, 1,1-dialkylparaffins) are less abundant than the isomers with two separated methyl groups.

Two bicyclic cycloparaffins were isolated, but not identified, in Ponca petroleum (Table 1).

As has been mentioned above, all aromatic hydrocarbons from benzene to C_9-alkylbenzenes were identified in Ponca petroleum; and, from benzene to C_8-alkylbenzenes, in other gasolines investigated. With few exceptions, the amount of benzene in crude oils is small, of the order of 0.2 per cent or less, whereas all crudes contain large percentages of toluene and C_8-alkylbenzenes. Of the C_8-isomers, meta-xylene is the most abundant.

Aromatic hydrocarbons of ten or more carbon atoms, identified in various crude oils, are either polynuclear aromatics or higher homologs of benzene. 1,2,3,4-Tetrahydronaphthalene, naphthalene, and numerous mono-, di-, and trimethyl (ethyl) alkyl derivatives of these hydrocarbons have been found in various petroleums of this country, Europe, and Asia. The fused (condensed) structure of polycyclic aromatic hydrocarbons seems to be predominant in petroleums. Phenylcyclopentane so far is the only nonfused dicyclic aromatic hydrocarbon separated from Ponca crude oil (identification is not complete). Biphenyl and 3-methylbiphenyl have been separated and identified in W. Edmond crude oil.[1]

Up to the present time, none of the unsaturated hydrocarbons has been identified in virgin crude oils. The possibility of the presence of olefins in crude oils will be discussed later.

The general similarity of the chemical composition of crude oils may lead one to the hypothesis that the hydrocarbons of crude oils approached equilibrium under temperature-pressure conditions of formation that were more or less similar for all crude oils. Generally speaking, this hypothesis is not compatible with the thermodynamic properties of hydrocarbons. As a matter of fact, all hydrocarbons of crude oils are thermally unstable and potentially convertible to such stable systems as, e.g., methane or ethane and carbon. Such reactions, however, require high values of acti-

DSW 297655
STLCOPCB4067568

produced fractions of significant 10.4-micron-band intensity. According to Lillard *et al.*, the unsaturate-type reactions observed for certain lubricating oils may be caused by some cycloparaffin structures undergoing this type of reaction.

It seems quite convincing that the 10.3-micron absorption band of lubricating oils is not due solely to olefins. If the intensity of the 10.3-micron absorption band is due to the combined effect of polycyclic cycloparaffins and trans-olefins, it is impossible at present to ascertain the part played by each of these constituents in the effect of absorption.

References

1. Adams, N. G., and Richardson, D. M., *Anal. Chem.*, **23**, 129 (1951); **25**, 1073 (1953).
2. Bell, M. F., Atlantic City Meeting, Am. Chem. Soc., Petr. Div., p. 77, Sept. 1949.
3. Charlet, E. M., Lanneau, K. P., and Johnson, F. B., Cleveland Meeting, Am. Chem. Soc., Petr. Div., p. 105, April, 1951.
4. Clere, R. J., Kincannon, C. B., and Wier, T. P. *Anal. Chem.*, **22**, 864 (1950).
5. Danaila, N., and Samuel, *Chem. Abs.*, **34**, 3059 (1941).
6. Donald, R. M., *Canadian J. Research*, **19**, 21 (1940).
7. Evans, A., Hibbard, R. R., and Powell, A. S., *Anal. Chem.*, **23**, 1604 (1951).
8. Forziati, A. F., Willinham, C. B., Mair, B. J., and Rossini, F. D., *Refiner* (November 1943).
9. Fred, M., and Putscher, R. E., *Anal. Chem.*, **21**, 900 (1949).
10. Gooding, R. M., Adams, W. G., Rall, H. T., and Smith, H. M. New York Meeting, Am. Chem. Soc., Petr. Div., September 1944.
11. Grosse, A. V., *Refiner* (April 1939).
12. Grosse, A. V., and Mavity, J. M., Boston Meeting, Am. Chem. Soc., Petr. Div., September 1939.
13. Haak, F. A., and van Nes, K., *J. Inst. Petroleum Tech.*, **37**, 245 (1951).
14. Hibbard, R. R., and Cleaves, A. P., *Anal. Chem.*, **21**, 486 (1949).
15. Komarewsky, V. I., and Riesz, C. H., *Oil Gas J.* (June 24, 1943).
16. Leslie, R. T., and Heuer, W. W., *J. Research Natl. Bur. Standards*, **21**, 515 (1938).
17. Lillard, J. G., Jines, W. C., and Anderson, J. A., Cleveland Meeting, Am. Chem. Soc., April 1951, Symposium on the Composition of Petroleum, p. 123.
18. Lipkin, M. R., and Kurtz, S. S., Detroit Meeting, Am. Chem. Soc., 1940.
19. Lipkin, M. R., Martin, C. C., and Hoffecker, W. A., Chicago Meeting, Am. Chem. Soc., April 1948, Petr. Div., p. 31.
20. Mabery, C. F., and Mathews, J. H., *J. Am. Chem. Soc.*, **30**, 992 (1908).
21. Mair, B. J., and Rossini, F. D., "The Science of Petroleum." Vol. 5, Part I, p. 126 (1950).
22. Mair, B. J., and Willingham, C. H., *J. Research Natl. Bur. Standards*, **17**, 926 (1936).
23. Mair, B. J., Willingham, C. H., and Streiff, A. J., *J. Research Natl. Bur. Standards*, **21**, 536 (1936).
24. Mair, B. J., Sweetman, A. J., and Rossini, F., D. *Ind. Eng. Chem.*, **41**, 2224 (1949).
25. Muller, J., and Neyman-Pilat, E., *J. Inst. Petroleum Tech.*, **23**, 669 (1937).
26. Putscher, R. E., *Anal. Chem.*, **24**, 1551 (1952).

DSW 297657

STLCOPCB4067569