Isolation and Identification of Biphenyls from West Edmond Crude Oil

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The sometimes adverse effects of aromatic hydrocarbons on the combustion characteristics and deposit-forming tendencies of Diesel fuels have stimulated interest in the aromatic hydrocarbon content of such fuels. Ultraviolet spectra of distilled fractions had indicated the probable presence of biphenyls. The present report confirms the presence of biphenyl and 3-methylbiphenyl, and indicates the probable presence of alkylated biphenyls of higher molecular weight. The separation and identification of the two biphenyls definitely found are described. As this is the first time these compounds have been reported in virgin stocks from crude oils, it establishes the presence of such a series of aromatic hydrocarbons in crude oil and is, therefore, important not only from a commercial or practical point of view, but also scientifically.

investigation of the presence of biphenyls in a crude oil
rt of an extensive Diesel-fuel program being conducted
ureau of Mines Petroleum Experiment Station, Bartles-
a. This program involves the determination and study
mposition and properties, including combustion charac-
of Diesel fuels (*1, 3, 4, 6, 7*).

arlier paper by the present authors (*2*) the presence of bi-
id one of its methyl derivatives in close-cut distillation
from a crude oil from the West Edmond field in Okla-
s strongly inferred by ultraviolet spectra. The present
s undertaken to prove the presence of biphenyl and its
in a straight-run distillate fuel.

EXPERIMENTAL

quence of operations followed in the investigation was:
ent fractional distillation of the crude oil, (*b*) isolation of
nyls from their respective fractions, and (*c*) identifica-
ese biphenyls by their infrared spectra.

nal Distillation of the Crude Oil. The fractional dis-
f the crude oil, as described in an earlier paper (*2*), pro-
ter fractions, each representing 0.25% of the crude oil,
olumn of approximately 80 theoretical plates at atmos-
ssure. The distillation was conducted at a pressure of
f mercury; it is believed that no significant cracking

n of Biphenyls. The ultraviolet absorption spectrum
was determined for each of 61 fractions, covering the boiling range of 207° to 290° C. (405° to 554° F.). These fractions exhibited, for the most part, absorption patterns common to alkylbenzenes and alkylnaphthalenes (*2*). Two fractions, Nos. 65 and 79, with corrected boiling points near 241° and 262° C. (466° and 504° F.), respectively, however, exhibited spectra radically different from the others, but similar to spectra of biphenyl and its homologs, with absorption maxima centered around 250 mμ. It had been learned previously (*2*) that the compounds responsible for these particular spectra could be concentrated by adsorption on silica gel. The biphenyl-containing subfractions from silica gel adsorption of fraction 65 solidified on cooling, and white crystals were separated and recrystallized repeatedly from alcohol.

The concentrate of fraction 79, however, was liquid, as are the three methyl derivatives of biphenyl. As alkylnaphthalenes composed the major contaminants, the concentrate was repeatedly treated with 1,3,5-trinitrobenzene solution for their removal by complexation.

Identification of Individual Biphenyls. The infrared spectrum of the white crystalline material, in solution in carbon disulfide, was determined and compared to a spectrum obtained similarly from a recrystallized Eastman sample of biphenyl. These comparison spectra are shown in Figure 1.

The infrared spectrum of the concentrate from fraction 79 was also determined and compared to those of 2-methyl- and 3-methylbiphenyl (*5*) furnished by the National Advisory Committee for Aeronautics. These spectra showed that the concentrate contained approximately 75% of the 3-isomer, while the 2-isomer could not be identified. The comparison spectra of the concentrate and 3-methylbiphenyl are shown in Figure 2. The spurious absorption around 13 microns and at 12.35 microns is attributed to the residual naphthalenes in the sample because the

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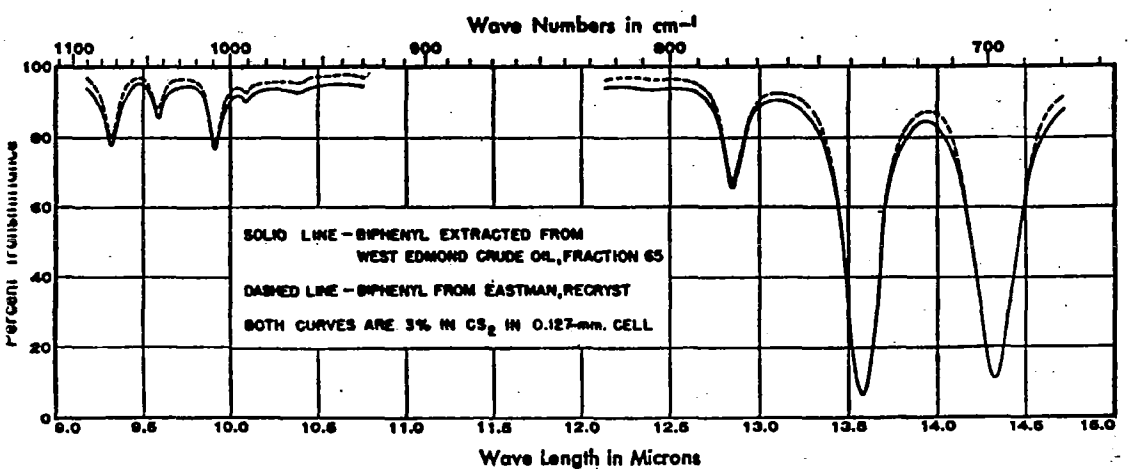

Figure 1. Comparison Spectra of Biphenyl

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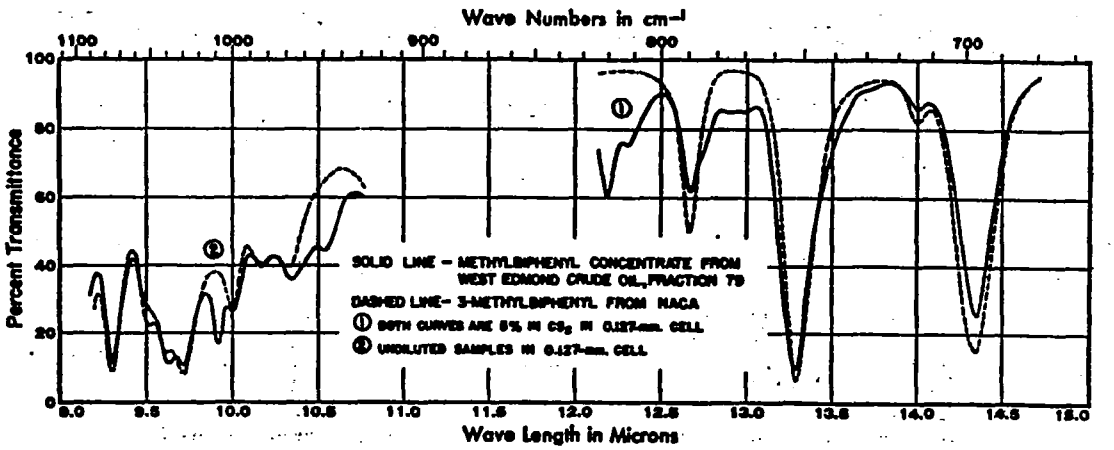

Figure 2. Comparison Spectra of 3-Methylbiphenyl

intensity of these absorption bands progressively decreased with the 1,3,5-trinitrobenzene treatments described above. The well-defined absorption band at 12.21 microns, however, does not decrease with removal of naphthalenes and is thought possibly to be caused by a small concentration of 4-methylbiphenyl for which a spectrum was not available.

DISCUSSION OF RESULTS

The infrared spectra presented here conclusively confirm the presence of biphenyl and 3-methylbiphenyl in fractions 65 and 79. The quantity of biphenyl is estimated as being 0.002 to 0.003% of the crude oil.

The presence, also, of some higher alkylated derivatives of biphenyl is inferred by the ultraviolet spectra of some higher-boiling fractions. A well-defined absorption band in the ultraviolet at 252 mμ appears superimposed upon an otherwise naphthalenic-type spectrum in 8 fractions with corrected boiling points from 283° to 290° C. (541° to 554° F.). In this case, however, this biphenyl-type absorption did not dominate the spectrum of the sample, as in fractions 65 and 79 (*2*). At present, the ultraviolet spectra have not been determined on fract boiling above this point, therefore, further recurrences of l boiling homologs have not been established.

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RECEIVED for review December 29, 1952. Accepted April 6, 1953. sented before the Southwest Regional Meeting, AMERICAN CHEM SOCIETY, Little Rock, Ark., December 1952.

Improved Electrophoresis Apparatus for Small Volumes

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ALTHOUGH several forms of micro- and semimicro electrophoresis apparatus are now available (*1*, *3*, *10*), the reduction in the volume of solution required for an analysis has in each case been made at a sacrifice in the resolving power and optical sensitivity of the standard 11-ml. cell. This report describes a cell requiring only 2 ml. of solution, together with the associated autocollimating optical system in which reflection of the light back through the channel of the cell compensates, in large part, for the reduced dimensions. Tests of the new equipment indicate that the resulting patterns are comparable in quality with those obtained in the conventional apparatus.

APPARATUS AND PROCEDURE

The 2-Ml. Cell. In the standard 11-ml. cell the width, w, of the channel is 3 mm., the depth, a, is 25 mm., and the clear height, h, of each side is 86 mm. Here the width is the critical dimension in controlling convection, the depth determines the optical sensitivity, and the height determines the resolving power for ions whose mobili[illegible]

w = 2 mm., a = 10 mm., and h = 70 mm. The considerati leading to this choice of values are given below.

Although the convective circulation of the solution in the ch nel resulting from the dissipation of the Joule heat decreases w the width, the ratio of the surface to the volume is ther increased and electro-osmosis and other wall effects become a turbing factor in narrow channels. There is, therefore, an o mum width. From tests on the resolution of the two compone of ovalbumin in channels of 3-, 1.5-, and 0.85-mm. width, optimum appears to be about 2 mm. (*9*).

In view of the recent progress in adapting interference meth for recording the refractive index as a function of the height in channel, a considerable reduction in the dimension, a, controll the optical sensitivity, appeared possible. Moreover, follow a suggestion made in 1939 by Chambers (*2*), and incorpora in one of the commercial instruments (*3*), this sensitivity can doubled by reflecting the light [illegible]

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