THE ISOLATION AND IDENTIFICATION OF 2,6-DIMETHYLNAPTHALENE FROM WEST EDMOND CRUDE OIL[1]

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The isolation and identification of 2,6-dimethylnapthalene described in this report are incidental to a larger and much more extensive program in which the Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla., is at present engaged. This program in its widest ramifications involves the determination and study of the composition and properties of Diesel fuels. West Edmond crude oil is one of the sources of the Diesel fuels being investigated.

In the course of this study, 518 gallons of West Edmond crude oil were processed in continuous (Ward and Schwartz, ms.) and batch stills at atmospheric pressure and at 15-mm pressure to yield a gas-oil cut representing 52.7 weight percent of the crude oil. An appropriate part of this was charged to a 100-gallon "superfractionating" unit described by Ward, Gooding, and Eccleston (1947) the performance of which has been found to be comparable to an 80-plate laboratory fractionating column also in use at the Bartlesville Station.

The distillation in the 100-gallon fractionating unit was conducted at atmospheric pressure up to 400°F, during which period forty 2-liter fractions were removed. At this point the pressure in the still was reduced to 50 mm, and further distillation provided 65 more 2-liter fractions (Nos. 41 to 106). These portions constituted 17.2 weight percent of the crude oil and included a boiling range, corrected to atmospheric pressure, of 400° to 568°F. The distillation was continued from this point at a lower pressure but as the subject of this paper concerns only fraction 69 from the 50-mm-pressure portion of the distillation nothing further need be mentioned of the remainder. Fig. 1 gives a graphic outline of the steps involved in the separation of this fraction from West Edmond crude oil.

Fraction 69 was removed from the column at a (corrected) top temperature of 471° to 475°F (244° to 246°C). It constituted 0.257 weight percent of the crude oil. According to the routine schedule of treatment previously planned for these fractions, it was subjected to silica-gel filtration to separate it into an aromatic portion and a paraffin-napthene portion. This process is now quite widely employed (Mair, Goboriault, and Rossini 1947) for this type of separation and need not be discussed in detail here. The essential steps of the procedure are to percolate the sample through an appropriately dimensioned column filled with silica gel, collect fractions as the percolate leaves the bottom of the column, and observe the progress of the percolation by measurements of volume and of some property of the percolate, usually refractive index. Fig. 2 shows an adsorptogram for fraction 69 and is typical of this type of data obtained from high-boiling petroleum fractions.

During filtration of fraction 69 through silica gel a crystalline solid formed in the receiver while the latter half of the aromatic portion was being collected. This material was isolated by repeatedly chilling and centrifuging combined subfractions 14, 15, and 16 (Fig. 2) in which the crystallization occurred. Following this the material was recrystallized from ethanol, centrifuged, and recrystallized from methanol. The product had a melting point uncorrected for stem exposure of 100.9° to 103.2°C at this stage, and repeated recrystallizations from methanol yielded a material with final melting point of 108.0° to 109.2°C (uncorrected).

From consideration of the boiling range of the portion from which the solid crystallized, and the occurrence of this material in the aromatic portion from the silica-gel adsorption, the crystalline unknown was thought to

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be one of the solid dimethylnapthalenes. On the basis of simple visual comparison of the fluorescences of the unknown and various commercial samples of dimethylnapthalenes in this laboratory the 2,6-isomer was chosen for further comparisons.

A sample of Edcan Laboratories' 2,6-dimethylnapthalene, m.p. 100.9°-103.2°C (uncorrected), was recrystallized until a constant melting point of 109.7°-109.9°C (uncorrected) was obtained. For final purification the sample was sublimed, but the melting point remained unchanged. The mixed melting point of this sample with an approximately equal quantity of the unknown was 109.8°-110.2°C (uncorrected).

Picrates of both the unknown material and the purified Edcan sample were prepared from methanol solution, as was also a mixed picrate from a solution containing equal quantities of both samples, giving the following uncorrected melting points: Picrate from the unkown, 141.4°-141.9°C; picrate from the purified Edcan sample, 141.4°-141.9°C; and picrate from the mixed sample, 141°-142°C. These data compare favorably with those of 2,6-dimenthylnapthalene synthesized by Bailey *et al.* (1947), who reported a melting point of 110°-110.5°C and for the picrate 140°C, all temperatures uncorrected for stem exposure.

TABLE I

Melting points of purified 2,6-dimethylnaphthalene and picrates prepared from them

Sample	Melting points (°C) obtained with: Hg thermometer (uncorrected stem)	Pt resistance thermometer
Edcan Laboratories 2,6-dimethylnapthalene	109.7-109.9	109.7-110.1
West Edmond 2,6-dimethylnapthalene	108.0-109.2	109.2-109.8
50-50 mixture of above	109.8-110.2	——
Picrate from Edcan 2,6-dimethylnaphthalene	141.4-141.9	141.4-141.9
Picrate from W. Edmond 2,6-dimethylnaphthalene	141.4-141.9	141.7-142.2
Picrate from 50-50 mixture of above	141.0-142.0	——

As another check on the identification, the ultraviolet absorption spectra were determined for both the unknown sample and the purified Edcan material. As shown in Fig. 3, the wavelengths of the absorption maxima coincide throughout the 215- to 330-millimicron region. The wavelengths in millimicrons of these absorption maxima were found to be 227.0, 274.0, 303.0, 310.0, 317.0, and 324.5. These spectra were then compared with spectra for all 10 dimethylnaphthalenes (Bailey, Bryant, Hancock, Morrell, and Smith 1947) and were found to be identical to only that for the 2,6-isomer.[2]

For determining the ultraviolet absorption spectra, measurements were taken on a Beckman *Model DU* photoelectric quartz spectrophotometer described by Carry and Beckman (1941). Calibration of the wavelength scale of the instrument with a mercury-vapor lamp indicated that over the range 238 to 365 millimicrons its error was less than ± 0.1 millimicron. Isooctane, filtered thru silica gel to remove interfering compounds, was used as the solvent.

The authors wish to express their appreciation for aid given by John Moore, Mary Nan Steel, and Dorothy Richardson who participated in various steps in the isolation, purification, and analysis of the hydrocarbon reported in this paper.

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[2]After completion of this report an ultraviolet spectrogram of 2.6-dimethylnapthalene was received from the American Petroleum Institute Research Project 44 contributed by the Socony-Vacuum Co. of Paulsboro, N. J. This is the only spectrogram for this compound in the A.P.I. collection and agrees with that of the hydrocarbon isolated from West Edmond crude oil.

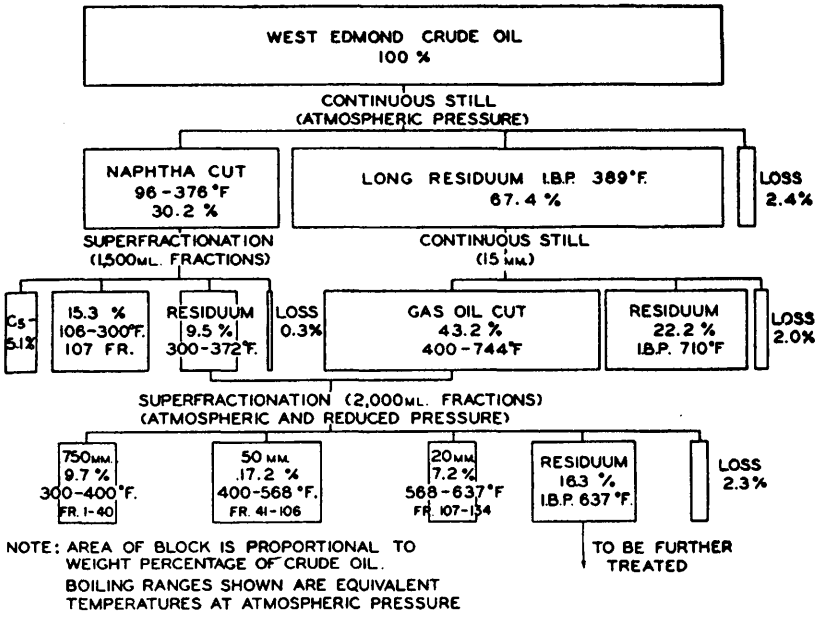

Fig. 1. Summary of treatment of West Edmond crude oil.

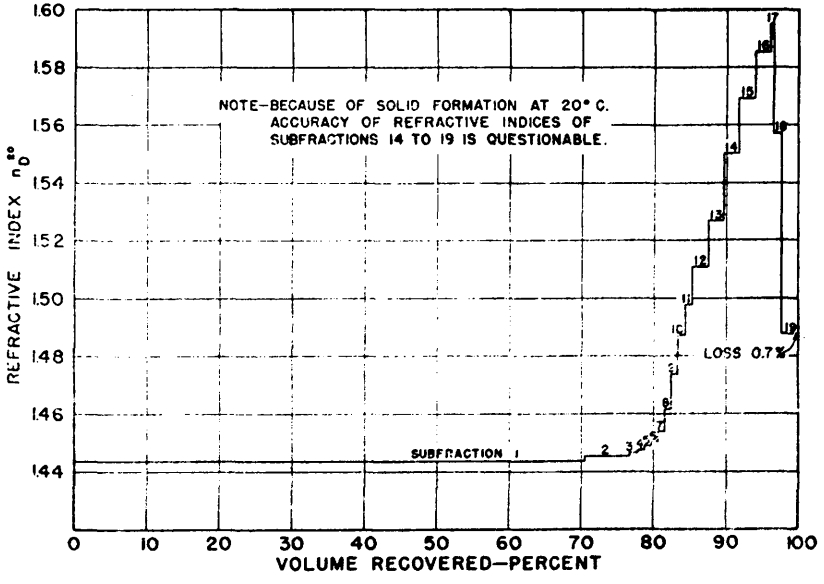

Fig. 2. Adsorption of silica-gel filtration of fraction 69.

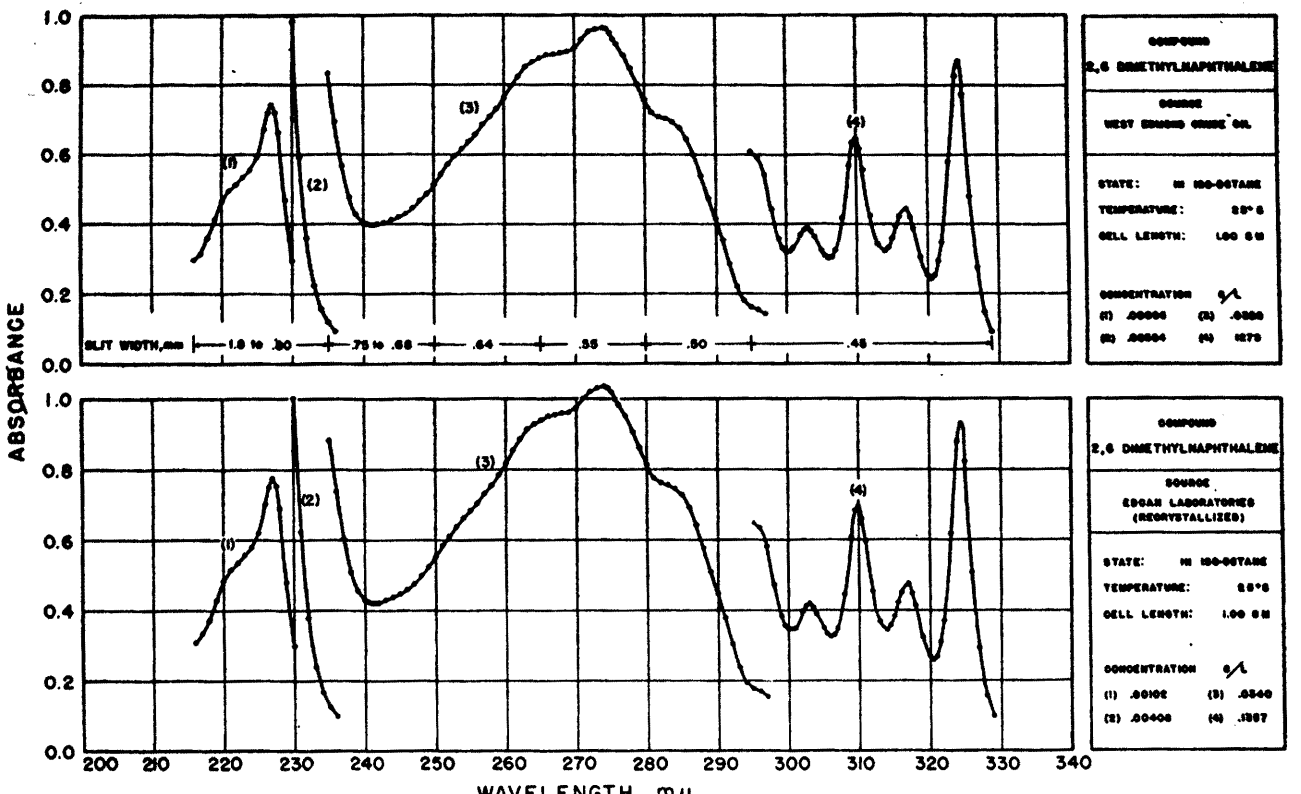

Fig. 3. Comparison of ultraviolet absorption curves.

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