

# On the Composition of Japanese Petroleum, II.

By

**Shigeru Komatsu and Naozo Tanaka.**

(Received Sept. 21, 1923)

---

In the first article, one of us and S. Kusumoto<sup>1</sup> made a communication on the isolation of cyclohexane and methylcyclopentane from the Nishiyama oil, Echigo. The present study is concerned with the identification of benzene and n-hexane isolated from the oil, which were regarded as having the most intimate relation to these naphthenes described in the previous article with respect to the genetic formation from the vegetable or animal kingdom.

The presence of benzene in the Nishiyama oil is undoubted since it has been proved that the main part of the fraction B. p. 70—90°, constitutes of cyclohexane which can be transformed catalytically into benzene and vice versa.

Moreover, S. Takano has reported that the fraction B. p. 80—82°, of the Amaze oil, Echigo, yielded by nitration 22% of dinitrobenzene<sup>2</sup>, and the results of other investigators<sup>3</sup> show that petroleum from many parts of the world contained benzene to some extent.

---

<sup>1</sup> These Memoirs, **7**, 77 (1923).

<sup>2</sup> Engler- Höfer : Das Erdöl, I, 360 ; There arises a question with the formation of the nitro compound, since naphthenes by treating with con. nitric acid yield some nitro aromatic compounds, (S. K) and also refer Balbiano : Chem. Z. 1902, II, 402 ; W. Markownikoff : Ber. D. Chem. Ges., **33**, 1908 (1900) ; Lieb. Ann., **307**, 342 (1899).

<sup>3</sup> Engler- Höfer : Das Erdöl, I, 361.

**BENZENE.**

The fraction B. p. 70—90°, of the Nishiyama oil was treated with fuming sulphuric acid containing 7% SO<sub>3</sub>, and the acidic solution separated from the oil part, was diluted with ice, neutralized with calcium hydroxide, filtered off calcium sulphate, and an excess of lime in the solution was removed by means of carbon dioxide, the filtrate free from the carbonate was treated with sodium carbonate to convert calcium benzene sulphonate formed in the solution by above treatments into the sodium salt, and then the solution was evaporated to dryness. It gave 12 grm. of the sodium salt which was subjected to the alkali fusion with 21 grm. caustic soda, and the oily substance generated by the fusion, amounting to 2.2 grm., was fractionated twice under ordinary pressure after drying with anhydrous sodium sulphate.

|               |            |          |
|---------------|------------|----------|
| 1st. fraction | below 182° | 0.6 grm. |
| 2nd. ,,       | 182—183°   | 0.8 ,,   |

The second fraction solidified in fine needle crystals, and shows the violet colour reaction with ferric chloride solution and the Liebermann reaction for the nitroso compounds. It was analysed and the results C=73.55 ; H=6.45, being small compared with the calculated value for phenol C=76.55 ; H=6.43, show that some aliphatic alcohols might be present as an impurity.

It was then treated with benzoyl chloride in the alkaline solution to get phenol in a pure state, according to the direction of Baumann<sup>1</sup>, and also of Behal and Choay,<sup>2</sup> and the benzoic acid ester thus formed after purification as usual, was found to melt at 69—69.5°.

It gave on analysis the following results C=78.95 ; H=5.22, which agree well with the theory C=78.8 ; H=5.1 required for C<sub>13</sub> H<sub>10</sub> O<sub>2</sub>.

<sup>1</sup> Ber. D. Chem. Ges., 19, 3218 (1886).

<sup>2</sup> C. R. 118, 1211 (1894).

By the treatment with fuming sulphuric acid, the benzene in the oil yields benzene sulphonic acid which, by alkali fusion and benzoylation, is transformed into phenol, and then into phenol denzoate successively. It was thus proved by chemical means that benzene is present in the Nishiyama oil.

**NOR. HEXANE.**

To isolate the hydrocarbon, the fraction B. p. 40—75°,  $d_4^{25} = 0.697$  of the Nishiyama oil was carefully fractionated under ordinary pressure seven times in a dephlegmator with two columns, and the fraction B. p. 66.5—71°,  $d_4^{25} = 0.6938$  weighing 94 grm. was subjected to oxidation with con. nitric acid (1.5), following the directions of S. Young<sup>1</sup>. Cyclopentane, its methyl derivatives, and isohexane, these isomeric substances of n-hexane were oxidized by this treatment, whereby n-hexane remains partly unaffected by the action of con. nitric acid. The reaction product washed with water and dilute alkali solution and dried with calcium chloride, and then it was subjected to fractional distillation on metallic sodium four times under ordinary pressure.

|    | Fraction.   | Yield.   |                     |
|----|-------------|----------|---------------------|
| 1. | below 68.5° | 1.9 grm. |                     |
| 2. | 68.5—69.5°  | 1.6 ,,   | $d_4^{25} = 0.6708$ |
| 3. | 69.5—70.5°  | 1.5 ,,   |                     |

To get n-hexane in a pure state, the fractionation was continued, and after the 7th. distillation under 749 m.m., the fraction B. p. 67. 5—68°.5 was analysed C=83.05 ; H=15.93,  $d_4^{25} = 0.66863$ .

---

<sup>1</sup> J. Chem. Soc., **73**, 906 (1898).

*146 S. Komatsu and N. Tanaka. On the Composition of Japanese Petroleum, II.*

The other fractions B. p. 66.5—67.5° and B. p. 68.5—69.5° were combined together, and the mixture fractionated nine times under ordinary pressure, and the fraction B. p. 71—73° was analysed with the following results :

$$C=83.80 ; H=15.80 ; d_4^{20} = 0.67178.$$

Thus, we may conclude that the Nishiyama oil surely contains n-hexane though the analytical figures and the density of the fraction B. p. 67.5—68.5 under 749 m.m. show a slight difference compared with the calculated percentage for n-hexane, and the density observed by other chemists of the hydrocarbon isolated from petroleum<sup>1</sup> and of the synthetic one<sup>2</sup>.

July 1923. Laboratory of Organic and Bio-chemistry.

---

<sup>1</sup> Engler and Höfer : *Das Erdöl*, I. 244 ; Brooks : *The non-benzenoid hydrocarbons*. p. 99, 548.

<sup>2</sup> Beilstein : *Handbuch d. Org. Chem.*, 4 auf. I, 143 (1918).