oil. Manifestly, it would not pay to attempt to extract these small proportions from the oil by distillation methods. Furthermore, investigation has proven the lower aromatic hydrocarbons, benzene and toluene, to be almost entirely absent from American crude oils, although appreciable amounts of aromatic hydrocarbons of higher molecular weight are present, particularly in oils of asphaltic base.

The existence of heavier aromatics in a natural state in certain oils, particularly Russian, Roumanian, Californian, and Japanese oils, has led a number of experimenters to attempt to devise methods whereby the yields of hydrocarbons of this series can be greatly increased from such oils. Probably the most work in this field has been done with Russian and Roumanian oils, because of the peculiarly favorable nature of these oils by reason of their content of hydrocarbons of the naphthene type. It is well known to chemists that hexahydrobenzene, for example, will readily split off six hydrogen atoms and leave benzene. This dehydrogenation process is relatively simple and is described in most textbooks of organic chemistry. The character of the reaction involved in making aromatic hydrocarbons from hydrocarbons of the naphthene type, involving a simple splitting off of hydrogen, must not be confused with that involved in making aromatic hydrocarbons from those American petroleums that contain practically no naphthene hydrocarbons.

PROCESSES PATENTED FOR PRODUCTION OF AROMATIC HYDROCARBONS FROM PETROLEUM.

The method devised by Letny [a] involved the passage of petroleum residues obtained from Baku crudes through a highly heated horizontal retort, 7 feet long and 1 inch in diameter, filled with wood charcoal. The residues were allowed to flow through the tubes, which were heated to approximately 700° to 800° C., the vapors coming from the tubes passing to a condenser. The claim was made that 50 to 60 per cent of gas and 40 to 50 per cent of tar was obtained. The tar, on distillation, gave some 17 per cent benzene, 0.4 per cent anthracene, and 7 per cent naphthalene. The oil was fed in slowly, as Letny considered it essential that a comparatively great heating surface be exposed.

Armstrong and Miller [b] reported that their experiments had shown that the liquid formed during the decomposition of petroleum gases contained a mixture of hydrocarbons of the C_nH_{2n-2} series. The

[a] Letny, Alexander, Ueber die Zersetzung des Petroleums und des Braunkohlentheers durch Ueberhitzen: Ber. Deut. chem. Gesell., Jahrg. 11, 1878, pp. 1210–1212; Decomposition of petroleum and lignite tar by superheating: Chem. News, vol. 38, 1878, p. 211.

[b] Armstrong, H. E., and Miller, A. K., On the decomposition and genesis of hydrocarbons at high temperatures; The products of manufacture of gas from petroleum: Chem. News, vol. 51, June 26, 1885, pp. 307–309.

liquid was rich in benzene and toluene and showed a trace of the higher aromatic compounds. They advanced the theory that the aromatic hydrocarbons are products in direct line with the paraffins, and are not built up from the acetylene series.

As previously pointed out, aromatic hydrocarbons have been found to exist in Russian and Roumanian oils; also considerable percentages of naphthene hydrocarbons, which are similar in structure to the benzene hydrocarbons. These naphthenes were contained more largely in the residuum than in the crude oil, and as a result most of the early investigators worked with the residual products.

In 1889 Intschik [a] patented a process for the manufacture of benzene and toluene, in which Russian petroleum residues are dropped into a highly heated vertical chamber where the oil is volatilized and the vapors decomposed. The fixed gases and vapors are drawn off and fractionally condensed.

During the early eighties, when the demand for benzene was high and the supply insufficient to meet the needs of the market, Nobel Brothers, Liebermann and Burg, [b] and Salzmann and Wichelhaus [c] investigated the possibilities of obtaining aromatic hydrocarbons from petroleum residues and are reported to have obtained excellent results.

Liebermann [d] reported in 1888 that the Nobel brothers were erecting a factory in the Baku field for the purpose of manufacturing aromatic hydrocarbons from petroleum residues.

Hlawaty, [e] in 1888, patented a process by means of which he claimed to obtain rich mixtures of benzene and its homologues, through the action of highly heated steam, or ethylene, methylethylene, or alcohol on petroleum residues, the mixed vapors being passed through red-hot tubes filled with charcoal and wood turnings.

A patent with the same object in view, granted to Dvorkovitz [f] in 1892 proposes to decompose steam passed into a gasifier in which the liquid hydrocarbon is vaporized. The water gas is there carbureted and passed into a condensing chamber where the benzene, toluene, and other aromatic compounds are separated.

A later patent issued to Dvorkovitz [g] states that the liquid hydrocarbon flows through a series of retorts in which the liquid is pro-

[a] Intschik, —, Russian Patent issued in 1889.

[b] Liebermann, C., and Burg, O., Ueber die Zersetzung des Braunkohlentheeröls in der Glühhitze: Ber. Deut. chem. Gesell., Jahrg. 11, 1878, pp. 723–726.

[c] Salzmann, M., and Wichelhaus, H., Ueber die Herstellung von Benzol aus Braunkohlentheeröl: Ber. Deut. chem. Gesell., Jahrg. 11, 1878, pp. 802, 1431–1434.

[d] Liebermann, C., Neue Gewinnungsmethode von Benzol, Naphtalin, und Anthracen: Dingl. Poly. Jour., Bd. 246, 1882, pp. 429–432.

[e] Hlawaty, Faustin, German Patent 51553, Aug. 11, 1888.

[f] Dvorkovitz, Paul, English Patent 21647, Nov. 26, 1892; also, Dvorkovitz, Paul, The distillation, cracking, and gasification of petroleum hydrocarbons: Petroleum Rev., vol. 17, Sept. 28, 1907, pp. 176–179; Gasification of coal and liquid hydrocarbons: Jour. Soc. Chem. Ind., vol. 12, May 31, 1893, pp. 403–412.

[g] Dvorkovitz, Paul, English Patent 23671, Dec. 5, 1894.