## DISTINCTION BETWEEN PRIOR PROCESSES AND THOSE DESCRIBED HEREIN.

References to a number of processes for benzene-toluene production not herein reviewed are contained in the bibliography at the end of this report. Those processes particularly mentioned here indicate sufficiently the prior development of the art, and the lines along which the problem has been approached.

The processes reviewed are primarily adapted to and dependent on the use of oils that are of a highly favorable character, and in connection with which the reaction necessary for benzene-toluene production is comparatively simple. In other words, the oils used were of the special varieties most favorable for the production of aromatic hydrocarbons. Either they contained the polycyclic (asphaltic) compounds that decompose on simple splitting into benzene and its homologues, or else naphthenes were present, which yield aromatic hydrocarbons through the simplest sort of dehydrogenation. Practically all of these prior processes are operated at atmospheric pressure, indicating the simplicity of reaction involved, as compared with the production of the low-boiling aromatic compounds from oils in which naphthenes and aromatics do not naturally occur, as accomplished by the process described later. The difference is that between a relatively simple alteration and an extensive and complex rearrangement.

In none of the descriptions of these prior processes is there the slightest mention of their availability for transforming hydrocarbons of the paraffin type into aromatic hydrocarbons, which is one of the characteristic advantages of the process discussed later. Otherwise stated, none of these processes is suitable for all types of oil. Although, as has been previously pointed out, it has long been known that benzene may be formed by the passing of petroleum at atmospheric pressure through a red-hot tube,[a] the quantities of benzene thus obtained are relatively small as compared with the quantities of by-products of little or no value, so that such processes, so far as is known, have not succeeded in industrial operations. This fact is pointed out by Hausman and Pilat,[b] and others.

## THEORIES OF FORMATION OF AROMATIC HYDROCARBONS.

In regard to the various theories concerning the character of reaction involved in producing aromatic hydrocarbons from petroleum hydrocarbons, as exemplified in processes of the type reviewed, there seems to be considerable difference of opinion. The three views most commonly discussed, which are probably all measurably correct, depending on the type of oil used and the conditions of time, temperature, and pressure in the reacting zone, are:

[a] Beilstein, F. K., Handbuch der organischer Chemie, Auflage 3, Bd. 2, p. 22.
[b] Hausman, Joachim, and Pilat, Stanislaus, German Patent 227178, Apr. 1, 1909.



(1) That there is a splitting off of cyclic nuclei;[a]

(2) That polymerization of ethylene and acetylene hydrocarbons occurs;[b]

(3) That dehydrogenation of naphthenes occurs.[c]

## OBJECT AND SCOPE OF BUREAU'S EXPERIMENTS WITH CRACKING PROCESSES.

The experimental work that resulted in the discovery of the processes described in this report was undertaken for the purpose of studying the reactions that occur in the cracking of liquid hydrocarbon mixtures.

The object of the bureau's experimental work, broadly stated, was to determine the effect of various combinations of temperature and pressure on the course of the cracking reaction, and to determine, if possible, *the most favorable conditions for the maximum yields of the various desired cracked products*, such as gas, gasoline, and low-boiling aromatic hydrocarbons.

The first phase of the work dealt with the production of ethylene hydrocarbons used in carbureting water gas.[d] In the production of carbureted water gas, petroleum distillates are commonly employed to increase the illuminating power of the product, and the increasing cost of "gas oils" has been a serious handicap to the continued existence of the carbureted water-gas industry.

Four to five gallons of oil is required per 1,000 cubic feet of carbureted gas produced. Consequently the addition of 1 cent per gallon at once becomes a serious matter to gas works, particularly in view of the fact that the numerous cracking processes for the production of gasoline will require the use of gas oil as the basic material, thereby greatly broadening the market for the latter, with resulting higher cost. Furthermore asphaltic distillates are not particularly desirable for use in carbureting gases. In fact the problem has become so serious that many gas men strongly favor coal-gas processes despite the fact that 75 per cent of the artificial gas produced in America to-day is carbureted water gas.

In the course of the experiments it was found that highly favorable conditions were obtained by having relatively high temperatures and low pressure in the cracking zone. The influence of pressure is clearly illustrated by the data in Table 1 following and by the curves shown in figures 2 to 5.

[a] Brooks, B. T., Bacon, R. F., and others, The preparation of gasoline and kerosene from heavier hydrocarbons: Jour. Ind. and Eng. Chem., vol. 7, Mar., 1915, p. 180; Lewes, V. B., The production of oil-gas from Russian petroleum: Jour. Soc. Chem. Ind., vol. 11, July 30, 1892, pp. 584–590.
[b] Ipatiew, W., Polymerisation der Äthylen-Kohlenwasserstoffe bei hohen Temperaturen und Drucken: Ber. Deut. chem. Gesell., Jahrg. 44, Bd. 3, 1911, pp. 2978–2987; Meyer, Richard, Pyrogene Acetylen-Kondensationen: Ber. Deut. chem. Gesell., Jahrg. 45, Bd. 2, 1912, pp. 1609–1633.
[c] Beilstein, F. K., Loc. cit.; Lewes, V. B., Loc. cit.
[d] Whitaker, M. C., and Rittman, W. F., Thermal reactions in carbureting water gas: Jour. Ind. and Eng. Chem., vol. 6, 1914, pp. 383–392, 472–479; Jour. Soc. Chem. Ind., vol. 33, July 15, 1914, p. 682.