

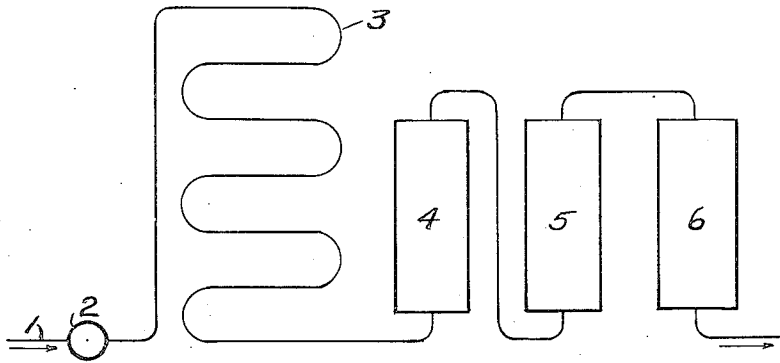
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H. M. SMITH ET AL

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PURIFICATION OF AROMATIC HYDROCARBONS

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PURIFICATION OF AROMATIC HYDROCARBONS

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2 Claims. (Cl. 260-674)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

This invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This invention which is a continuation in part of our pending application filed April 26, 1934, Serial No. 722,520, entitled Purification of aromatic hydrocarbons, relates to the refining of crude light oil and particularly the light oil produced by the pyrolysis of gaseous hydrocarbons, as described and claimed in Patent No. 1,995,330, issued March 26, 1935, and entitled Process for treating gaseous hydrocarbons wherein the gases issuing from the reaction tube and consisting largely of uncracked raw gas unsaturates such as ethylene and aromatic substances such as benzene, naphthalene, anthracene, pyrene and still heavier hydrocarbons and possibly small amounts of carbon together with a considerable amount of hydrogen are cooled to condense the heavier hydrocarbons to a liquid or solid condition, passed through an electrical precipitating chamber to remove the condensates and then under suitable conditions of temperature, pressure and rate of flow are directed to a catalytic hydrogenation chamber from which they are passed to a recovery system. Crude benzene from gas works contain numerous unsaturated compounds which polymerize and resinify upon standing, and it has been found that crude benzene from the pyrolysis of gaseous hydrocarbons turns yellow and deposits gums; indicating that it also contains the same or similar unstable compounds as gas-works benzene.

The usual methods employed for treating gas-works benzene result in high losses ranging from 5 to 20 percent. Various methods have been suggested for treatment including the use of: sulfuric, boric and hydrofluoric acids; aluminum, zinc and iron chlorides; chlorine; sulfur; heat and pressure. Often several of these agencies are combined, but in all cases the principle is to remove the harmful material in some form, and as a consequence, losses result. In some instances the methods are costly or cumbersome.

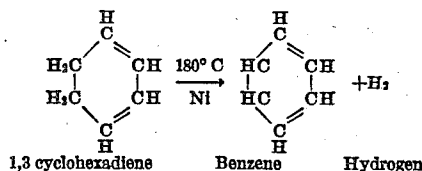
It is apparent that much of this loss could be prevented if the unsaturated compounds which are responsible for the color and gums in the benzene could be converted to useful products. In view of these facts it is the object of this invention to provide a method whereby crude benzene may be refined without loss, and we have discovered that this object may be attained by causing the benzene vapors containing the unsaturated compounds to traverse a nickel catalyst under suitable conditions.

A great many olefins and other unsaturated compounds have been identified among the products of gaseous hydrocarbon pyrolysis. Certain types of unsaturated compounds, such as the di-

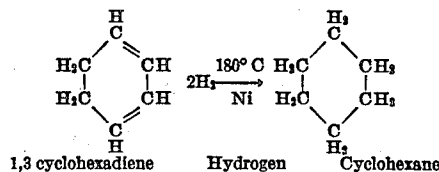
clefins, are well known gumforming agents. This property also extends to the cyclo-diolefins or cyclo-dienes, and certain aromatic olefins such as phenyl ethylene or styrene. Among the compounds which have been found in the liquids resulting from pyrolysis of gaseous hydrocarbons are cyclohexadiene, methyl cyclohexadiene and styrene. These compounds are unstable and are subject to polymerization reactions. Richter (Richter's Organic Chemistry, Translated by D'Albe, P. Blakeston's Son & Co. Vol. II) says of cyclohexadienes "They are easily polymerized and resinified", while of styrene he says "it is polymerized to meta-styrene on standing or in the sunlight."

Thus it appears probable that gum formation, at least in crude benzene produced by natural gas pyrolysis, is due to the presence of these and related compounds. One theory dealing with the formation of benzene from the pyrolysis of hydrocarbon gases postulates a series of condensation and dehydrogenation reactions, and one of the intermediate products suggested is a cyclohexadiene. If this theory is correct, and it has many facts to support it, then the presence of small amounts of such compounds as cyclohexadiene should be expected. The method which we have discovered for treating crude benzene may be illustrated by reactions which 1,3 cyclohexadiene would undergo when subjected to catalytic treatment such as we propose.

1,3 cyclohexadiene, when passed with an inert gas over a nickel catalyst at 180° C., is dehydrogenated completely and benzene is produced according to the following equation:



On the other hand if the diene is vaporized with a current of hydrogen then the completely hydrogenated product, cyclohexane, is the result:



The product of the first reaction, benzene, is identical with the material which we are purifying and therefore exceedingly desirable. The product of the second reaction, cyclohexane, is a liquid which boils very close to the boiling point of benzene, is an excellent motor fuel, and has no detrimental qualities. We have assumed that

these reactions are typical for the various unsaturated compounds present in the crude benzene produced by pyrolysis, and they are the basis for our invention. When hydrocarbon gases are pyrolyzed to produce benzene different amounts of hydrogen are formed depending upon operating conditions, but there are also present considerable amounts of methane and possibly ethane. These gases are inert so far as the reactions discussed above are concerned, so that the type of reaction which takes place probably depends upon the hydrogen concentration and operating conditions in the catalyst chamber. Due to the relatively small amounts of reactive compounds present and their close relationship to the major product benzene, we have been unable to determine which type of reaction occurs, but the net overall result from either or both of these reactions is the production of gum-free color-stable benzene.

Coming now to a more detailed account of the process, the pyrolyzed gas containing the light-oil vapors and even naphthalene is desired, but free of heavier compounds such as anthracene, pyrene and tars, is passed over a nickel catalyst within a temperature range of 180 to 220° C., and at a pressure ranging from 0-75 pounds gauge pressure. Here the unsaturated gumforming compounds are either completely hydrogenated or dehydrogenated according to their individual reactive properties under the operating conditions. In either case the gas with the light-oil vapors next enters a light-oil recovery system where the gum-free color-stable benzene is recovered. We have been able to recover amounts of treated benzene equivalent to the amount of crude benzene which can be recovered without treating, so that there is a negligible loss. Untreated benzene rapidly turns yellow, deposits gums and has a disagreeable odor, whereas the treated benzene retains its water-white color indefinitely.

Reference will now be made to Figure 1, which shows a diagrammatic drawing in elevation of an assembly of apparatus suitable for the conduction of the treating method described. The gas enters the system at 1, passes through the measuring devices 2 into the cracking chamber 3. The cracked gas next passes through a high-temperature scrubber or electrical precipitator 4 to remove heavy tars and carbon, and then into the catalyst chamber 5 where the reactions discussed pre-

viously occur. The gas and vapors pass from the treating or catalyst chamber to a recovery unit 6 for removing the light-oil (benzene). The light-oil as recovered here should be suitable for use without any further treatment except distillation to segregate the desired fractions.

In conclusion, it will be apparent, that we have devised a simple, inexpensive method for the purification of crude benzene which affords a yield free from objectional odor, coloring agents and gums.

Having described our invention, what we claim as new and wish to secure by Letters Patent is:

1. A process for converting and otherwise rendering ineffective the gum and color forming constituents present in the tar-free light oil produced by the catalytic hydrogenation of the pyrolyzed products of natural gas after such products have been treated to effect condensing of the heavier hydrocarbons and passed through a high potential electrical field to remove the condensates by electrical precipitation and which comprises recycling the products of hydrogenation through the initial pyrolyzing, condensing and electrical precipitation stages and then passing the resulting products in a vapor stage and in the presence of hydrogen over a metallic catalyst at atmospheric pressure and within a temperature range of 180 to 220° C., whereby to produce water white and gum stable benzene.
2. A process for converting and otherwise rendering ineffective the gum and color forming constituents present in the tar-free light oil produced by the catalytic hydrogenation of the pyrolyzed products of natural gas after such products have been treated to effect condensing of the heavier hydrocarbons and passed through a high potential electrical field to remove the condensates by electrical precipitation and which comprises recycling the products of hydrogenation through the initial pyrolyzing, condensing and electrical precipitation stages and then passing the resulting products in a vapor stage and in the presence of hydrogen over a metal catalyst at a pressure ranging from 0 to 75 pounds gauge pressure and within a temperature range of 180 to 220° C., whereby to produce water white and gum stable benzene.

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