

UNITED STATES PATENT OFFICE

2,367,535

PROCESS FOR THE MANUFACTURE OF AROMATIC HYDROCARBONS

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No Drawing. Application January 13, 1941,
Serial No. 374,204

3 Claims. (Cl. 260—671)

The invention relates in general to the manufacture of aromatic hydrocarbons and, in particular, to a process for the manufacture and recovery of toluene, the xylenes, mesitylene and their homologues.

High grade toluene is the basic raw material used for the manufacture of trinitrotoluene, hereinafter called "TNT." Such high grade toluene is therefore in great demand during periods of warfare. Before the last World War, the by-product coke oven was the sole source of toluene, but recently petroleum has become a secondary source. However, the quantity of petroleum oils containing appreciable amounts of toluene is quite limited. The production of toluene from such oils by cracking is tedious, expensive and troublesome. Accordingly, a method for the production of toluene from petroleum oils by methods other than cracking is very desirable.

On the other hand, there are available large quantities of oils which contain a major proportion of benzene and a minor proportion of aliphatic hydrocarbons, for example, the so-called "light oils" of coal tar, and the benzene fraction from petroleum. However, toluene intended for the manufacture of "TNT" must meet rigid specifications as to properties and purity. Among the essential requirements of toluene for "TNT" manufacture is that the toluene must be absolutely free of aliphatic hydrocarbons since these compounds, when present, adversely affect the properties and stability of the "TNT." The removal of such impurities from toluene by extraction with solvents, scrubbing, etc., is laborious and expensive.

Accordingly, it is a general object of the present invention to produce aromatic hydrocarbons, such as toluene, of high purity from oils containing benzene and aliphatic hydrocarbons.

A specific object of the invention is to produce toluene containing insufficient aliphatic hydrocarbons to prevent its use for the manufacture of "TNT."

According to the present invention, toluene of purity sufficiently high for use directly in the manufacture of "TNT" is obtained by fractionally distilling a benzene-containing oil, such as coal tar oil or petroleum oil, collecting a fraction containing benzene, which fraction also contains a minor proportion of aliphatic hydrocarbons, chemically converting the benzene in such oil to toluene and separating the residual benzene and the aliphatic hydrocarbons from the toluene by fractional distillation. Since the aliphatic hydrocarbons distilled over with the benzene frac-

tion they will have boiling points near that of benzene, i. e. about 75° C. to 85° C. so that the separation of the toluene (B. P. 110.7° C.) from such low boiling compounds will be quite complete.

As the source of benzene, there may be used any oil containing substantial quantities of benzene such, for example, as coal tar oil, preferably the so-called "Light oil" fraction boiling up to 170° C. from which the benzene fraction containing some aliphatic hydrocarbons and boiling between 75° C. and 85° C. is obtained by fractional distillation. On the other hand, one may distill petroleum oils and collect the fraction boiling between 78° C. and 84° C. which contains benzene and some aliphatic hydrocarbons. The petroleum oil treated may be derived from an asphaltic base, a paraffin base or a mixed base. The conversion of the benzene to toluene is not carried out after the separation from such oils of the components which boil in the range of toluene, that is, the conversion to toluene is carried out on a benzene-containing oil which has a boiling range below 110° C., preferably of between 75° C. and 85° C., whether derived from coal tar or petroleum oils.

The conversion of the benzene in such oil to toluene is accomplished in a suitable manner. By way of illustrating but not by way of limiting the scope of the present invention, there will be given three methods of chemically converting the benzene to toluene:

Method I.—This method involves the action of a dehydrating agent on a mixture of the benzene and an aliphatic alcohol, more particularly methyl alcohol if toluene is to be prepared. Suitable dehydrating agents are sulphuric acid, zinc chloride and phosphorus pentoxide. Of these substances, sulphuric acid has the advantage of being cheap and functioning at lower temperatures than the others. The function of the dehydrating agent may be two-fold: To split off and bind water by hydration, and to effect condensation by intermediate compound formation, but the present invention is independent of the mechanism of the reaction or the theoretical explanation thereof. This method will be illustrated by the following specific example:

195 grams of a petroleum oil fraction boiling between 78° C. and 84° C. and containing substantial quantities of benzene and minor quantities of aliphatic hydrocarbons are mixed with 64 grams of methyl alcohol and 25 grams of concentrated sulphuric acid. The mixture is heated in an autoclave to a temperature of above

150° C. until reaction is completed, for example, about 3 hours. The autoclave is opened and the upper layer of liquid therein is washed with water and caustic alkali. The mixture is now distilled, the benzene and aliphatic hydrocarbons distilling at between 75° C. and 85° C. and the toluene distilling at between 109° C. and 110° C. The toluene thus obtained is free of aliphatic hydrocarbons. The same method may be employed with the benzene fraction obtained from the "light" oil of coal tar.

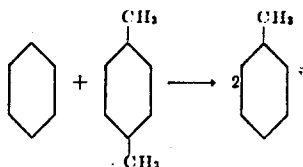
Method II.—This method involves the action of metallic halides on a mixture of an alkyl halide and an oil containing benzene. Any reactive metallic halide may be employed, such, for example, as zinc chloride, aluminum chloride, silicon chloride, and the like. The alkyl halide may be an alkyl fluoride, chloride, or bromide. This method will be illustrated by the following specific example:

An oil containing benzene and aliphatic hydrocarbons and boiling between 78° C. and 84° C. is mixed with a mole proportion of methyl chloride (based on the benzene content) and a mole proportion of aluminum chloride. The mixture is placed in a vessel provided with a reflux condenser. After warming to initiate the reaction, heating is discontinued since the reaction is exothermic. The hydrogen chloride generated by the reaction is distilled off and the aluminum chloride is extracted with water. The toluene is separated from the reaction products by fractional distillation as described under Method I. By this method, the toluene is completely separated from the residual benzene and the lower-boiling aliphatic hydrocarbons.

Method III.—In this embodiment of the invention, use is made of the unique coupling properties of boron fluoride. The process comprises mixing a poly-methylated phenolic compound with benzene and boron fluoride, heating the mixture under pressure whereby one or more methyl radicals transfer from the phenolic compound to the benzene ring. The poly-methylated phenolic compound may comprise di, tri, tetra, or penta alkyl phenols and its derivatives, alkyl catechol and its homologues, alkyl derivative of pyrogallol and its homologues, etc. The boron fluoride, BF₃, is believed to form intermediate compounds with the reactants, the formation of which cause the alkyl (methyl) group to migrate to the benzene ring. The following specific example will show the application of this method to the production of nitration-grade toluene:

Method IV

This method relates to the preparation of toluene from benzene and a polymethylated benzene such as xylene or its higher homologues by heating the mixture preferably in the presence of catalysts in the liquid or vapor phase. In general, this reaction is illustrated by the following equation:



and by the following specific examples:

Example A.—318 grams of xylene, 936 grams of toluene-free benzene, and 266 grams of anhydrous aluminum chloride were placed in a three-

necked flask fitted with an inlet tube, a mechanical stirrer and a reflux condenser. Dry hydrogen chloride was added until the mixture was saturated. The contents were heated to a gentle reflux for 12 hours.

The contents can then be distilled to remove the benzene and toluene or washed with water, caustic soda, dried and fractionated to remove the benzene and toluene and reclaim the xylene and other methylated benzenes. The following results were obtained under the above conditions of reaction:

	Boiling range, °C.	
Fraction I	80-85	650 grams recovered benzene
Fraction II	105-115	145 grams toluene
Fraction III	Above 115	150 grams recovered xylene

The fractionation serves to separate the toluene also from any aliphatic hydrocarbons which may have existed in the benzene or xylene used.

Example B.—The reaction of Example A was repeated in an autoclave at 115° C. for 1.5 hours. The purification was carried out as above described. After fractionation, the yield was 152 grams of toluene which was substantially free of aliphatic hydrocarbons.

Example C.—A solution of xylene in benzene in the molecular ratio of one to four is flash vaporized into a reaction chamber heated above 175° C. and the product fractionated to recover toluene as above described. The transference of the methyl groups to the benzene takes place at these higher temperatures without a catalyst, but is considerably increased by having anhydrous aluminum chloride present in the reaction chamber. The yield is still further increased by adding small quantities of hydrogen chloride to the mixture of vapors of xylene and excess benzene. Other catalysts also accelerate this reaction. For example, small quantities of gaseous boron trifluoride may be advantageously mixed with the xylene-benzene vapor mixture at the time that the mixture enters the reaction chamber.

An oil containing a major proportion of benzene and a minor proportion of aliphatic hydrocarbons is mixed with a mole equivalent of trimethyl phenol and a mole equivalent of boron fluoride, BF₃, (a gas) based on the mole proportion of benzene in the oil. Preferably an excess of benzene should be present to insure the production of the monoalkyl derivative, i. e. toluene. The mixture is heated to 100° C. in an autoclave, whereupon the methyl radical transfers from the tri-methyl phenol to the benzene with the formation of toluene. The toluene is separated from the other reaction products and from the aliphatic hydrocarbons by fractional distillation. This process has the advantage that it may be carried out under atmospheric pressures.

Various changes can be made in the process within the scope of the invention. The invention is adapted to produce toluene which is substantially free of aliphatic hydrocarbons or which may contain from a trace up to 1% of such impurity depending largely on the care used in the final fractionation of the reaction product.

Having described my invention, what I claim is:

1. In a process for the production of alkyl derivatives of benzene of high purity from an oil containing benzene and aliphatic hydrocarbons, the steps comprising distilling said oil, collecting a fraction of said oil boiling between 75° C. and 85° C., mixing with the fraction thus obtained a poly-alkyl benzene, subjecting said mixture to the action of a catalyst under conditions promoting the transference of an alkyl group from the

poly-alkyl benzene to the benzene and thereafter fractionating the reaction product and separately collecting aliphatic hydrocarbons, mono-alkylated benzene, and poly-alkylated benzene.

2. In a process for the production of toluene of high purity from oils containing benzene and aliphatic hydrocarbons, the steps comprising distilling said oil, collecting a fraction of said oil boiling between 75° C. and 85° C., mixing with the fraction thus obtained a poly-methyl benzene, 5
subjecting said mixture to the action of a catalyst under conditions promoting the transference of a methyl group from the poly-methyl benzene to the benzene and thereafter fractionating the reaction product and separately collecting aliphatic hydrocarbons, toluene, and poly-methylated benzene. 10

3. In a process for the production of alkyl derivatives of benzene of high purity from an oil containing benzene and aliphatic hydrocarbons, the steps comprising distilling said oil, collecting a fraction of said oil boiling between 75° C. and 85° C., mixing with the fraction thus obtained a compound selected from the group consisting of poly-alkyl benzenes and poly-alkyl phenols, subjecting said mixture to the action of a catalyst 10
under conditions promoting the transference of an alkyl group from the poly-alkyl compound to the benzene and thereafter fractionating the reaction product and separately collecting aliphatic hydrocarbons, mono-alkylated benzene, 15
and poly-alkylated compounds.

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