

UNITED STATES PATENT OFFICE

2,438,570

PRODUCTION OF TOLUENE BY CATALYTIC
CRACKING OF MONOALKYL BENZENESWilliam J. Mattox, La Grange, Ill., assignor to
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8 Claims. (Cl. 260-672)

1

This invention is a continuation-in-part of my copending application Serial Number 510,885, filed November 19, 1943, now U. S. Patent 2,386,969, issued October 16, 1945, and relates to the conversion of mono- or poly-alkyl aromatic hydrocarbons in which at least one of the alkyl groups contains two or more carbon atoms into mono- or poly-methylated aromatic hydrocarbons by reducing the length of the alkyl group or groups to methyl substituents.

In the production of motor fuels by the distillation of petroleum it has long been recognized that the fractions boiling above gasoline contain alkyl aromatic hydrocarbons in which the alkyl groups are long chain hydrocarbon radicals. The said high molecular weight hydrocarbons are frequently the components which render these higher boiling fractions unsuitable for use as gasoline because of their low volatility. Consequently, a process for converting the long chain alkyl radicals to shorter chain length groups, thereby lowering the boiling points of the aromatic hydrocarbons to the gasoline boiling range, would have a widespread application in the refining industry for increasing the yields of gasoline from petroleum. Further, in the production of aviation fuels various specifications and standards have been established to insure the proper performance of aviation engines, among which is included the specification that such fuels have a maximum end boiling point of 300° F. Any components of the fuel having a boiling point above the said specified maximum, therefore, are considered unsuitable for aviation use. Many aromatic hydrocarbons containing a single or a multiple number of long chain alkyl groups attached to the aromatic nucleus are considered undesirable aviation fuel components because of the above mentioned restriction on their boiling points. It is an object of this invention, therefore, to obtain the conversion of the higher boiling fractions of petroleum containing the said long chain alkylated aromatic hydrocarbons to increase the yields of gasoline, particularly aviation gasoline, therefrom by reducing the chain length of the alkyl groups to methyl substituents while retaining the desirable aromatic structure of the hydrocarbon. As a typical application of the present process, may be cited the dealkanation of normal propylbenzene (boiling point 320° F./760 mm.) to produce therefrom toluene (boiling point 231° F./760 mm.) thereby converting a hydrocarbon which boils at a temperature too high to meet aviation gasoline specifications

2

into a hydrocarbon which boils at a temperature within the specified range.

It is well known in the art of alkylating aromatic hydrocarbons that the production of methylated aromatic hydrocarbons by purely alkylation procedures is more difficult, relatively speaking, than the formation of aromatic hydrocarbons in which the alkyl group contains two or more carbon atoms. Thus, it is apparent that for ease of manufacture and for minimum cost of production, the problem of producing methylated aromatic hydrocarbons from benzene may be more advantageously attacked by producing the longer chain aromatic hydrocarbons, and devising a means for subsequently reducing the length of the alkyl group to leave the methyl radical attached to the aromatic ring. The term "dealkanation" defines such a reaction in which an alkyl side chain of two or more carbon atoms undergoes scission at the bond between the alpha and beta carbon atoms of the side chain, leaving a methyl group attached in the position originally occupied by the alkyl group. It is intended that the term as used in the present specifications and claims be limited to such a definition. The process of dealkanating a mono- or poly-alkyl aromatic hydrocarbon is the proposed process of the present invention.

It is another object of the present invention to subject petroleum fractions boiling above gasoline and containing mono- or poly-alkyl aromatic hydrocarbons to dealkanation in the presence of a dealkanation catalyst, and under specific process conditions to reduce the length of one or more of the alkyl side chains on the said higher boiling aromatic hydrocarbons to a methyl group or groups.

In one embodiment, the present invention comprises a process for the dealkanation of an alkyl aromatic hydrocarbon having at least one alkyl group containing two or more carbon atoms by contacting said hydrocarbon with a catalyst comprising an oxide of an element from the left-hand column of group VI of the periodic table at a temperature of from about 400° C. to about 650° C., at a pressure of from atmospheric to about 1000 pounds per square inch, and at a hourly weight space velocity of from about 0.1 to about 5 whereby to split said alkyl group at the bond between its alpha and beta carbon atoms and leave a methyl substituent attached to the aromatic nucleus.

One specific embodiment of the present invention relates to a process for producing toluene, which comprises subjecting propylbenzene to de-

alkanation in the presence of hydrogen, and a catalyst comprising a composite of alumina and an oxide of a metal selected from the elements in the left-hand column of group VI of the periodic table at a temperature of from about 400° to about 650° C.

In another specific embodiment the present invention comprises a process for manufacturing xylene by subjecting di-ethylbenzene to dealkanation in the presence of a naphthene hydrocarbon and a catalyst comprising a composite of alumina and an oxide of a metal selected from the group of elements in the left-hand column of group VI of the periodic table at a temperature of from about 400° to about 650° C.

The mono- or poly-alkyl aromatic charging stock suitable for treatment by the process of the present invention may comprise an aromatic hydrocarbon in which at least one of the alkyl side chains contains two or more carbon atoms (preferably more than two carbon atoms); thus, such compounds as ethylbenzene, propylbenzene, butylbenzene, etc. may be converted into toluene. Methyl-ethylbenzene, ethyl-propylbenzene, methyl-butylbenzene, etc. or such compounds as di-ethylbenzene, ethyl-propylbenzene, ethyl-butylbenzene, ethyl-amybenzene, etc., or such compounds as di-propylbenzene, propyl-butylbenzene, etc., or such compounds as di-butylbenzene, butyl-amybenzene, etc., may be converted in accordance with the present invention to form xylene. It is understood that the yields of toluene or xylene produced from these various alternative compounds are not necessarily equivalent. It is generally preferable, however, that the alkyl side chain contain between 3 and 5 carbon atoms, such as normal propylbenzene. Furthermore, the present invention is also applicable to treatment of more highly alkyl-substituted aromatic hydrocarbons, such as the tri-alkyl or tetra-alkylbenzene derivatives, in which at least one of the alkyl side chains contains two or more carbon atoms to produce therefrom, a methylated aromatic hydrocarbon containing as many methyl groups as the number of alkyl groups in the original aromatic hydrocarbon and in the same position.

In the following further explanation of the invention, the description will be based on a process in which propylbenzene is subjected to dealkanation, with the understanding that the process may be applied to the other mono- or poly-alkylated benzenes heretofore set forth. It is also to be understood that the specific operating conditions may require modification when treating the other alkyl benzenes as compared to the treatment of propylbenzene. However, the conditions for treating these other mono- or poly-alkylated benzenes will be within the range hereinafter set forth.

In accordance with the present invention dealkanation of propylbenzene to produce toluene is effected in the presence of a catalyst comprising a composite of an oxide of a metal selected from the group of elements in the left-hand column of group VI of the periodic table with alumina or another suitable supporting material such as an oxide of zinc, zirconium, magnesium, silicon, titanium, or thorium. A particularly preferred catalyst comprises a composite of alumina with chromia or molybdenum oxide.

The dealkanation is effected in the presence of the hereinbefore specified catalyst at a temperature from about 400° to about 650° C. (preferably from about 500° to about 600° C.), a pressure of

from atmospheric to 1000 pounds, or more, per square inch (preferably from about 100 to about 400 pounds per square inch), and an hourly weight space velocity of from about 0.1 to 5, or more (preferably from about 0.2 to about 2). As used herein, the term "hourly weight space velocity" is intended to mean the weight of hydrocarbon per hour per weight of catalyst in the reaction zone.

The dealkanation reaction is preferably effected in the presence of hydrogen which may be introduced from an extraneous source, from the excess of hydrogen recycled within the system, or from a hydrocarbon which is capable of donating hydrogen in situ under the operating conditions of the process. Such hydrocarbons include the naphthenes or cycloaliphatic hydrocarbons, a naphthene fraction of a straight-run petroleum distillate or, in general, a saturated hydrocarbon capable of donating hydrogen under the proper conditions of temperature and pressure to the reactants undergoing conversion. The amount of hydrogen, if introduced from an extraneous source, is within the range of from about 0.5 to about 15 mols or more (preferably of from about 1 to 10 mols) per mol of propylbenzene. The amount of saturated hydrocarbon introduced for the purpose of supplying a hydrogen donor in the reaction, in general, must be sufficient to produce a mol of hydrogen for each mol of alkyl group removed from the alkyl aromatic hydrocarbon. Thus, the available hydrogen from a naphthene, such as cyclohexane, would be sufficient to donate 3 mols of hydrogen per mol of cyclohexane, or enough to supply the requirements for the dealkanation of a mol of a tri-alkyl aromatic hydrocarbon. The quantity of saturated hydrocarbon charge in admixture with the alkyl aromatic undergoing dealkanation will, therefore, depend upon the particular charging stocks employed, but generally an excess is preferred. During the dealkanation reaction, and particularly in connection with a relatively high conversion per pass, some hydrogen will be produced as a result of side reactions, and in certain cases, the hydrogen so produced may be sufficient for the intended purpose of the invention. In such cases it may be unnecessary to introduce hydrogen from an extraneous source and even in some extreme cases it may be unnecessary to recycle hydrogen within the system. Usually, however, it will be advisable to recycle the hydrogen from the separation step of the process to the dealkanation step.

The dealkanation reactor may be of any suitable design in which the catalyst is disposed and in which the reactants are satisfactorily contacted therewith. The catalyst bed employed in the present invention may be of any of the common types employed in catalytic processes, but the invention is particularly adaptable to "fixed bed" and "fluidized" types of operation, the latter including both the "fluidized fixed bed" and the "fluidized moving bed" reactor systems. The fixed bed type of operation effects conversion of the reactants by allowing vapors of the charge stock to flow over or through a stationary bed of catalyst, while in the fluidized types of operation a stream of reactants is fed at a relatively high velocity of flow and at the desired conversion temperature into a reactor containing the catalyst, the velocity of flow being such that the vapors of reactants maintain the catalyst in a more or less violent state of agitation. The fluidized fixed bed method is characterized by the fact that the catalyst remains in one reactor

5

where it is contacted by a continuous flow of charge stock during the conversion operation, whereas in the moving bed method the charge stock and catalyst flow out of the reactor and are separated in a subsequent unit of apparatus, such as, cyclone precipitator. The fluidized type of operation is particularly advantageous in that it results in more uniform heat distribution in the reactor bed and better contact between the catalyst and the charge stock.

The catalysts of the present invention may also be employed in a "suspensoid" type of conversion in which the catalyst is suspended within the charge stock or its vapors and the mixture fed into a conversion zone maintained at the desired temperature for reaction. In still another method of operation, the so-called "compact" or "dense" moving bed may be employed in which the charge stock vapors flowing in one direction are contacted with a bed of catalyst moving in either a concurrent or countercurrent direction.

The reaction products from the dealkanation reactor are directed into a separation zone which may comprise one or a plurality of suitable fractionating, distilling, absorbing, and/or stripping zones whereby the products introduced thereto may be separated into a hydrogen-containing fraction, a toluene-containing fraction, and unconverted propylbenzene. The hydrogen-containing fraction which may also contain light hydrocarbon gases such as methane, ethane, or ethylene may be withdrawn from the separating zone and removed from the process, but preferably at least a portion thereof is recycled with or without intermediate purification or other treatment in order to concentrate the hydrogen prior to recycling. The toluene-containing fraction is withdrawn from the separating zone and may, when desired, be subjected to any further fractionation or other treatment in order to separate the toluene from other constituents, if any. Unconverted propylbenzene is usually recycled through the process to increase the overall yield of desirable products from the charge stock. Likewise this fraction may be subjected to fractionation or other treatment to effect its purification or concentration prior to recycling.

The following examples are introduced for the purpose of further illustrating the novelty and utility of the present invention, but should not be construed as limiting the invention strictly in accordance thereto.

Example I

Propylbenzene may be subjected to dealkanation in the presence of an alumina-chromia catalyst at a temperature of 525° C., a pressure of 200 pounds per square inch, and a space velocity of 0.5 in the presence of a mol for mol ratio of cyclohexane as the hydrogen donor hydrocarbon. 89% by weight of liquid products per pass is recovered from the reaction products and the alkyl aromatic fraction from these will comprise about 38% by weight of toluene and about 43% by weight of unconverted propylbenzene. The latter may be recycled to the dealkanation zone in order to produce an ultimate yield of toluene from propylbenzene of 70% or more by weight.

Example II

A di-ethylbenzene charging stock was subjected to dealkanation in the presence of an alumina-molybdenum oxide catalyst at a temperature of about 525° C., a pressure of 200 pounds per square inch, a space velocity of 0.5, and in

6

the presence of an equivalent quantity of a straight-run naphtha fraction to yield 81% by weight of liquid products, the aromatic portion of which contained 40% by weight of xylene and 35% by weight of unconverted di-ethylbenzene.

Example III

Mono-ethylbenzene may be dealkanated to toluene by passing the said ethylbenzene through a fixed bed reactor containing a catalyst comprising a composite of the oxides of magnesium and chromium at a temperature of 500° C., at a pressure of 300 pounds per square inch, at a space velocity of 0.5, and in the presence of 3 mols of hydrogen per mol of the hydrocarbon. A condensable fraction, corresponding to a theoretical yield of 85% based on the hydrocarbon charged, contains 58% by weight of toluene and 21% by weight of unconverted mono-ethylbenzene.

I claim is my invention:

1. A process for the dealkanation of a mono-alkyl aromatic hydrocarbon wherein the alkyl group contains two or more carbon atoms, which comprises contacting said hydrocarbon with a catalyst comprising an oxide of an element from the left-hand column of group VI of the periodic table at a temperature of from about 400° C. to about 650° C., a pressure of from atmospheric to about 1000 pounds per square inch, and a hourly weight space velocity of from about 0.1 to about 5, whereby to split said alkyl group at the bond between its alpha and beta carbon atoms and leave a methyl substituent attached to the aromatic nucleus.

2. The process of claim 1 further characterized in that the said hydrocarbon is contacted with the catalyst in the presence of a hydrocarbon capable of donating hydrogen at the said reaction conditions.

3. A process for producing toluene from a mono-alkyl benzene hydrocarbon having an alkyl group containing at least two carbon atoms which comprises contacting said hydrocarbon with a catalyst comprising an oxide of an element from the left-hand column of group VI of the periodic table at a temperature of from about 400° C. to about 650° C., a pressure of from atmospheric to about 1000 pounds per square inch, and an hourly weight space velocity of from about 0.1 to about 5, whereby to reduce the number of carbon atoms of said alkyl group to one.

4. The process of claim 3 further characterized in that the mono-alkylbenzene hydrocarbon is contacted with the said catalyst in the presence of a hydrocarbon capable of donating hydrogen at the said reaction conditions.

5. The process as defined in claim 3 further characterized in that said hydrocarbon is contacted with the catalyst in the presence of hydrogen in the amount of from about 0.5 to about 15 mols per mol of the hydrocarbon.

6. A process for producing toluene which comprises contacting normal propylbenzene with a catalyst comprising an oxide of an element from the left-hand column of group VI of the periodic table at a temperature of from about 400° to about 650° C., a pressure of from about atmospheric to about 1000 pounds per square inch, and a hourly weight space velocity of from about 0.1 to about 5 in the presence of a hydrocarbon capable of donating hydrogen, whereby to split the propyl group of said propylbenzene at the bond between its alpha and beta carbon atoms and leave a methyl substituent attached to the benzene nucleus.

2,438,570

7

7. The process as defined in claim 1 further characterized in that said catalyst comprises alumina and chromia.

8. The process of claim 1 further characterized in that said catalyst comprises alumina and molybdenum oxide.

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8

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