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TREATMENT OF ALKYL AROMATIC
HYDROCARBONS

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This invention relates to the preparation of aromatic and naphthenic hydrocarbons having a smaller alkyl group or smaller number of alkyl groups from an alkyl aromatic hydrocarbon containing at least 1 carbon atom more than the number of carbon atoms present in each molecule of the aromatic and naphthenic hydrocarbons produced therefrom. More specifically the invention is concerned with a process for treating an aromatic hydrocarbon containing at least 7 carbon atoms per molecule to effect demethylation and to produce an aromatic or naphthenic hydrocarbon of lower molecular weight containing at least 6 carbon atoms per molecule.

An object of this invention is to provide an improved process for demethylating aromatic hydrocarbons.

Another object of this invention is the demethylation of an alkyl aromatic hydrocarbon in the presence of hydrogen and of a catalyst at a temperature substantially precluding the splitting from said aromatic hydrocarbon of radicals containing more than one carbon atom.

A further object of this invention is the treatment of an alkyl aromatic hydrocarbon in the presence of a mixture of hydrogen and methane and of a demethylation catalyst at a temperature sufficient to effect demethylation but to preclude the splitting from said aromatic hydrocarbon of radicals containing more than one carbon atom.

In one specific embodiment the present invention relates to a process for demethylating an alkyl aromatic hydrocarbon which comprises reacting said alkyl aromatic hydrocarbon and hydrogen in the presence of a demethylating catalyst at a temperature of from about 350° to about 650° F.

In a further embodiment the present invention relates to a process for demethylating an alkyl aromatic hydrocarbon which comprises reacting said alkyl aromatic hydrocarbon and hydrogen in the presence of methane and a demethylating catalyst at a temperature of from about 350° to about 650° F.

By the term "demethylation" we mean the herein described process by which an alkyl aromatic hydrocarbon and hydrogen or a mixture of hydrogen and methane are reacted to produce methane and an aromatic hydrocarbon containing at least one carbon atom less than present in the alkyl aromatic hydrocarbon charged to the process. Demethylation thus involves the scission of a methyl group from an alkyl side chain of an alkylated aromatic hydrocarbon or the scission of a methyl group from a methylated aromatic hydrocarbon.

In the presence of hydrogen, such a scission of a methyl group is accompanied by hydrogen addition whereby methane and an aromatic hydrocarbon of lower molecular weight are produced.

Demethylation of an alkyl aromatic hydrocarbon is clearly differentiated from pyrolysis or cracking which yield propane, butane, and other gaseous products while our process forms essentially only methane and the aromatic hydrocarbon of lower molecular weight.

The aromatic hydrocarbons which may be treated by the process of this invention include monoalkyl and polyalkyl aromatic hydrocarbons which are monocyclic or polycyclic. The process is particularly applicable to the treatment of cracked petroleum hydrocarbon fractions containing a relatively high proportion of aromatic hydrocarbons. Alkyl aromatic hydrocarbons which boil too high to be included in aviation gasoline may be demethylated and converted into lower boiling hydrocarbons utilizable in aviation gasoline. Thus benzene hydrocarbons such as monopropyl-, butyl-, and amylbenzenes may be converted into substantial yields of benzene, toluene, ethylbenzene, etc.

A particularly suitable charging stock for the present process comprises aromatic hydrocarbon fractions obtained by catalytic cracking of hydrocarbon oils such as gas oil. Thus such a highly aromatic fraction boiling from about 300° to about 400° F. is converted by our process into an aromatic hydrocarbon fraction boiling below 300° F. and thus utilizable as a blending stock in the production of aviation gasoline.

Demethylation catalysts which we prefer to use in the process of this invention comprise the metals of the iron group including iron, nickel, and cobalt and their oxides either used as such or supported by carriers as diatomaceous earth, alumina, silica, crushed porcelain, or some other refractory material which has substantially no adverse affect on the demethylation reaction. Catalysts containing copper composited with iron, nickel, or cobalt are also utilizable in the process.

A highly active nickel catalyst which we have employed in the demethylation treatment of alkyl aromatic hydrocarbons contains approximately 66% by weight of total nickel, 30% of diatomaceous earth, and 4% of oxygen, the latter present with the nickel as nickel oxide. This catalyst is made by the general steps of suspending diatomaceous earth, also known as kieselguhr, in a dilute solution of nickel sulfate and then gradually add-

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ing thereto an excess of a hot saturated solution of sodium carbonate. The mixture of nickel sulfate solution and diatomaceous earth is agitated vigorously while the sodium carbonate solution is introduced thereto to form a precipitate which is then removed from the solution by filtration and then washed, dried, and reduced with hydrogen. Other nickel catalysts may also be prepared from different proportions of the nickel compound and carrier. The different catalysts so produced are not necessarily equivalent in activity.

The resultant nickel-diatomaceous earth catalyst is employed in powder form when demethylation is effected in batch type treatment or in fluidized or fluidized fixed bed type of operation. When pelleted or formed catalyst particles are desired, the powdered mixture, preferably before being subjected to reduction with hydrogen, is mixed with graphite or some other lubricant and formed into pellets by a pilling machine. Other nickel-containing catalysts which may be employed similarly may be prepared to contain proportions of nickel different than those aforementioned.

Cobalt catalysts are produced by essentially the same series of steps as used in producing nickel-diatomaceous earth catalyst composites. Diatomaceous earth and cobalt nitrate so proportioned as to give essentially the same ratio of cobalt to silica as of nickel to silica in the above described catalyst, were mixed with water and then treated with an excess of a hot saturated solution of sodium carbonate. The mixture of cobalt nitrate solution and diatomaceous earth suspended therein is agitated vigorously while the sodium carbonate solution is added thereto to form a precipitate which is then removed by filtration and washed, dried, and reduced to give an active cobalt-diatomaceous earth catalyst, utilizable in the form of powder or pellets in essentially the same manner as the nickel-diatomaceous earth catalyst.

The process of this invention is carried out under carefully correlated conditions of temperature and pressure. Operating temperatures utilizable in the process are from about 350° to about 650° F. at a pressure of from subatmospheric to about 1000 pounds per square inch. The operating conditions used in batch type treatments are generally somewhat different from those employed in continuous operation. It is generally advisable to carry out the process under a relatively low pressure of hydrogen so as to obtain a relatively high proportion of demethylation and a relatively small amount of hydrogenation of aromatic hydrocarbons to naphthenic hydrocarbons. At higher pressures the demethylation reaction is accompanied by a greater amount of hydrogenation and the resultant product contains both aromatic and naphthenic hydrocarbons. Under certain correlated conditions of temperature, pressure, and partial pressure of hydrogen the demethylation of the aromatic hydrocarbon occurs as the principal reaction of the process.

Batch type treatment of alkyl aromatic hydrocarbons may be made in reactors or autoclaves of suitable design in which the hydrocarbons and catalyst are treated with hydrogen or with a hydrogen-methane mixture under the desired conditions of operation and for a time sufficient to effect the removal of one or more methyl groups, said removal being accompanied by addition of hydrogen so as to produce methane and an aromatic hydrocarbon containing fewer carbon

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atoms than those present in the aromatic hydrocarbon charged to the process.

The demethylation process may be operated continuously in a suitable chamber or tubular reactor containing a fixed bed or layer of the catalyst and through which the hydrocarbon charging stock and hydrogen-containing gas are passed under chosen conditions of temperature and pressure. Thus the reaction products are discharged continuously from the reactor at substantially the same rate as that at which they are charged thereto. The products of demethylation are fractionated by suitable means to separate the desired lower boiling aromatic hydrocarbons from the unconverted portion of the aromatic hydrocarbon material charged to the process, and said unconverted material is recycled to commingle with the hydrocarbon material charged.

Also, the process may be carried out continuously in the presence of powdered catalyst by employing what may be termed a fluid or fluidized fixed bed type of operation. For example, an aromatic hydrocarbon or mixture containing alkyl aromatic hydrocarbons and a hydrogen-containing gas are preheated to a chosen reaction temperature of from about 350° to about 650° F. and the resultant mixture of gas and hydrocarbon vapor is charged to a reaction zone containing a powdered demethylation catalyst. The reaction zone may also be provided with suitable means for introducing or removing heat such as heat exchanger coils containing a fluid heat transfer medium in order to maintain the reaction zone at a substantially constant temperature. The effluent hydrocarbon vapors and gases are directed from the reaction zone to a catalyst separating zone such as a cyclone separator or other suitable separator in order to substantially remove therefrom the finely powdered catalyst which is then returned to the reactor. The mixture of hydrocarbon vapors and gas so freed from finely divided catalyst is then directed to a second separating zone in which the gases are separated from the liquid hydrocarbons. In some cases the use of powdered catalysts in the so-called fluid type of operation simplifies the control of the reaction temperature so that relatively high yields of demethylation products of high antiknock value can be obtained per pass without an excessive increase in temperature in the reaction zone due to the exothermic heat of reaction.

The demethylation of an alkyl aromatic hydrocarbon may also be carried out continuously by contacting said hydrocarbon, hydrogen, and powdered demethylation catalyst in a tubular reactor of relatively small diameter surrounded by a jacket through which a cooling fluid is circulated in order to remove part of the exothermic heat of reaction and thus assist in controlling the reaction temperature. The resultant reaction mixture is directed from such tubular reactors through one or more suitable separators, such as cyclone separators, in which catalyst powder is removed from the mixture of methane, hydrogen, and vapors of liquid aromatic hydrocarbons. The recovered catalyst is suitable for recycling to the process. Fractional distillation methods are employed for separating gaseous products and desired demethylated products from unconverted hydrocarbon charging stock which is recycled to further treatment in the presence of the catalyst and hydrogen.

We have found that the partial pressure of hydrogen in the reaction mixture has an impor-

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tant influence upon the demethylation of an alkyl aromatic hydrocarbon. Furthermore, we have observed that the speed and amount of demethylation are affected greatly by the partial pressure of hydrogen existing at various points in the catalyst zone. More specifically we have found that for each partial pressure of hydrogen there is an optimum operating temperature for a given alkyl aromatic hydrocarbon undergoing reaction. In the case of the demethylation of alkyl aromatic hydrocarbons, a suitable operating temperature for demethylation to aromatic hydrocarbons with shorter side chains is defined as a temperature range at the lower limit of which the conversion is relatively low, such as from about 5 to about 10% per pass, while at the higher temperature range the reaction becomes difficult to control because of the high conversion, such as 40 to 50% per pass, since this conversion is accompanied by a high evolution of heat.

It is thus apparent that as a reaction mixture of alkyl aromatic hydrocarbons and hydrogen proceeds through a reaction zone containing a demethylation catalyst, the hydrogen is consumed continuously to form methane; and consequently the partial pressure of hydrogen decreases continuously as the reaction mixture approaches the exit end of the reaction zone. In general there is a relatively narrow range of temperature which should be maintained throughout the entire reaction zone in order to control the demethylation reaction and to prevent the reaction temperature from increasing rapidly and excessively because of the relatively high exothermic heat of reaction. A high partial pressure of hydrogen in the reaction mixture increases the ease of control of the reaction temperature. Sometimes hydrogen or a mixture of hydrogen and methane is introduced at intermediate points along the line of flow in the reaction zone as a means of controlling the reaction temperature.

Although relatively pure hydrogen is utilizable for treating an alkyl aromatic hydrocarbon in the presence of a catalyst to effect demethylation as herein described, it is sometimes advantageous to similarly utilize a mixture of hydrogen and methane or to employ a gas mixture containing hydrogen admixed with a substantially inert gaseous diluent. The methane or other gas admixed with hydrogen apparently serves as a heat absorbing medium and thereby assists in the control of the reaction temperature. Accurate control of the reaction temperature is necessary since otherwise the desired products undergo further demethylation and decomposition reactions. Such temperature control may be accomplished or aided by recycling a portion of the methane or methane-hydrogen mixture separated from the hydrocarbon products of the process.

The following example is given to illustrate the process of the invention although with no intention of unduly limiting its generally broad scope.

Hydrogen and isopropylbenzene in the molecular ratios of 3.8:1 were passed continuously at atmospheric pressure through a steel reactor containing a fixed bed of nickel-diatomaceous earth catalyst in the form of 3 x 3 mm. pellets. This catalyst had been reduced previously with hydrogen at 1000° F. The catalyst reactor was surrounded with a jacket containing tetralin under its vapor pressure maintained at a temperature of from 548° to 561° F., but during the reaction the temperature of the catalyst was between 563° and 578° F. because of the heat given off by the reaction. During this run, 1.4 liquid volumes of

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isopropylbenzene were charged per hour per volume of catalyst in the reactor. The liquid product recovered had 90% of the volume of the isopropylbenzene charged.

Investigation of the recovered liquid product showed that it contained benzene, toluene, ethylbenzene, unconverted isopropylbenzene (also known as cumene), and small amounts of naphthenic hydrocarbons. From the following table which shows the boiling ranges at atmospheric pressure and refractive indices of the different fractions of the liquid product, it is evident that approximately 14% of the isopropylbenzene was converted into aromatic hydrocarbons of lower molecular weight with only a small amount of hydrogenation to cyclohexane and other naphthenic hydrocarbons.

Fraction No.	Boiling Range, °C.	Per cent by Volume	n_D^{20}
1.....	74-90	1.4	1.4760
2.....	90-118	9.4	1.4925
3.....	118-125	0.6	1.4919
4.....	125-140	3.0	1.4904
5.....	Above 140	85.6	1.4901

Fraction 1 consisted essentially of benzene admixed with small amounts of cyclohexane and fraction 2 contained a major proportion of toluene and a small amount of methylcyclohexane. Fraction 3 which boiled between toluene and ethylbenzene consisted of a mixture of these two hydrocarbons, while fraction 4 which boiled between 125° and 140° C. was largely ethylbenzene admixed with naphthenic hydrocarbons comprising essentially ethylcyclohexane. The remaining 85.6% of the recovered liquid product was unchanged isopropylbenzene suitable for recycling to further demethylation treatment. The gaseous products of the reaction consisted of the excess of hydrogen admixed with methane formed in the hydrocarbon demethylation reaction.

The foregoing specification and example indicate the character and value of the present process although it is not intended that either section should limit unduly the broad scope of the invention.

We claim as our invention:

1. A process for producing a lower molecular weight alkyl aromatic hydrocarbon from an aromatic hydrocarbon having an alkyl side chain of at least 2 carbon atoms, which comprises reacting the last-named hydrocarbon with hydrogen in the presence of a catalyst comprising a metal of the iron group at a temperature of from about 350° F. to about 650° F. and a pressure not greater than about 1000 pounds per square inch to remove at least one methyl group from said alkyl side chain while retaining a portion of said side chain on the aromatic nucleus.

2. The process as defined in claim 1 further characterized in that the catalyst employed in the reaction comprises nickel.

3. The process as defined in claim 1 further characterized in that the catalyst employed in the reaction comprises cobalt.

4. The process as defined in claim 1 further characterized in that the catalyst employed in the reaction comprises iron.

5. A process for producing a lower molecular weight alkyl aromatic hydrocarbon from an aromatic hydrocarbon having an alkyl side chain of more than 2 carbon atoms, which comprises reacting the last-named hydrocarbon with hydrogen at a temperature of from about 350° F. to

about 650° F. and a pressure not greater than about 1000 pounds per square inch in the presence of a catalyst comprising a reduced metal of the iron group to remove a methyl group from said alkyl side chain while retaining at least one methyl group in said side chain.

6. The process as defined in claim 5 further characterized in that said metal is nickel.

7. A process for producing an ethyl benzene which comprises reacting a propyl benzene with hydrogen at a temperature of from about 350° F. to about 650° F. and a pressure not greater than about 1000 pounds per square inch in the presence of a catalyst comprising a reduced metal of the iron group to remove only a methyl group from the propyl radical of a substantial portion of said propyl benzene, thereby forming an ethyl benzene, and recovering from the resultant products a fraction containing said ethyl benzene.

8. The process as defined in claim 7 further characterized in that said propyl benzene is cumene.

9. The process as defined in claim 7 further characterized in that said metal is nickel.

10. The process as defined in claim 7 further characterized in that said propyl benzene is cumene and said metal is nickel.

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