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DEALKYLATION OF ALKYL-SUBSTITUTED AROMATICS

Jack M. Gill and William G. Juhl, St. Louis, Mo., assignors to Monsanto Company, a corporation of Delaware

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The present invention relates to the non-catalytic conversion of hydrocarbons. More particularly, the present invention relates to a process for the non-catalytic dealkylation of alkyl-substituted aromatic compounds.

The dealkylation of alkyl-substituted aromatic hydrocarbons is relatively well known. The dealkylation processes disclosed in the prior art are generally of two types, those carried out in the presence of a catalyst and those carried out by purely thermal means. The vast majority of the known dealkylation processes are of the catalytic type. However, several processes exist in the prior art for the thermal dealkylation of alkyl-substituted aromatic compounds. Generally, however, these non-catalytic processes operate at relatively high temperatures and are vapor phase processes. Of course, the higher the temperature necessary for a hydrocarbon conversion process, the more expensive the process becomes. Also, to operate a process as a vapor phase process significantly reduces the capacity of the reaction unit. Further, present catalytic and thermal dealkylation processes reduce the alkyl substituents on the aromatic ring to methane, thus losing the economic value of the alkyl hydrocarbons which could potentially otherwise be produced. As a result of these and other deficiencies found in the existing processes for the dealkylation of alkyl substituted aromatic compounds by thermal means, very few of such processes have been found to be commercially acceptable.

It is an object of the present invention to provide a process for the dealkylation of alkyl-substituted aromatic compounds. It is another object of the present invention to provide a process for the non-catalytic thermal dealkylation of alkyl-substituted aromatic compounds. Another object of the present invention is to provide a process for the concurrent dealkylation of feed stocks comprised of both alkyl-substituted mono-nuclear and alkyl-substituted poly-nuclear aromatic compounds. Yet another object of the present invention is to provide a process whereby alkyl substituents of aromatic compounds may be substantially reduced in carbon number by the non-catalytic thermal dealkylation of alkyl-substituted aromatic compounds. A particular object of the present invention is to provide a process whereby the alkyl substitutents of alkyl mono-nuclear and alkyl poly-nuclear aromatics may be removed without benefit of a catalyst and at lower temperatures. Another particular object of the present invention is to provide a liquid phase process for the dealkylation of alkyl aromatic compounds. Additional objects will become apparent from the following description of the invention herein disclosed.

In fulfillment of these and other objects it has been found that alkyl aromatic compounds may be successfully dealkylated at high conversions by thermal means according to the process of the present invention which process comprises subjecting a feed stock containing alkyl-substituted aromatic compounds to a temperature of 750 to 1000° F. and a pressure of 400 to 2500 p.s.i.g. in the presence of a hydrogen donor, said hydrogen donor being a partially-hydrogenated aromatic compound. The present invention provides a method for the thermal dealkylation of alkyl aromatic compounds at somewhat lower temperatures than those conventional to other processes. Further, the present invention operated under the conditions above set forth is a liquid phase process thereby providing the advantage of higher capacity for the reaction chamber. Another advantage of the present invention is that alkyl substituents generally are severed from the alkyl aromatic compound as one molecule rather than as several lower molecular weight molecules thereby preserving the alkyl molecule and reducing the hydrogen consumption.

To further illustrate the present invention, the following examples are presented. These examples are not to be construed in any manner as limiting the conditions, application or objects of the present invention.

EXAMPLE I

To demonstrate the present invention, approximately 3 mls. of a mixture of 1-methylnaphthalene and tetralin was placed in a thermal dealkylation chamber of 20 ml. capacity. The 1-methylnaphthalene was present in a mole ratio to the tetralin of 2.25:1. The thermal dealkylation chamber was heated to a temperature of 932° F. The pressure was the sum of the partial pressures of the reactants under the temperature conditions of the dealkylation chamber. The residence time of the reactants in the thermal dealkylation chamber was 15 minutes. The reaction product was found to contain 35.6 mole percent naphthalene.

EXAMPLE II

Example I was substantially repeated with the exception that the temperature was 842° F. and the residence time 30 minutes. The reaction product was found to contain approximately 27.6 mole percent naphthalene. No coke was formed.

EXAMPLE III

Example II was substantially repeated with the exception that the alkyl naphthalene was 2-methylnaphthalene. The reaction product was found to contain 18.8 mole percent of naphthalene. No coke was formed.

EXAMPLE IV

1,6-dimethylnaphthalene and tetralin were placed in the thermal dealkylation chamber of Example I in a mole ratio of 1,6-dimethylnaphthalene to tetralin of approximately 2.67:1 and heated to a temperature of 932° F. The pressure was the sum of the partial pressures of the reactants under the conditions of the reaction zone. The residence time of the reactants in the dealkylation chamber was about 15 minutes. The reaction product collected was found to contain 31.6 mole percent naphthalene, 33.3 mole percent 2-methylnaphthalene, and 3.5 mole percent 1-methylnaphthalene. Some coking occurred.

EXAMPLE V

Example IV was substantially repeated with the exception that the temperature was 842° F. and the residence time of the reactants in the reaction chamber 60 minutes. The reaction product was found to contain 18.6 mole percent naphthalene, 22.7 mole percent 2-methylnaphthalene and 3.7 mole percent 1-methylnaphthalene. No coking occurred.

The temperatures at which the present process is opera-

ble are generally within the range of from approximately 750 to 1000° F. At temperatures below the lower temperature the desired dealkylation reaction falls to a rate too low for practical utilization. At temperatures above 1000° F. the aromatic nucleus of the various alkyl aromatics as well as the hydrogen donors will begin to rupture excessively causing loss of aromatic product and severe carbon formation and coking of the reaction chamber. A particularly preferred range of temperatures for operating the present invention is within the range of from approximately 800 to 950° F.

The pressures at which the present thermal dealkylation process may be successfully carried out range from approximately 400 to 2500 p.s.i.g. Preferably, however, the pressure at which the present thermal dealkylation process is operated is within the range of from about 600 to 1200 p.s.i.g.

The hydrogen donors which are a necessary part of the present thermal dealkylation process are partially-hydrogenated aromatic hydrocarbons. Generally, these hydrocarbons are di-nuclear or poly-nuclear aromatics having one or more of the nuclei partially or totally saturated. A particularly useful group of hydrogen donors are the di-nuclear aromatics in which either one of the nuclei has been partially or completely hydrogenated. As examples of such compounds are tetralin, dihydronaphthalene, di- and tetrahydroalkylnaphthalenes, and the like. Another particularly useful group of hydrogen donor compounds are the tri-nuclear aromatics having one or two of the aromatic nuclei partially or completely hydrogenated to form a saturated ring or rings. Examples of such hydrogen donors are 9, 10-dihydrophenanthrene, tetrahydrophenanthrenes, octahydrophenanthrenes, tetrahydrophenylnaphthalenes and the like. Still another particularly useful group of hydrogen donor compounds are the tetranuclear aromatics having one, two or three of the aromatic nuclei partially or completely hydrogenated. Non-limiting examples of such compounds are dihydrochrysenes, tetrahydrochrysenes, octahydrochrysenes, tetrahydropyrenes, octahydropyrenes, tetrahydrofluoranthenes, octahydrofluoranthenes and the like.

The mole ratio of hydrogen donor to the alkyl aromatic compounds in the dealkylation zone should be within the range of from 0.1:1 to 10:1. The mole ratio of hydrogen donor to the alkyl aromatic compound is determined by the moles of hydrogen potentially available per mole of donor and the moles of alkyl substituents of the alkyl aromatic compounds. Preferably, there should be a stoichiometric equivalent of the alkyl substituents of the alkyl aromatic compounds and the hydrogen available from the hydrogen donors. However, where complex hydrocarbon mixtures are subjected to the dealkylation process of the present invention, the number of alkyl substituents per aromatic nucleus cannot readily be determined. Thus, from a process standpoint, a mole ratio of hydrogen donor to alkyl aromatic compound of 0.25:1 to 5:1 generally is used with a ratio of 0.5:1 to 2:1 being preferred.

The residence time of the reactants within the thermal dealkylation zone is generally within the range of from 0.2 to 60 seconds. If longer residence times are used, there is a liklihood of destruction of a part of the feed material, products and hydrogen donor compounds. At lower residence times, the conversions and yields are far too low for practical application of the present invention. The residence time, of course, is largely dependent upon the temperature. If higher temperatures are used, lower residence times are required. The present invention may be operated as a bath operation or as a continuous flow system. Usually the temperatures are somewhat lower in the former, thus requiring longer residence times. Conversely, in the continuous flow system, higher temperatures with shorter residence times are used. However, in batch operation, the residence time is usually within the range of 15 to 60 minutes and the residence time for the continuous flow system, preferably, within the range of 1 to 12 minutes.

The feed stocks which may be dealkylated in accordance with the present invention include practically any aromatic compound containing alkyl substituents of one or more carbon atom per alkyl substituent. The aromatic compounds may be mono-nuclear or poly-nuclear and may contain one or more alkyl substituents. For example, the feeds to the present invention may be mono-, di-, tri-, or tetra-alkyl substituted aromatic hydrocarbons, such as dimethylbenzenes, trimethylbenzenes, dimethylnaphthalenes, trimethylnaphthalenes, tetramethylnaphthalenes, diethylbenzenes or mono-methylbenzenes, monoethylbenzenes, mono-methylnaphthalenes, diethylnaphthalenes, methyl phenanthrene, dimethyl anthracenes, dimethyl pyrenes, tetraethyl phenanthrenes, dimethylchrysenes, tetraethyl pyrenes, trimethyl anthracenes, diethyl-dimethyl phenanthrenes, methyl ethylbenzene, methyl ethyl naphthalene, and the like. If the alkyl substituents have 3 or more carbon atoms per alkyl group, it is not necessary that the alkyl group be in a straight chain. The alkyl substituent may be either branched-chain or straight-chain. The present invention is equally applicable to the dealkylation of alkyl benzenes and/or alkyl naphthalenes and/or alkyl phenanthrenes and/or alkyl anthracenes and/or alkyl pyrenes and/or alkyl chrysenes, and the like. Also, the present invention finds application in the dealkylation of alkyl aromatic compounds containing substituents other than alkyl groups. For example, the alkyl aromatic compounds may contain hydroxyl, alkoxy, alkoxycarbonyl, halogen, sulfide, sulfate, nitrate, amino, nitrile, nitro, and other such radicals as substituents in addition to the alkyl substituents. Also, the aromatic compound may contain elements other than carbon in the aromatic nucleus. For example, the present invention may be utilized in the dealkylation of alkyl pyridines, alkyl pyrans, alkyl furans and alkyl substituted thiophenes. Also, the present invention has utility in the dealkylation of complex mixtures of the above alkyl aromatic compounds as well as to the pure compounds.

The hydrogen donors of the present invention may be obtained by separating hydrocarbon fractions to obtain the partially-hydrogenated aromatics. Generally, however, the hydrogen donors are obtained by hydrogenating aromatic hydrocarbons by conventional hydrogenation means. The present invention is not, however, to be limited to any particular source or method for obtaining the hydrogen donors.

The individual equipment which may be used in the present invention is not critical as long as it conforms to good engineering principles and will allow efficient operation under the conditions set forth herein.

What is claimed is:

1. A process for the dealkylation of alkyl substituted aromatic hydrocarbons which comprises passing an alkyl substituted aromatic hydrocarbon feed consisting essentially of alkyl aromatic hydrocarbons selected from the group consisting of alkyl benzenes, alkyl naphthalenes, alkyl phenanthrenes, alkyl anthracenes, alkyl pyrenes, alkyl chrysenes, and mixtures thereof, through a dealkylation zone which is maintained at a temperature of 750 to 1000° F. and a pressure of 400 to 2500 p.s.i.g., said alkyl substituted aromatic hydrocarbons being passed into the dealkylation zone concurrently with a hydrogen donor, said hydrogen donor being a partially-hydrogenated aromatic hydrocarbon, and recovering from said dealkylation zone aromatic hydrocarbons of reduced molecular weight.

2. The process of claim 1 wherein the hydrogen donor is a di-nuclear partially-hydrogenated aromatic hydrocarbon.

3. The process of claim 1 wherein the hydrogen donor is a tri-nuclear partially-hydrogenated aromatic hydrocarbon.

4. The process of claim 1 wherein the residence time of the reactants within the dealkylation zone is 0.2 to 60 minutes.

5. The process of claim 1 wherein the temperature is 850 to 950° F.

6. The process of claim 1 wherein the pressure is 600 to 1200 p.s.i.g.

7. The process of claim 1 wherein the alkyl aromatic hydrocarbons are mono-alkyl substituted aromatic hydrocarbons.

References Cited by the Examiner

UNITED STATES PATENTS

3,147,206	9/1964	Tulleners	208—56
3,177,262	4/1965	Calkins	260—672

DELBERT E. GANTZ, *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*