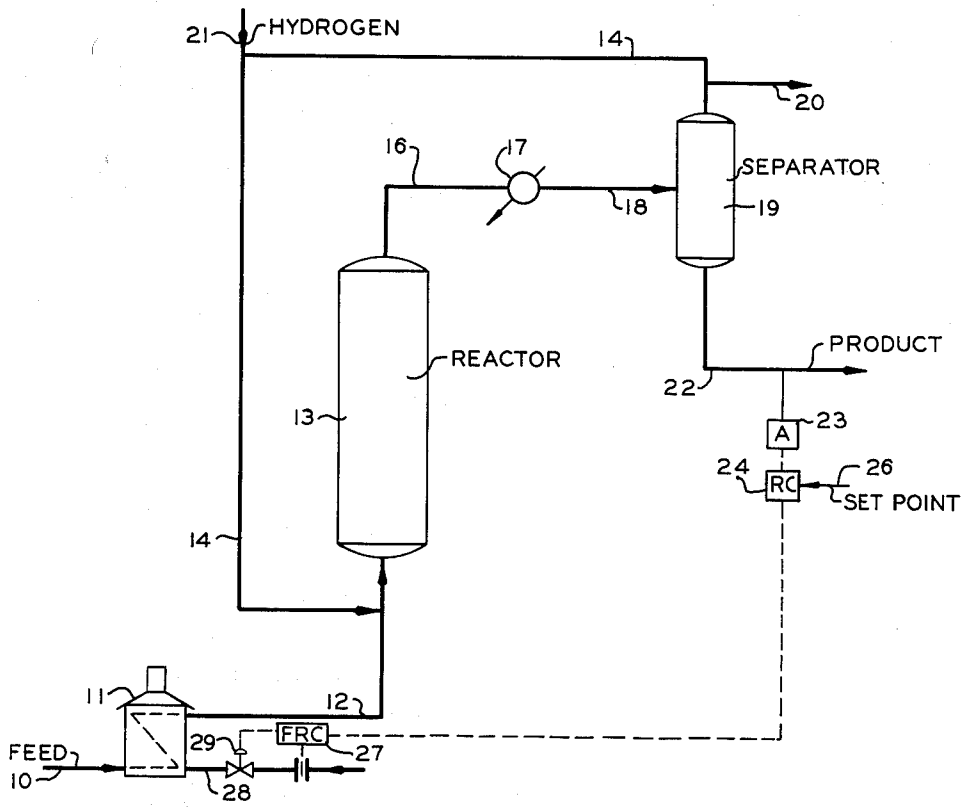
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HYDRODEALKYLATION OF ALKYL NAPHTHALENES

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# HYDRODEALKYLATION OF ALKYL NAPHTHALENES

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This invention relates to the conversion of alkyl-substituted aromatic compounds. In another aspect, this invention relates to the hydrodealkylation of alkyl naphthalenes to produce naphthalene and benzenoid hydrocarbons. In another aspect, this invention relates to the hydrodealkylation of aromatic extract oils obtained from catlytic cracking processes to produce naphthalene and benzenoid hydrocarbons.

In the petroleum industry attention is being directed more and more toward the conversion of light distillates to products other than the conventional burner oils and diesel fuels. The use of light cycle oil (conventionallly a 420–600° F. fraction obtained upon the catalytic cracking of gas-oil) in a burner oil or diesel fuel does not realize the potential value of the 10–50 percent bicyclic aromatics contained in the light cycle oil. The concentration of bicyclic aromatics contained in the light cycle oil fraction depends upon the source of the crude and the depth of conversion. The refractory light catalytic cycle oils high in sulfur and nitrogen content are difficult to market either alone or in blends other than burner oils or diesel fuels.

Moreover, during periods of low demand for burner oil and/or diesel fuel, it becomes necessary to utilize the light cycle oil fraction in other ways. A conventional process comprises recycling the light cycle oil fraction to extinction in the catalytic cracking step. This recycle operation, which results in the conversion of the aromatics to coke, motor fuel, LPG and like gases, again does not realize the potential value of the aromatics contained in the light cycle oil fraction.

The bicyclic aromatics contained in the light cycle oil fraction are too high-boiling to be employed either as a preferred motor fuel, a petrochemical, or a chemical intermediate. Hydrodealkylation of the light cycle oil fraction to produce lower-boiling aromatics is not feasible as the less stable non-aromatic materials in the light cycle oil is converted entirely to gas and coke under the relatively severe conditions required for hydrodealkylation of the aromatic material. It would thus be desirable to provide a process for the extraction of the high-boiling aromatics from the light cycle oil fraction and the hydrodealkylation of the extracted aromatics to produce lower-boiling aromatics.

Due to fluctuations in the market demand for the various aromatics, it would also be highly desirable to control the hydrodealkylation step to produce either preferentially naphthalene or preferentially alkylbenzenes that could be employed as such or subsequently hydrodealkylated to benzene.

I have by my invention provided a process for the hydrodealkylation of bicyclic aromatics to favor the production of naphthalene or to favor the production of alkylbenzenes and/or benzene by controlling the temperature of the hydrodealkylation zone.

Accordingly, an object of my invention is to provide a process and apparatus for the conversion of alkyl naphthalenes to naphthalene and benzenoid hydrocarbons.

Another object of my invention is a process and apparatus for the catalytic conversion of alkyl napthalenes selectively to naphthalene and benzenoid hydrocarbons.

Another object of my invention is to provide a process and apparatus for the hydrodealkylation of alkyl napthalenes selectively to naphthalene and benzenoid hydrocarbons.



Other objects, advantages and features of my invention will be readily apparent to those skilled in the art from the following description and the appended claims.

I have discovered that by proper selection of process conditions during the hydrodealkylation of alkyl naphthalenes the production of either naphthalene or benzene and alkylbenzenes (benzenoid hydrocarbons) can be favored in the same catalytic system. Thus, as relatively high temperatures—other conditions being substantially identical—alkyl naphthalenes are preferentially hydrodealkylated to naphthalene, and at lower temperatures—other conditions again being substantially identical—one ring of the naphthalene is saturated, the saturated ring is opened to form an alkylbenzene, and the alkylbenzene is partially dealkylated to benzene.

Broadly, the invention comprises a process for the hydrodealkylation of alkyl naphthalenes to other valuable aromatic hydrocarbons, which comprises contacting the alkyl naphthalenes with a hydrodealkylation catalyst at an elevated temperature and in the presence of hydrogen gas under super-atmospheric pressures.

The process of this invention can be applied to any alkyl naphthalene. Non-limiting examples are 1-methylnaphthalene; 2-methylnaphthalene; 1,4-dimethylnaphthalene; 2,3-dimethylnaphthalene; 2,7-dimethylnapthalene; 1,2,5-trimethylnapthalene; 1-methyl-4-ethylnaphthalene; 1-methyl-7-isopropylnaphthalene; 1,4-dimethyl-6-ethylnaphthalene; and mixtures containing two or more parts of the foregoing. The invention is particularly applicable to the hydrodealkylation of bicyclic aromatics extracted from a light cycle oil fraction, said light cycle oil fraction obtained from the catalytic cracking of a petroleum gas oil.

The bicyclic aromatic fraction can be obtained from the light cycle oil fraction by employing a selective solvent such as sulfur dioxide to extract the bicyclic aromatic fraction. Conventionally, the light cycle oil fraction is countercurrently contacted with sulfur dioxide at a temperature in the range of 70–100° F., a sulfur dioxide to oil weight ratio in the range of 0.5:1 to 1.5:1, and a pressure in the range of 75–125 p.s.i.g. The bicyclic aromatic fraction can then be separated from the sulfur dioxide by a conventional stripping operation, the bicyclic aromatic fraction hereinafter referred to as an aromatic extract oil.

Suitable hydrodealkylation catalysts can be selected from the Group VIA oxides and sulfides and from the Group VIII metals, oxides and sulfides, and are normally supported on well-known supports such as alumina, acid-treated alumina, silica-alumina, boria-alumina, silica-zirconia, silica-magnesia, or magnesia. Examples of specific catalysts that can be employed are chromia-alumina comprising 20 weight percent chromia and 80 weight percent alumina, and palladium-alumina comprising 0.1 weight percent palladium and 99.9 weight percent alumina.

The process of this invention is carried out at temperatures of between about 900° F. and about 1400° F., preferably at between about 1000° F. and about 1250° F. It has been discovered that the production of naphthalene is favored with a temperature in the range of 1100–1400° F., preferably in the range of 1100–1250° F., and the production of alkylbenzenes and benzene is favored with a temperature in the range of 900–1080° F., preferably in the range of 1000–1080° F. The contact or reaction time depends upon the temperature and the pressure employed. Generally the time of contact will vary indirectly with the temperature and directly with the pressure. The liquid

hourly space velocity (LHSV) is between 0.1 and 10.0, preferably between 0.5 and 3.0.

The inventive process is conducted in the presence of hydrogen gas. Hydrogen can be supplied to the reaction zone in the form of relatively pure hydrogen gas, or of a gas rich in hydrogen, such as refinery gases. The mol ratio of hydrogen to alkyl naphthalene to produce naphthalene and alkylbenzenes can vary between about 1:1 and about 15:1 and preferably between about 4:1 and about 10:1.

The pressure of the hydrodealkylation zone is maintained in the range of from about 50 p.s.i.g. to about 1500 p.s.i.g., preferably in the range from about 500 p.s.i.g. to about 1000 p.s.i.g.

The drawing is a schematic representation of one embodiment of the inventive process.

Referring to the drawing, an alkyl naphthalene feed is passed via conduit means **10** to a means **11** for preheating the alkyl naphthalene feed, such as a furnace. The preheated alkyl naphthalene feed is passed from furnace means **11** via conduit means **12** to reactor **13**. The preheated alkyl naphthalene feed is mixed with hydrogen passed to conduit means **12** via conduit means **14** and the combined hydrogen and alkyl naphthalene feed passed to reactor **13**.

Reactor **13** contains a fixed catalyst bed, the composition of the catalyst as heretofore described. The temperature within reactor **13** is maintained in the range of 900–1400° F. by preheating the alkyl naphthalene feed in the heretofore described manner. A pressure in the range of 50–1500 p.s.i.g. is maintained within reactor **13**.

A vaporous reaction zone effluent is withdrawn from reactor **13** via conduit means **16** and partially condensed by heat exchange means **17**. The temperature of the vaporous and liquid mixture withdrawn from heat exchange means **17** is maintained in the range of 100–600° F. The vaporous and liquid mixture is passed from heat exchange means **17** via conduit means **18** to a separator **19**.

The pressure of separator **19** is in the range of 100–200 p.s.i.g. less than the pressure in reactor **13**. A vaporous stream comprising hydrogen, ethane and methane is withdrawn from separator **19** via conduit means **14** and recycled to reactor **13** via conduit means **12**. To prevent the build-up of light hydrocarbons within the reaction zone, a portion of the vaporous stream can be removed from the process via conduit means **20** and passed to a conventional hydrogen recovery process such as a hydrocarbon absorption process wherein the light hydrocarbons are extracted from the feedstream by an absorption oil such as kerosene. Make-up hydrogen as required can be passed to the recycle hydrogen stream in conduit **14** via conduit means **21**.

A liquid stream comprising naphthalene, alkylbenzenes and benzene is withdrawn from separator **19** via conduit means **22**. The product stream withdrawn from separator **19** via conduit means **22** can be passed to a conventional means of separation such as a fractionation zone. The product stream flowing through conduit **22** is analyzed by a conventional analyzer **23** such as a chromatographic analyzer, which includes a transmitter. Instrumentation of this type is manufactured by Perkin-Elmer Corporation and others. When employing a chromatographic analyzer-transmitter, a programmed holding device such as described in ISA Journal 9, page 28, October 1958, will transmit the analog of the concentration of the component of interest to a conventional recorder-controller **24**.

Recorder-controller **24** compares this input signal with a set point signal **26** representative of the desired concentration of the constituent of interest and transmits a reset signal responsive to said comparison to a conventional flow-recorder-controller **27**. Flow-recorder-controller **27** opens or closes control valve **29** responsive to the reset signal received from recorder-controller **24** and the rate of flow measurement of a heating medium flowing through conduit **28**. Thus, the temperature of the reaction zone within reactor **13** is manipulated in response to the analysis of the product stream flowing through conduit **22**.

If, for example, it is desired to increase the concentration of naphthalene flowing through conduit **22**, the reset signal transmitted by recorder-controller **24** to flow-recorder-controller **27** will cause flow-recorder-controller **27** to open contol valve **29**, thereby increasing the reaction zone temperature within reactor **13**. If it is desired to increase the production of alkylbenzenes and benzene, the reset signal transmitted by recorder-controller **24** will result in the closing of control valve **29** to thereby decrease the reaction zone temperature within reactor **13**.

It is within the scope of this invention to analyze the effluent flowing through conduit **16** and to manipulate the flow through conduit **28** responsive to said analysis so as to maintain the concentration of naphthalene and/or alkylbenzenes at the desired concentration level.

A preferred methot of manipulating the temperature of the hydrodealkylation zone has been illustrated. It is also within the scope of this invention to otherwise manipulate the hydrodealkylation zone temperature. The rate of flow of alkyl naphthalene and hydrogen feed to reactor **13** can be manipulated, thereby manipulating the temperature of the hydrodealkylation zone.

The following examples are presented as illustrative of the inventive process. It is not intended, however, that the invention should be limited thereto.

*Example I*

An aromatic extract obtained from a light cycle oil fraction, which contained 82.4 weight percent substituted alkyl naphthalenes and 17.6 weight percent non-aromatics, was hydrodealkylated in the presence of a catalyst comprising 0.1 weight percent palladium and 99.9 weight percent alumina under the following conditions and with the following yields:

| Catalyst | Palladium-alumina | |
|---|---|---|
| | Run 1 | Run 2 |
| Temperature, ° F | 1,080 | 1,160 |
| Pressure, p.s.i.g | 1,000 | 1,000 |
| $H_2$/aromatic, mol ratio | 8 | 8 |
| $H_2$ rate, c.f./bbl | 6,000 | 6,000 |
| LHSV | 0.8 | 0.8 |
| Product, weight percent: | | |
| Alkylbenzenes [a] | 13.8 | 8.6 |
| Naphthalene | 7.5 | 27.5 |

[a] Including benzene.

Comparison of the results obtained in Runs 1 and 2 illustrates that the high temperature of Run No. 2 favored naphthalene production and that the low temperature of Run No. 1 favored benzene and alkylbenzene production.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of the foregoing disclosure and discussion without departing from the spirit or scope thereof.

I claim:

1. A process for converting alkyl naphthalenes into other aromatic hydrocarbons which comprises contacting an alkyl naphthalene with hydrogen in a hydrodealkylation zone in the presence of a hydrodealkylation catalyst selected from the Group VIA oxides and sulfides and from the Group VIII metals, oxides and sulfides, maintaining the temperature in said hydrodealkylation zone in the range of 900–1080° F., and withdrawing a product effluent from said hydrodealkylation zone containing a constituent of interest selected from the group consisting of alkylbenzenes and benzene.

2. The process of claim 1 wherein the temperature of said hydrodealkylation zone is maintained in the range of 1000–1080° F.

3. The process of claim 1 wherein said alkyl naphthalene is an aromatic extract obtained from a light cycle

oil fraction, and said hydrodealkylation catalyst consists of palladium supported upon alumina.

4. A process for converting alkyl naphthalenes into other aromatic hydrocarbons which comprises passing an alkyl naphthalene to a hydrodealkylation zone, said hydrodealkylation zone containing a hydrodealkylation catalyst selected from the Group VIA oxides and sulfides and from the Group VIII metals, oxides and sulfides, maintaining the temperature of said hydrodealkylation zone within the range of 900–1080° F., passing hydrogen to said hydrodealkylation zone, withdrawing a product effluent from said hydrodealkylation zone, partially condensing said effluent, passing said partially condensed effluent to a separation zone, withdrawing a vapor from said separation zone, passing at least a portion of said withdrawn vapor to said hydrodealkylation zone, and withdrawing a liquid from said separation zone containing a constituent of interest selected from the group consisting of alkylbenzenes and benzene.



5. The process of claim 4 wherein the temperature of said hydrodealkylation zone is manipulated by preheating the alkyl naphthalene feed to said hydrodealkylation zone.

6. The process of claim 4 wherein said alkyl naphthalene is an aromatic extract oil.

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