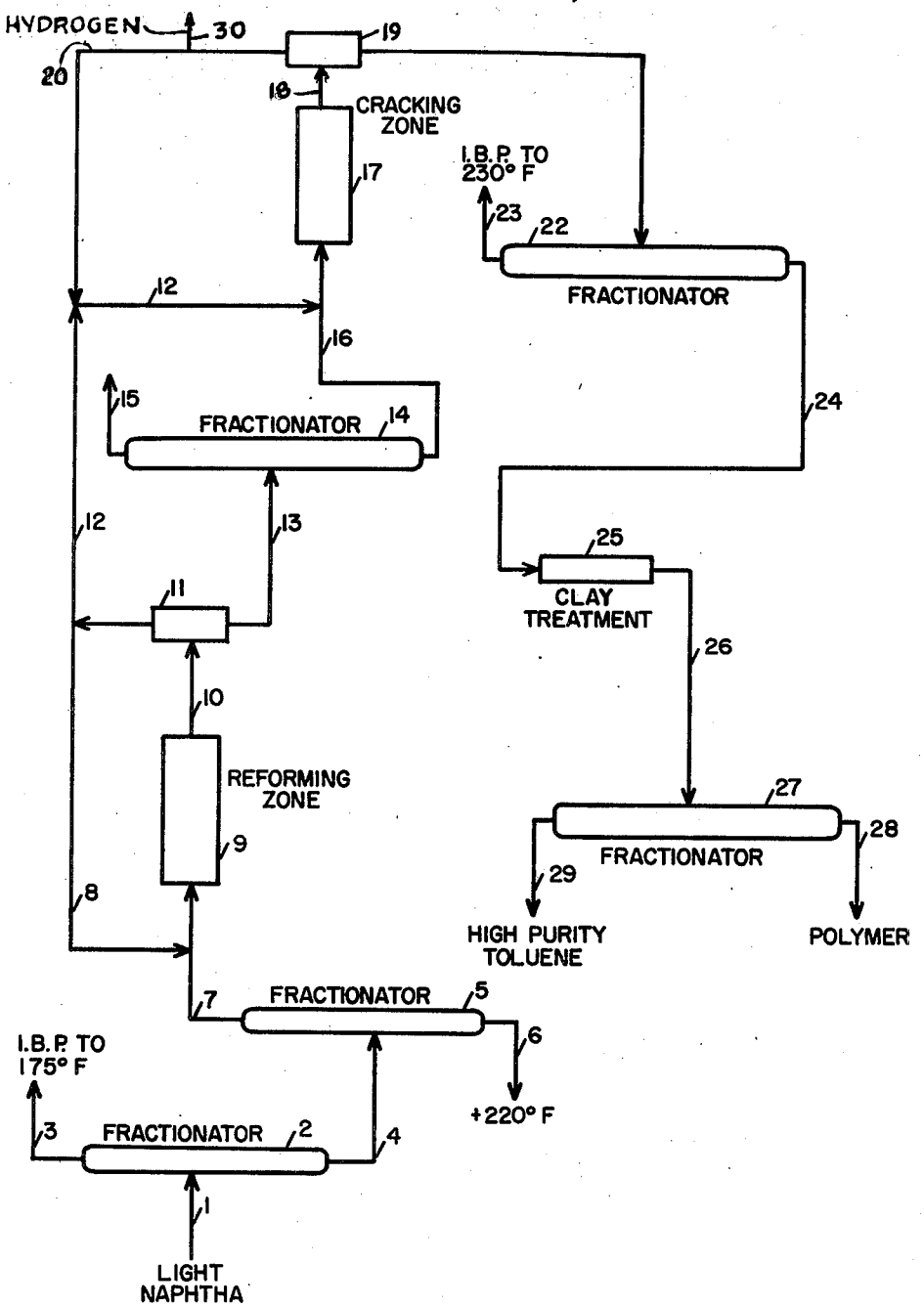
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PRODUCING HIGH PURITY TOLUENE FROM PETROLEUM NAPHTHA

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PRODUCING HIGH PURITY TOLUENE FROM PETROLEUM NAPHTHA

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ABSTRACT OF THE DISCLOSURE

The specification discloses a method of producing nitration grade toluene. The method comprises fractionating a petroleum naphtha to produce a C_7 naphthenic containing fraction which is then subjected to reforming to substantially convert the naphthenes to toluene. Unconverted naphthenic compounds are removed from the reformate by distillation and the resulting toluene concentrate is thermally cracked to convert olefins and paraffins in the fraction to low boiling, easily removable hydrocarbons which are separated in a final distillation.

This invention relates to a process for preparing high purity, nitration grade toluene from a light naphtha petroleum fraction. The invention more specifically involves a combined reforming—thermal cracking operation, conducted under selected conditions, on particular petroleum fractions with intermediate separations between steps.

Although catalytic cracking has been used in combination with reforming to produce a highly aromatic gasoline, the combination has not been used to make a nitration grade toluene, an application which has been found, according to the present invention, to be particularly advantageous.

Aromatics have been produced from petroleum by various procedures including thermal and catalytic conversions in combination with suitable procedures for separating and concentrating the aromatics. It is usually necessary to combine these procedures with additional purification steps such as extraction with a selective solvent or treatment with acid. Even then the aromatic often fails to meet nitration grade specifications. The present invention makes possible the production of nitration grade toluene from a light naphtha by a combination of reforming, thermal cracking and clay treatment, each operation conducted on a critically selected fraction. The invention comprises first fractionating a petroleum naphtha to produce a fraction boiling in the range below 175° F., an intermediate fraction boiling between about 175° and 220° F., and a bottoms fraction boiling above about 220° F. The intermediate fraction contains most of the toluene precursors which are to be converted in a subsequent reforming step. The exact boiling range of this intermediate fraction can be broader than the specified 175 to 220° F. range so long as it does not include precursors of aromatics other than those of toluene which would compete with the toluene formers for the heat required for dehydrogenation in reforming. Also the intermediate fraction should be chosen to provide a high concentration of the toluene formers to make the subsequent reforming step economically feasible.

The intermediate fraction is then subjected to reforming. This step comprises any conventional reforming used on petroleum naphtha and substantially converts toluene precursors, such as C_7 naphthenes, to toluene. The reformate from this step is then fractionated to produce a bottoms fraction boiling above about 225° F. and containing toluene and about 5 to 10 percent paraffins. This fraction is substantially free of benzene, alkylaromatics other than toluene, and naphthenic compounds. The distillation also produces a fraction boiling up to about 225° F. which contains the unconverted toluene precursors, other naphthenic compounds, benzene and the lighter paraffins.

The bottoms fraction is then subjected to thermal cracking at a temperature of from 450 to 1075° F., at a pressure of from atmospheric to 600 p.s.i.g., in the presence of hydrogen in a molar ratio of hydrogen to hydrocarbon between 1:1 and 20:1, and at a liquid hourly space velocity of 0.5 to 10. The conditions of this step must be correlated to produce a cracking severity insufficient to substantially demethylate aromatics but sufficient to crack paraffins to gaseous hydrocarbons. The paraffins are cracked to lower boiling hydrocarbons which can be easily removed by fractionating the crackate to produce a fraction boiling up to about 230° F. and comprising the light paraffins and a fraction boiling at 230° F. and above and comprising toluene of about 99.5 percent purity. The toluene concentrate is then treated to remove residual impurities and to give toluene of nitration grade.

Certain aspects of the present invention should be noted. Firstly, the reforming step is particularly suitable for converting toluene precursors to the aromatic. In the reforming step, the naphthenic C_7's are significantly different in boiling point, from toluene, making the resulting toluene easily separable from unconverted naphthenes. Many other naphthenes are not significantly altered in boiling point with conversion to the aromatic. For example, in the conversion of cyclohexane to benzene, the boiling point of cyclohexane is not changed significantly to make the resulting benzene easily separable from the unconverted cyclohexane.

Thomas, U.S. Patent 2,908,629, teaches reforming a straight run gasoline and catalytically cracking the reformate under conditions which convert paraffins to easily removable low-boiling olefins or light paraffins without affecting aromatics. A highly aromatic gasoline is then easily recovered from the crackate product. This patent contrasts to the process of the present invention which utilizes critical fractionating steps to produce the feeds to the reforming and to the cracking steps. The purpose of the Thomas patent is to produce a highly aromatic gasoline while the present invention is utilized to produce a highly pure, single component, toluene. It is therefore necessary in the present invention to first distill the naphtha feed to give a fraction which is high in toluene precursors, i.e., components which under reforming conditions are converted to toluene. If the reforming step were conducted on a fraction containing C_6 naphthenes, unreacted naphthenes could not easily be removed from the reformate. Again, for example, the dehydrogenation of cyclohexane produces benzene which boils at about the same temperature as cyclohexane. The benzene could not be separated from unconverted cyclohexane in the reformate by distillation. In contrast, the C_7 naphthenes boil, as random examples; methylcyclohexane at 214° F., 1,cis,2,dimethyl cyclopentane at 211° F., and 1,1 dimethylcyclopentane at 190° F., while toluene boils at about 231° F. Toluene, produced by converting C_7 naphthenes, is easily separated by distillation from the unconverted formers.

Another advantage of reforming only the particular toluene precursor-containing fraction is that other aromatic precursors are not present to compete with the C_7 naphthenes for the heat necessary in dehydrogenation for conversion to the aromatics. A higher conversion is therefore possible for a given amount of heat.

Finally, it should be noted that the Thomas catalytic cracking step cracks some of the side chains of alkylaromatics and ends up with a concentrate of about 50 to 85 percent aromatics while the fraction, thermally cracked in the present invention, contains substantially no alkyl-

aromatics other than toluene and produces a crackate of about 90 to 95 percent toluene. Also since catalytic cracking tends to dealkylate aromatics more than thermal cracking, it would appear that some toluene would be demethylated to benzene in the Thomas process.

In Wilson, Jr., et al., U.S. Patent 2,455,634, an aromatic with about 5 percent impurities including paraffins, sulfur compounds, naphthenes and cyclohexanes is subjected to a dual function cracking-dehydrogenation catalyst to convert the impurities to easily separable compounds. The fraction which undergoes cracking according to the present invention contains substantially only toluene as the aromatic. Furthermore, with the novel combination of steps of the present process, in the cracking step, no dehydrogenation catalyst is needed because there are substantially no naphthenic or cycloparaffinic compounds in the impurities. These have been removed in the preceding reforming and distillation steps. This removal is possible with toluene because its precursors are significantly changed in boiling point in reforming as they are converted to toluene.

The invention will be described in reference to the drawing which shows the process of the present invention utilizing reforming and cracking of particular hydrocarbon fractions.

A light naphtha is fed **1** to a fractionator **2** which distills the naphtha to an initial boiling point to 175° F. cut **3** and a cut boiling above 175° F. **4**. The latter fraction is distilled in fractionator **5** to give a bottoms boiling above 220° F. **6** and a fraction boiling between about 175° and 220° F. **7**. This latter fraction is mixed with hydrogen from **8** and is fed into reforming zone **9**.

Suitable processes for reforming petroleum stocks to produce aromatics are well known in the art. This reforming **9** can comprise any known or suitable reforming procedure. Preferably the reforming step **9** uses a platinum type catalyst. This catalyst can be any of the conventional type platinum-on-alumina catalysts which generally contain between about 0.1 to 2.0 percent platinum. Catalysts of this type are available commercially and are extensively described in the literature. The compositions may include various active forms of alumina, such as gamma, eta, and kappa, and the aluminas may vary considerably in surface characteristics depending upon how the catalyst was made. The combination of platinum and the alumina produces a catalyst having a plurality of functions whereby such reactions as dehydrogenation, isomerization, cyclization and hydrocracking are promoted. In some cases a minor amount of a halogen, such as chlorine or fluorine, is incorporated in the catalyst to control the catalytic activity for promoting certain types of these reactions.

The conditions of the reforming step **9** can be varied rather widely, thus temperatures of about 600° to about 1050° F. are suitable and the preferred range is from about 800° to about 950° F. Within these temperature limits weight space velocities of about 0.05 to about 10.0 pounds of naphtha per hour per pound of catalyst in the reaction zone may be employed advantageously, however, space velocities of about 0.25 to about 5.0 provide the best results. Hydrogen should be introduced into the reforming reactor at rates running from about 0.5 to about 20.0 mols of hydrogen per mol of hydrocarbon reactant. While the total reaction pressure in the reformer may be maintained at any value between about 50 and about 1000 pounds per square inch gauge (p.s.i.g.), the best results are obtained by holding the reaction pressure within the range between about 100 and about 750 p.s.i.g. In any event, the reaction conditions should be adjusted to effect a net production of hydrogen in the reaction.

The product from the reforming step **9** is removed from the reforming zone via **10**. Hydrogen is removed from the product via a high pressure separator **11**. The hydrogen is recycled to the reformer feed via **8** or is added via **12** to the feed to the cracking step as hereinafter specifically described,

The product removed from the high pressure separator **11** via **13** contains toluene and saturated compounds. This product is distilled in fractionator **14** to remove saturates in the range boiling up to about 225° F. **15**. The bottoms fraction **16** contains toluene and about 5 to 10 percent saturates. The bottoms is then combined with hydrogen from **12** and thermally cracked in **17** at conditions which are correlated to produce a cracking severity insufficient to demethylate the toluene to a significant degree but sufficient to crack the saturated compounds to lower boiling hydrocarbons.

The thermal cracking of paraffin requires temperatures above about 450° F., with elevated pressures, feed rates of over 0.5 liquid hourly space velocity, and a hydrogen feed of at least, in a molar ratio of hydrogen to saturate, of 1 to 1. On the other hand thermal cracking begins to cause significant demethylation of toluene at temperatures above about 1075°, in combination with pressures of about 600 p.s.i.g. See U.S. Patent 3,193,595. The conditions for the thermal cracking step of this invention then are those conditions at which paraffin will crack but no significant demethylation of toluene will occur. Broadly these conditions would be temperatures of between about 450° and 1075° F. and pressures of between atmospheric and 600 p.s.i.g., these conditions correlated to produce the specified result. Preferably the thermal cracking step should be conducted at temperatures between about 900° and 1000° F., at pressures between about 200 to 400 p.s.i.g. One or the other of the conditions can lie outside these specified ranges so long as, in combination with the other condition, significant cracking of saturates occurs with insignificant demethylation of toluene.

Additionally, the thermal cracking step **17** of the present invention should utilize a liquid hourly space velocity (LHSV) of between 0.5 and 10 and a H_2 to saturate hydrocarbon ratio of between 1:1 to 20:1. Liquid hourly space velocities of between 5 and 8, and H_2 ratios of 4:1 to 6:1 are preferred.

Some art of thermal cracking teaches that significant demethylation of substituted aromatics occurs with the conditions specified by this invention. However the significant demethylation is due to an additional expedient which makes demethylation possible under less severe conditions. For example U.S. Patent 2,776,326 to Schneider teaches operating above about 900° F. at pressures at about 75 p.s.i.g. and above. However operation under these conditions is probably due to the addition of acyclic hydrocarbon in large amounts, which addition is an expedient of the Schneider invention. The feed in the present invention contains 15 percent or less saturates in contrast to the Schneider patent in which acyclic hydrocarbons make up at least one-third of the feed.

After thermal cracking in zone **17**, the crackate is removed via **18** to a high pressure separator **19** where hydrogen is removed and recycled **20**. Excess hydrogen is removed via **30**. The liquid from separator **19** is then sent via **21** to fractionating zone **22** where it is distilled to remove benzene and light paraffins and olefins in an initial boiling point to 230° F. cut **23**, and a toluene containing bottoms **24**. The bottoms are then treated by a conventional clay treatment **25** to improve the acid wash color of the toluene. This step comprises treatment at elevated temperature with ordinary adsorptive clay, such as naturally occurring aluminum silicate clays such as is available commercially under the trademark name of Attapulgus clay. Also suitable and commercially available are Floridin Milwhite and Filtrol. Contact of the bottoms with clay causes olefinic constituents to polymerize. The polymers are then separated from the toluene by distillation.

In the clay treatment step **25** the temperature should be above 275° F. and preferably is maintained within the range of 300–370° F. Sufficient pressure is used to keep the toluene in liquid phase. Contact of the toluene stock with the clay at the elevated temperature employed

causes olefinic constituents to polymerize to form higher boiling materials which can then be separated from the treated aromatic by distillation. A high yield of nitration grade product is obtained in this manner. The clay treated product can be removed from zone **25** via **26** and distilled in fractionator **27** to separate the polymerized olefin **28** to give a high purity toluene **29**.

What is claimed is:

1. A process for producing high purity, nitration grade toluene which comprises:

(a) fractionating a petroleum naphtha to produce a fraction boiling in the range below 175° F., a fraction boiling between 175° to 220° F. and a bottoms fraction boiling above 220° F.;

(b) subjecting the fraction boiling between 175° to 220° F. to reforming whereby hydrocarbon components, which are capable of conversion to toluene under reforming conditions are substantially converted thereto;

(c) fractionating the reformate from said reforming to produce a bottoms fraction boiling above about 225° F. and containing toluene olefins and paraffins and substantially free of other alkylaromatic compounds besides toluene and a fraction boiling up to about 225° F.;

(d) subjecting said bottoms fraction boiling above about 225° F., and containing olefins, paraffins, a high concentration of toluene and being substantially free of other alkylaromatics, to thermal cracking at a temperature of from about 450° to about 1075° F., at a pressure of from about amtospheric to about 600 p.s.i.g., in the presence of hydrogen in a molar ratio of hydrogen to saturate hydrocarbon between 1:1 and 20:1, and at a liquid hourly space velocity of 0.5 to 10, volume of feed per hour per volume of reactor, said conditions being correlated to produce a cracking severity insufficient to demethylate toluene to a significant degree but sufficient to crack said paraffins to lower boiling hydrocarbons;

(e) fractionating the product from said thermal cracking to produce a fraction boiling up to 230° F. comprising light paraffins and olefins, and a fraction boiling at 230° F. and above and comprising toluene and some residual olefins; and

(f) treating said toluene to remove residual olefins to produce a high purity, nitration grade toluene.

2. The process of claim **1** in which Step (d) comprises subjecting the said bottoms fraction boiling above about 225° F., and containing a high concentration of toluene and being substantially free of other alkylaromatics, to thermal cracking at a temperature of from about 900 to about 1000° F., at a pressure of from about 200 to 400 p.s.i.g. in the presence of hydrogen in a molar ratio of hydrogen to saturate hydrocarbon between 4:1 to 6:1, and at a liquid hourly space velocity of 5 to 8 volume of feed per hour per volume of reactor, said conditions being correlated to produce a cracking severity insufficient to demethylene toluene to a significant degree but sufficient to crack said paraffins to lower boiling hydrocarbons.

3. The process of claim **1** in which Step (b) comprises subjecting the fraction boiling between 175° to 220° F. to catalytic reforming in the presence of a platinum on alumina catalyst at temperatures in the range of 600 and 1050° F., and 50 to 1000 p.s.i.g., in the presence of hydrogen in a molar ratio of hydrogen to hydrocarbon between 0.5 and 20.0 and at a liquid hourly space velocity of between 0.05 and 10.0.

4. The process of claim **3** in which Step (b) comprises subjecting the fraction boiling between 175° to 220° F. to catalytic reforming in the presence of a platinum on alumina catalyst at temperatures in the range of about 800° to about 950° F., and 100 to 750 p.s.i.g., in the presence of hydrogen in a molar ratio of hydrogen to hydrocarbon between 0.5 and 20.0, and at a liquid hourly space velocity of between 0.25 and 5.0.

5. The process of claim **1** in which Step (f) comprises contacting said toluene with clay at temperatures above 275° F. to polymerize said residual olefins and distilling to separate said olefins to produce a high purity, nitration grade toluene.

6. The process of claim **1** in which Step (f) comprises contacting said toluene with clay at temperatures within the range of 300 to 375° F. to polymerize said residual olefins and distilling to separate said olefins to produce a high purity nitration grade toluene.

7. The process of claim **2** in which Step (b) comprises subjecting the fraction boiling between 175° to 220° F. to catalytic reforming in the presence of a platinum on alumina catalyst at temperatures in the range of about 800 to about 950° F., and 100 to 750 p.s.i.g., in the presence of hydrogen in a molar ratio of hydrogen to hydrocarbon between 0.5 to and 20.0, and at a liquid hourly space velocity of between 0.25 and 5.0.

8. The process of claim **2** in which Step (f) comprises contacting said toluene with clay at temperatures within the range of 300 to 375° F. to polymerize said residual olefins and distilling to separate said olefins to produce a high purity nitration grade toluene.

9. The process of claim **7** in which Step (f) comprises contacting said toluene with clay at temperatures within the range of 300 to 375° F. to polymerize said residual olefins and distilling to separate said olefins to produce a high purity nitrogen grade toluene.

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