

INTEGRATED HYDROGENATION/DEHYDROGENATION REACTOR
IN A PLATFORMING PROCESS

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 13/327,185 which was
5 filed on December 15, 2011.

FIELD OF THE INVENTION

[0002] The present invention relates to a process for enhancing the production of
aromatics compounds. In particular the improvement and enhancement of aromatic
compounds such as benzene, toluene and xylenes from a naphtha feedstream.

10 BACKGROUND OF THE INVENTION

[0003] The reforming of petroleum raw materials is an important process for producing
useful products. One important process is the separation and upgrading of hydrocarbons for a
motor fuel, such as producing a naphtha feedstream and upgrading the octane value of the
naphtha in the production of gasoline. However, hydrocarbon feedstreams from a raw
15 petroleum source include the production of useful chemical precursors for use in the
production of plastics, detergents and other products.

[0004] The upgrading of gasoline is an important process, and improvements for the
conversion of naphtha feedstreams to increase the octane number have been presented in
US 3,729,409, US 3,753,891, US 3,767,568, US 4,839,024, US 4,882,040 and US 5,242,576.
20 These processes involve a variety of means to enhance octane number, and particularly for
enhancing the aromatic content of gasoline.

[0005] While there is a move to reduce the aromatics in gasoline, aromatics have many
important commercial uses. Among them include the production of detergents in the form of
alkyl-aryl sulfonates, and plastics. These commercial uses require more and purer grades of
25 aromatics. The production and separation of aromatics from hydrocarbons streams are
increasingly important.

[0006] Processes include splitting feeds and operating several reformers using different
catalysts, such as a monometallic catalyst or a non-acidic catalyst for lower boiling point

hydrocarbons and bi-metallic catalysts for higher boiling point hydrocarbons. Other improvements include new catalysts, as presented in US 4,677,094, US 6,809,061 and US 7,799,729. However, there are limits to the methods and catalysts presented in these patents, and which can entail significant increases in costs.

- 5 **[0007]** Improved processes are needed to reduce the costs and energy usage in the production of aromatic compounds.

SUMMARY OF THE INVENTION

[0008] The present invention is a process for improving the yields of aromatic compounds from a hydrocarbon feedstream. In particular, a preferred feedstream is a full
10 boiling range naphtha. The increase in demand for aromatic compounds enhances the value of converting paraffins, olefins and naphthenes to aromatics.

[0009] The process includes passing the hydrocarbon feedstream to a fractionation unit to generate a light stream comprising C7 and lighter hydrocarbons and a heavy stream comprising C8 and heavier hydrocarbons. The process includes passing the light stream to a
15 hydrogenation/dehydrogenation reactor system to generate an intermediate process stream having C6 and C7 aromatics with a reduced olefin content. The heavy stream is passed to a reforming reactor system, to convert the heavier paraffins to aromatic compounds and generate a reformate stream. The reformate stream and the intermediate process stream are sent to a second reforming reactor system to generate a reformate product stream. The
20 reformate product stream is passed to a reformate splitter to generate a reformate overhead stream comprising C7 and lighter aromatics, and lighter hydrocarbons, and a reformate bottoms stream comprising C8 and heavier hydrocarbons. The reformate overhead stream is passed to a aromatics recovery unit to generate an aromatics product stream.

[0010] In one embodiment, the hydrogenation/dehydrogenation reactor system uses a
25 metal catalyst on a support to hydrogenate the olefins present in the process stream and to dehydrogenate the naphthenes present in the process stream.

[0011] Other objects, advantages and applications of the present invention will become apparent to those skilled in the art from the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWING

[0012] Figure 1 is a diagram of a first process for increasing aromatics yields by separately processing and reforming light naphthenic and olefinic compounds; and

[0013] Figure 2 is a diagram of a second process for increasing aromatics yields by processing the light and heavy hydrocarbon streams separately.

DETAILED DESCRIPTION OF THE INVENTION

[0014] There is an increased demand for aromatics. Important aromatics include benzene, toluene, and xylenes. These aromatics are important components in the production of detergents, plastics, and other high value products. With increasing energy costs, energy efficiency is an important aspect for improving the yields of aromatics. The present invention provides for understanding the differences in the properties of the different components in a hydrocarbon mixture to develop a better process.

[0015] The feedstock comprises many compounds and the reforming process proceeds along numerous pathways. The reaction rates vary with temperature, and the Arrhenius equation captures the relationship between the reaction rate and temperature. The reaction rate is controlled by the activation energy for a particular reaction, and with the many reactions in the reforming process, there are many, dissimilar activation energies for the different reactions. For the different reactions, it is possible to manipulate the conversion of one hydrocarbon to a desired product, e.g. hexane to benzene. A process is best operated at isothermal conditions, and produces the highest yields if the reactions are controlled to a narrow temperature range to simulate near isothermal conditions.

[0016] The reforming process is substantially endothermic, and requires a continuous addition of heat to maintain the temperature of reaction. Different components within a hydrocarbon mixture have different endothermicities during the reforming process. Separating out the components with the highest endothermicities reduces the heat load to the process. In addition, separate processing of components that take in the most heat allows for more isothermal control of the reforming process downstream. While the description herein describes the reaction temperatures in the reactors, the reaction temperatures refer to the reactor inlet temperatures. The actual reactor temperatures will fluctuate, and drop somewhat from the reactor inlet temperatures. The control of the process is to maintain a

relatively constant inlet temperature, with the reactor sized and process controls directed to minimize the temperature drop within the reactors.

[0017] While all of the components react differently, it would be impossible to separate out each component. But it has been found that some of the types of components have different properties which significantly affect the reaction process. Dehydrogenation is an important process for the production of aromatics. Generally, naphthenes are highly endothermic, and this requires a continuous addition of heat to the process. By separating the naphthenes from the bulk of the feedstock, and processing the naphthene rich stream separately, downstream reactors can be held in a more near isothermal operation. The process can be utilized with a variety of hydrocarbon feedstreams, but a full boiling range naphtha feedstream having a significant amount of naphthenes and aromatics provides a useful preferred source of hydrocarbons for the generation and recovery of aromatics.

[0018] The present invention, as shown in Figure 1, includes passing a hydrocarbon feedstream 8 to a fractionation unit 10. The fractionation unit 10 is operated to separate the feedstream into an overhead stream 12 having C7 and lighter hydrocarbons, and a bottoms stream 14 having C8 and heavier hydrocarbons. In particular, the operation is for separating light naphthenes, such as cyclohexane, to the overhead stream 12. The overhead stream 12 is passed to a hydrogenation/dehydrogenation reactor system 20, to dehydrogenate the naphthenes and to hydrogenate some of the olefins, to generate a first stream 22 having C6 and C7 aromatics and with a low olefin content. The bottoms stream is passed to a bottoms, or heavy, reforming unit 30 to generate a bottoms reformat 32 having aromatic compounds. The first stream 22 and the bottoms reformat stream 32 are passed to an isothermal reactor system 40 to further convert paraffins to aromatics and to generate an aromatics process stream 42. The aromatics process stream 42 is passed to a reformat splitter 50 to recover the lighter aromatics. The reformat splitter 50 generates a reformat overhead stream 52 having C7 and lighter aromatics, and C7 and lighter compounds such as paraffins. The reformat splitter 50 also generates a reformat bottoms stream 54 having C8 and heavier hydrocarbons. The reformat overhead stream 52 is passed to an aromatics recovery unit 60 to generate an aromatics product stream 62 comprising benzene and toluene. The remainder of the hydrocarbons from the aromatics recovery unit 60 are passed out as a raffinate stream 64 comprising paraffins.

[0019] The aromatics recovery unit 60 can comprise different methods of separating aromatics from a hydrocarbon stream. One industry standard is the SulfolaneTM process, which is an extractive distillation process utilizing sulfolane to facilitate high purity extraction of aromatics. The SulfolaneTM process is well known to those skilled in the art.

5 **[0020]** The process can further include passing the raffinate stream 64 to the hydrogenation/dehydrogenation reactor 20 for further conversion of the hydrocarbons in the raffinate stream 64. The need to pass the raffinate stream 64 to the hydrogenation/dehydrogenation reactor 20 can depend on the amount of naphthenes and olefins in the raffinate stream 64. When the raffinate stream 64 has an olefinic content of at least 10 wt%, the raffinate stream 64 is passed to the hydrogenation/dehydrogenation reactor 20. For a raffinate stream 64 having low naphthene content, the raffinate stream 64 can, in an alternative, be passed to the isothermal reactor system 40.

[0021] The passing of high olefinic content streams to the hydrogenation/dehydrogenation reactor system 20 removes olefins that can reduce the reforming catalyst deactivation due to the presence of the olefins in the hydrocarbon stream.

[0022] The hydrogenation/dehydrogenation reactor system 20 uses a single catalyst. The catalyst is a non-acid catalyst and has a metal function. The preferred catalyst is a metal deposited on an inert support. The catalyst is non-chlorided. The catalyst performs two functions, while it is a single catalyst. The catalyst will hydrogenate olefins and also dehydrogenate naphthenes. In studying the reaction rates various classes of hydrocarbons and for various reactions were looked at for catalytic reactions over a catalyst with a platinum metal. For hydrogenation the reaction rates run from 10^{-2} to 10^2 molecules/site-s, and has an operating window generally from 200°C to 450°C. Dehydrogenation has reaction rates from 10^{-3} to 10 molecules/site-s, and has an operating window generally from 425°C to 780°C.

20 There is an overlap of these reaction windows where both reactions occur when the temperature in the reactor is held to between 400°C and 500°C, and preferably 420°C and 460°C, and more preferably between 425°C and 450°C. A wider range can be employed depending on the relative amounts of naphthenes and olefins. This allows for the simultaneous reactions of hydrogenation of some hydrocarbon components, while dehydrogenating other hydrocarbon components. In particular, olefins present can be hydrogenated while naphthenes are dehydrogenated.

[0023] Preferably, the hydrogenation/dehydrogenation reactor system 20 is a fixed bed reactor system, but it is intended to include other types of reactor bed structures within this invention, including, but not limited to, moving bed systems, bubbling bed systems, and stirred reactor bed systems.

5 **[0024]** The catalyst in the hydrogenation/dehydrogenation reactor system 20 is preferably a metal only catalyst on a support, where the choice of catalyst metal is from a Group VIII noble elements of the periodic table. The Group VIII noble metal may be selected from the group consisting of platinum, palladium, iridium, rhodium, osmium, ruthenium, or mixtures thereof. Platinum, however, is the preferred Group VIII noble metal component. It is believed
10 that substantially all of the Group VIII noble metal component exists within the catalyst in the elemental metallic state. Preferably, the catalyst in the hydrogenation/dehydrogenation reactor has no acid function.

[0025] Preferably the Group VIII noble metal component is well dispersed throughout the catalyst. It generally will comprise 0.01 to 5 wt.%, calculated on an elemental basis, of the
15 final catalytic composite. Preferably, the catalyst comprises 0.1 to 2.0 wt.% Group VIII noble metal component, especially 0.1 to 2.0 wt.% platinum.

[0026] The Group VIII noble metal component may be incorporated in the catalytic composite in any suitable manner such as, for example, by coprecipitation or cogelation, ion exchange or impregnation, or deposition from a vapor phase or from an atomic source or by
20 like procedures either before, while, or after other catalytic components are incorporated. The preferred method of incorporating the Group VIII noble metal component is to impregnate the support with a solution or suspension of a decomposable compound of a Group VIII noble metal. For example, platinum may be added to the support by commingling the latter with an aqueous solution of chloroplatinic acid. Another acid, for example, nitric acid or
25 other optional components, may be added to the impregnating solution to further assist in evenly dispersing or fixing the Group VIII noble metal component in the final catalyst composite.

[0027] The support can include a porous material, such as an inorganic oxide or a molecular sieve, and a binder with a weight ratio from 1:99 to 99:1. The weight ratio is
30 preferably from 1:9 to 9:1. Inorganic oxides used for support include, but are not limited to, alumina, magnesia, titania, zirconia, chromia, zinc oxide, thoria, boria, ceramic, porcelain,

bauxite, silica, silica-alumina, silicon carbide, clays, crystalline zeolitic aluminasilicates, and mixtures thereof. Porous materials and binders are known in the art and are not presented in detail here.

5 **[0028]** The isothermal reactor system 40 can comprise a plurality of smaller reactors operated sequentially, with inter-reactor heat exchangers between sequential reactors. This provides for maintaining the process nearer to isothermal conditions.

10 **[0029]** The process can further include passing the feedstream 8 to a hydrotreater (not shown) before passing the feedstream to the fractionation unit 10. The hydrotreater removes sulfur compounds prior to passing the hydrocarbon stream to the catalytic reactors, thereby providing protection to the catalysts by removing common catalytic poisons.

15 **[0030]** The isothermal reactor system 40 utilizes a reforming catalyst and is operated at a temperature between 520°C and 600°C, with a preferred operating temperature between 540°C and 560°C, with the reaction conditions controlled to maintain the isothermal reactions at or near 540°C. A plurality of reactor with inter-reactor heaters provides for setting the reaction inlet temperatures to a narrow range, and multiple, smaller reactors allow for limiting the residence time and therefore limiting the temperature variation across the reactor system 40. The process or reforming also includes a space velocity between 0.6 hr⁻¹ and 10 hr⁻¹. Preferably the space velocity is between 0.6 hr⁻¹ and 8 hr⁻¹, and more preferably, the space velocity is between 0.6 hr⁻¹ and 5 hr⁻¹. Due to the elevated temperature, the problems of potential increased thermal cracking are addressed by having a shorter residence time of the process stream in the isothermal reactor system 40. An aspect of the process can use a reactor with an internal coating made of a non-coking material. The non-coking material can comprise an inorganic refractory material, such as ceramics, metal oxides, metal sulfides, glasses, silicas, and other high temperature resistant non-metallic materials. The process can also utilize piping, heater internals, and reactor internals using a stainless steel having a high chromium content. Stainless steels having a chromium content of 17% or more have a reduced coking ability.

25 **[0031]** Reforming catalysts generally comprise a metal on a support. The support can include a porous material, such as an inorganic oxide or a molecular sieve, and a binder with a weight ratio from 1:99 to 99:1. The weight ratio is preferably from 1:9 to 9:1. Inorganic oxides used for support include, but are not limited to, alumina, magnesia, titania, zirconia,

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chromia, zinc oxide, thoria, boria, ceramic, porcelain, bauxite, silica, silica-alumina, silicon carbide, clays, crystalline zeolitic aluminasilicates, and mixtures thereof. Porous materials and binders are known in the art and are not presented in detail here. The metals preferably are one or more Group VIII noble metals, and include platinum, iridium, rhodium, and palladium. Typically, the catalyst contains an amount of the metal from 0.01% to 2% by weight, based on the total weight of the catalyst. The catalyst can also include a promoter element from Group IIIA or Group IVA. These metals include gallium, germanium, indium, tin, thallium and lead.

[0032] A second process for improving the production of aromatic compounds from a full boiling range naphtha is presented as shown in Figure 2. The process includes passing the naphtha feedstream 8 to a fractionation unit 10 to generate an overhead stream 12 having C7 and lighter hydrocarbons and a bottoms stream 14 having C8 and heavier hydrocarbons. The overhead stream 12 is passed to a hydrogenation/dehydrogenation reactor system 20, where a first stream 22 is generated having a low olefin content, a reduced naphthene content and an increased C6 and C7 aromatics content. The first stream 22 is passed to a light reforming reactor system 44 to generate a first aromatics stream 47. The light reforming reactor system 44 is operated to be a substantially isothermal system.

[0033] The bottoms stream 14 is passed to a bottoms reforming unit 30 for conversion of some of the hydrocarbons, including the naphthenes to aromatics, and generates a second stream 32 having a reduced naphthene content. The second stream 32 is passed to a heavy reforming reactor system 46, thereby generating a second aromatics stream 48. The first 47 and second 48 aromatics streams are passed to a reformate splitter 50. The reformate splitter 50 generates a reformate overhead stream 52 having C7 and lighter aromatics and hydrocarbons, and a reformate bottoms stream 54 having C8 and heavier hydrocarbons. The reformate overhead stream 52 is passed to an aromatics recovery unit 60 to generate an aromatics product stream 62, and a raffinate stream 64. The aromatics product stream 62 comprises benzene and toluene, and can include small amounts of xylenes.

[0034] The process can further include passing the raffinate stream 64 to the hydrogenation/dehydrogenation reactor system 20 for hydrogenating the olefins. In an alternative, if the raffinate stream 64 is sufficiently low in olefin content, the raffinate stream 64 can be passed to the light reforming reactor system 44.

[0035] The hydrogenation/dehydrogenation reactor system 20 uses a single catalyst that will perform both the function of hydrogenating olefins and dehydrogenating naphthenes. The hydrogenation/dehydrogenation reaction is operated in a relatively narrow temperature window where both reactions occur when the temperature in the reactor is held to between
5 400°C and 500°C , and preferably 420°C and 460°C , and more preferably between 425°C and 450°C. When the catalyst contacts an olefin, it performs a hydrogenation of the olefin, but if the catalyst contacts a naphthene, it performs a dehydrogenation of the naphthene. This reactor also processes the hydrocarbon components that have the greatest amount of endothermicity in the conversion to aromatics. The conversion of these components before
10 passing the first stream 22 on to the isothermal system 44 reduces the energy input to the light reforming reactor system 44. The isothermal system 44 can comprise a plurality of smaller reactors with inter-reactor heaters for maintaining a substantially isothermal reaction system.

[0036] The bottoms reforming unit 30 is operated at a temperature lower than the heavy reforming reactor system 46. The heavy reforming reactor system 46 can comprise a
15 plurality of reactors with inter-reactor heaters, and is operated as a substantially isothermal process. The preferred operating temperature range for the heavy reforming reactor system 46 is between 520°C and 600°C, with a preferred operating temperature between 540°C and 560°C, with the reaction conditions controlled to maintain the isothermal reactions at or near
20 540°C. The bottoms reforming unit 30 is operated at a lower temperature and a temperature range for the bottoms unit 30 is from 420°C to 540°C, with a preferred temperature between 440°C and 500°C. The bottoms reforming unit 30 provides for the conversion of higher endothermic components before passing the second stream 32 on to the isothermal heavy reforming reactor system 46.

25 **[0037]** In an alternate embodiment, the heavy reforming reactor system 46 is operated at a lower temperature, such as in the temperature range from 420°C to 540°C.

[0038] This process is useful for a hydrocarbon feedstream having a substantial amount of naphthenic compounds, such as a full boiling range naphtha. The naphtha feedstream 8
30 can be passed to a hydrotreater for removing sulfur compounds and other compounds that will act as poisons to the catalysts in the reforming reactors.

[0039] Therefore, increases can be achieved through innovative flow schemes that allow for process control of the reactions. While the invention has been described with what are presently considered the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

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CLAIMS:

1. A process for producing aromatic compounds from a hydrocarbon feedstream, comprising:

5 passing the hydrocarbon feedstream to a fractionation unit to generate an overhead stream comprising C7 and lighter hydrocarbons, and a bottoms stream comprising C8 and heavier hydrocarbons;

 passing the overhead stream to a hydrogenation/dehydrogenation reactor system thereby generating a first stream having C6 and C7 aromatics with low olefin content;

10 passing the bottoms stream to a bottoms reforming unit, to generate bottoms reformate comprising aromatics;

 passing the first stream and the bottoms reformate to a substantially isothermal reactor system, thereby generating an aromatics stream; and

15 passing the aromatics stream to a reformate splitter, to generate a reformate overhead stream comprising C7 and lighter aromatics and C7 and lighter paraffins, and a bottoms stream comprising C8 and higher hydrocarbons.

20 2. The process of claim 1 further comprising passing the reformate overhead stream to an aromatics recovery unit to generate an aromatics product stream comprising benzene and toluene, and a raffinate stream.

3. The process of claim 2 further comprising passing the raffinate stream to the hydrogenation/dehydrogenation reactor system.

25 4. The process of claim 2 further comprising passing the raffinate stream to the substantially isothermal reactor system.

5. The process of any of claims 1 to 4 wherein the hydrocarbon feedstream is a full boiling range naphtha.

6. The process of any of claims 1 to 5 wherein the hydrogenation/dehydrogenation reactor system uses a catalyst that has a metal function to hydrogenate olefins and to dehydrogenate naphthenes.
- 5 7. The process of any of claims 1 to 6 wherein the isothermal reactor system comprises a plurality of reactors with inter-reactor heaters, and the reactor system is operated at a temperature greater than 540°C.
8. The process of any of claims 1 to 7 wherein the hydrogenation/dehydrogenation reactor
10 system is operated at a temperature between 420°C and 460°C.
9. The process of any of claims 1 to 8 wherein the hydrogenation/dehydrogenation system comprises a metal only catalyst on an inert support material.
- 15 10. The process of any of claims 1 to 9 further comprising the hydrocarbon feedstream to a hydrotreater before passing the hydrocarbon feedstream to the fractionation unit.