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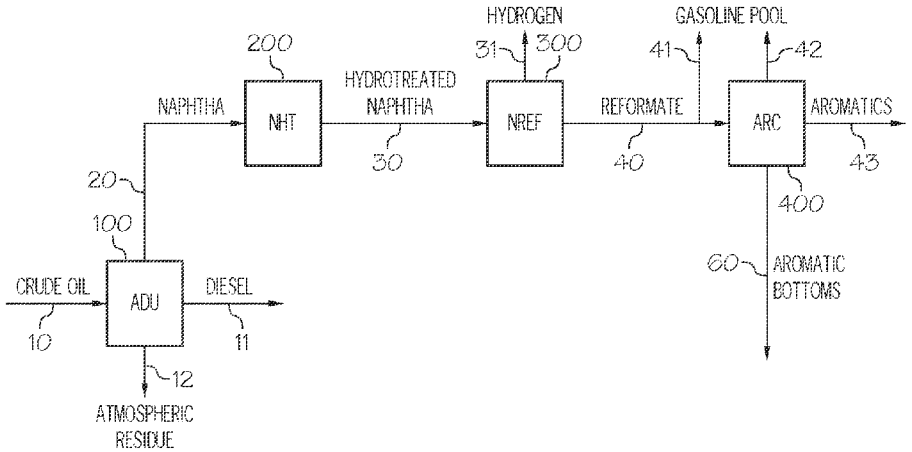

FIG. 1

(57) **Abstract:** The invention relates to a process and system arrangement to generate benzene, toluene and xylenes in a refinery. The process relies on recycling a C_{9+} aromatic bottoms stream from an aromatic recovery complex back to rejoining a hydrotreated naphtha stream as it enters a catalytic reformer. The aromatic bottoms can be further reacted through both the reformer and the subsequent aromatic recovery complex to transform to higher value compounds, thereby reducing waste or reducing bottoms' presence in gasoline pools.

[Continued on next page]

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RECYCLE CATALYTIC REFORMING PROCESS TO INCREASE AROMATICS YIELD

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Patent Application Serial Number 16/944,494, filed on July 31, 2020, entitled "RECYCLE CATALYTIC REFORMING PROCESS TO INCREASE AROMATICS YIELD," the entire contents of which are incorporated by reference in the present disclosure.

TECHNICAL FIELD

[0002] The present disclosure generally relates to processes and systems for the recycling or recirculation of a C_{9+} hydrocarbon aromatic bottoms stream to a catalytic reformer to improve recovery of high value product within a refinery complex.

BACKGROUND

[0003] Refinery products used for producing fuels receive increasing levels of attention, particularly with respect to minimizing waste and emissions. National and international concerns and regulations continue to evolve concerning gasoline specifications, and automakers have further set limitations for gasoline and diesel to allow them to provide vehicles that produce minimal emissions over their lifetime. Goals are set such as a maximum levels for sulfur, aromatics, and benzene levels of 10 ppmw (parts per million per weight), 35 V %, and 1 V % or less, respectively.

[0004] When the use of lead to increase octane was phased out due to environmental concerns, no direct gasoline substitute existed, and refiners instead looked to convert certain hydrocarbon molecules to higher octane ratings. Catalytic reforming of naphtha is now a widely used process for refining hydrocarbon mixtures to increase the yield of higher octane gasoline.

[0005] In a typical refinery, naphtha is reformed after hydrodesulfurization to increase the octane number of the gasoline. The naphtha reformate, however, contains a high level of benzene, up to or above 10 V % in reformate. However, no more than 1-3 V % or less can be present in typical gasoline pools. Methods to remove benzene from reformate currently exist, including separation processes and hydrogenation reaction processes. In separation processes, benzene is typically extracted with a solvent and then separated from the solvent through a membrane separation unit or other suitable unit operation. In hydrogenation reaction processes, the reformate

is divided into fractions to concentrate the benzene followed by hydrogenation of one or more of the benzene-rich fractions.

[0006] In a typical catalytic reforming unit, a naphtha stream is first hydrotreated in a hydrotreating unit to produce a hydrotreated naphtha stream. The hydrotreating unit operates under conditions (e.g., temperature, pressure, hydrogen partial pressure, liquid hourly space velocity (LHSV), catalyst selection/loading) that are effective to remove at least enough sulfur and nitrogen to meet requisite specifications. For instance, hydrotreating in conventional naphtha reforming systems generally occurs under relatively mild conditions that are effective to lower sulfur and nitrogen to less than 0.5 ppmw levels.

[0007] The hydrotreated naphtha stream is then reformed in a reforming unit to produce a gasoline reformate product stream. In general, the operating conditions for the catalytic naphtha reforming unit include a temperature in the range of from about 260 °C to about 560 °C, a pressure in the range of from about 1 bar to about 50 bars, and a LHSV in the range of from about 0.5 h^{-1} to about 40 h^{-1}.

[0008] In the catalytic reforming process, paraffins (alkanes) and naphthenes (cycloalkanes) are restructured to produce isomerized paraffins and aromatics of relatively higher octane numbers. Aromatics are left essentially unchanged or some may be hydrogenated to form naphthenes due to reverse reactions taking place in the presence of hydrogen. The reactions involved in catalytic reforming are commonly grouped into the four categories of cracking, dehydrocyclization, dehydrogenation and isomerization in parallel. A particular hydrocarbon/naphtha feed compound may undergo more than one form of reaction and/or may form more than one product. The catalysts for catalytic reforming processes are either mono-functional or bi-functional reforming catalysts that contain precious metals, such as IUPAC Groups 8-10, as active components. A bi-functional catalyst features both metal and acidic sites. Refineries generally use a platinum catalyst or platinum alloy supported on alumina as the reforming catalyst. The resulting reformate is sent to the gasoline pool to be blended with other gasoline components to meet the specifications. A typical gasoline blending pool includes C_4 and heavier hydrocarbons that have boiling points of less than about 205 °C.

[0009] The hydrocarbon/naphtha feed composition, the impurities present therein, and the desired products determine the processing parameters with regard to choice of catalyst(s), process

type etc. Particular types of chemical reactions can be targeted through a selection of catalyst or operating conditions known to those of ordinary skill in the art to influence both yield and selectivity of conversion of paraffinic and naphthenic hydrocarbon precursors to particular aromatic hydrocarbon structures.

SUMMARY

[0010] The reformate is usually sent to an aromatics recovery complex (ARC) where it undergoes several further processing steps in order to recover high value products, such as xylenes and benzene, and to convert lower value products, such as toluene, into higher value products. Aromatics present in the reformate are usually separated into different fractions by carbon number; for example benzene, toluene, xylenes, and ethylbenzene, etc. The C_8 fraction is subjected to a processing scheme to make more high value para-xylene by separating the para-xylene from the ortho-xylene, meta-xylene, and ethylbenzene using selective adsorption or crystallization. The ortho-xylene and meta-xylene remaining after para-xylene separation are isomerized to produce an equilibrium mixture of xylenes. The ethylbenzene is isomerized into xylenes or is dealkylated to benzene and ethane. The para-xylene is then again separated with the remaining para-xylene-depleted-stream being recycled to extinction through the isomerization unit and then to the para-xylene recovery unit until all are converted to para-xylene and recovered.

[0011] Toluene is typically recovered as a separate fraction and converted into higher value products, such benzene and/or xylenes through conversion processes such as disproportionation of toluene to make benzene and xylenes. Further processes involve hydrodealkylation of toluene to make benzene. Both toluene disproportionation and toluene hydrodealkylation result in the formation of benzene.

[0012] However, with current and future anticipated environmental regulations involving benzene, it is desirable that the toluene conversion not result in the formation of significant quantities of benzene. The problem faced by refineries is now how to most economically reduce benzene content in the reformate products sent to the gasoline pool by modifying the processes and apparatus of existing systems practicing the prior art processes described above.

[0013] Currently, the aromatics bottoms from an ARC is currently added to the gasoline fraction, although it has very high final boiling point, as it is a small volume. However, it deteriorates the gasoline quality and in the long run impacts the engine performance negatively.

Therefore a solution is required to improve the quality of the aromatics fraction. As set forth in US 10,053,401 (incorporated by reference herein in its entirety), hydrodearylation offers an approach to convert bridged noncondensed di- or multi- aromatics to mono-aromatics. Further, US 10,093,873 (incorporated by reference herein in its entirety) contemplates returning aromatic bottoms to the atmospheric distillation unit. However, given the temperatures therein and the fractioning of heavier hydrocarbons (e.g. C_{9+}) in a diesel fraction, heavier compounds returned to the ADU may be fractioned therewith. As such, a further approach is needed to recover or obtain higher value mono-aromatics (e.g. benzene, toluene and xylene "BTX") from a refinery complex.

[0014] Accordingly, ongoing needs exist deriving and/or recovering higher value hydrocarbons from the refining complex and for reducing waste and/or production of low value hydrocarbons. The present disclosure achieves such by recycling the heavier aromatics back into the system to be processed further.

[0015] The present disclosure provides a method to increase recovery of benzene, toluene and xylene. The method may include supplying to a naphtha reforming unit (NREF) a stream of hydrotreated naphtha and then allowing the stream to flow through the NREF to generate reformate and hydrogen gas. At least a portion of reformate is then supplied from the NREF to an aromatics recovery complex (ARC). A portion of the reformate then may flow in the ARC through a reformate splitter to generate a C_{8+} stream. The C_{8+} stream may then flow through a xylene re-run splitter to obtain a C_8 stream and a C_{9+} stream. The C_{9+} stream may then be redirected back to enter the stream of hydrotreated naphtha to thereby reprocess the C_{9+} stream and recover a higher yield of benzene, toluene and xylene.

[0016] In some instances, the C_{9+} stream is recycled to the stream of hydrotreated naphtha prior to entering the NREF. In other instances, the C_{9+} stream is recycled to the stream of hydrotreated naphtha within the NREF.

[0017] In certain aspects, the C_{9+} stream feeds into the NREF equally before each reactor unit contained therein. In other aspects, the NREF provides a temperature and a catalyst suitable to provide sufficient energy to sever an alkyl carbon-carbon bond, such as from about 490 °C to about 520 °C. In some instances, the catalyst in the NREF includes an acidic catalyst.

[0018] The present disclosure may further include flowing the C_8 stream to a para-xylene extraction unit to obtain a para-xylene stream and a xylene isomer stream. The xylene isomer stream may then flow to a xylene isomerization unit coupled to a further splitter. The xylene isomer stream may then be recycled to the xylene re-run splitter to provide further C_{9+} compounds to join the C_{9+} stream.

[0019] In some aspects, the catalyst of the NREF is selected from a zeolite, a platinum compound, a palladium compound or combinations thereof. In some instances, a zeolite may features a framework selected from Faujasite (FAU), beta (BEA), Mordenite (MOR), Mordenite Framework Inverted (MFI) or combinations thereof.

[0020] In other aspects, the NREF may have a hydrogen/oil operating ratio of about 100 to about 2500 L/L, including of about 100 to about 1000 L/L and of about 100 to about 750 L/L. In some aspects, the NREF may have an operating LHSV of about 0.5 to about 40 h^{-1}, including of about 0.5 to about 10 h^{-1} and about 0.5 to about 4 h^{-1}. The NREF may further have an operating pressure of about 1 to about 50 bar, including of about 1 to about 30 bar and of about 1 to about 20 bar. The NREF may further have an operating temperature of about 250 to about 575 °C, including of about 400 to about 575 °C and of about 450 to about 575 °C.

[0021] Additional features and advantages of the described embodiments will be set forth in the detailed description, which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the described embodiments, including the detailed description, which follows, the claims, as well as the appended drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] Figure 1 shows a schematic overview of a typical refinery arrangement of systems.

[0023] Figure 2 shows a more detailed schematic of the various processing units present in a typical aromatics recovery complex.

[0024] Figure 3 shows a schematic of an example of the present disclosure, wherein an aromatic bottoms stream of C_{9+} hydrocarbons from the aromatics recovery complex is recycled back to the hydrotreated naphtha feed into the catalytic reformer.

[0025] Figure 4 shows in greater detail possible inputs for the aromatic bottoms C_{9+} hydrocarbons back into a fixed bed catalytic reformer.

[0026] Figure 5 shows in greater detail possible inputs for the aromatic bottoms C_{9+} hydrocarbons back into a circulating catalytic reformer.

[0027] The embodiments set forth in the drawing are illustrative in nature and not intended to be limiting to the claims. Moreover, individual features of the drawing will be more fully apparent and understood in view of the detailed description.

DETAILED DESCRIPTION

[0028] As used herein, the term "aromatics" includes C_6-C_8 aromatics, such as, for example, benzene and xylenes, whereas "aromatic bottoms" refer to the heavier fraction of C_{9+} compounds, including but not limited to C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, and C_{16} compounds.

[0029] A typical refinery complex is presented in Figure 1 and a closer schematic of an aromatics recovery complex (ARC) from such is depicted in Figure 2. The crude oil feed is distilled in an atmospheric distillation unit (ADU) to recover a naphtha fraction boiling in the range 36-180 °C, a diesel fraction boiling in the range 180-370 °C and an atmospheric residue fraction boiling at 370 °C and higher. The naphtha fraction is then hydrotreated in a naphtha hydrotreating unit (NHT) to reduce the sulfur and nitrogen content to less than 0.5 ppmw. In general, the operating conditions of a NHT include a temperature in the range of from about 260 °C to about 400 °C; a pressure in the range of from about 1 bar to about 50 bars; and an LHSV in the range of from about 0.5 h^{-1} to about 40 h^{-1}.

[0030] The hydrotreated naphtha fraction is then sent to a catalytic reforming unit (NREF) to improve its quality, i.e., increase octane number to produce gasoline blending stream or feedstock for an aromatics recovery unit. Similarly, the diesel fraction is hydrotreated in a separate diesel hydrotreating unit (DHT) to desulfurize the diesel oil to obtain diesel fraction meeting the stringent specifications. The atmospheric residue fraction is either used as a fuel oil component or sent to other separation/conversion units to convert them from low value hydrocarbons to various fuel oil products.

[0031] The reformate fraction from the catalytic reforming unit can be used as gasoline blending component or sent to an aromatic recovery complex (ARC) to recover high value aromatics, i.e., benzene, toluene, and xylenes, commonly called BTX. Figure 2 shows more detail of the processes present in an aromatic recovery complex (ARC). The reformate stream flowing from the catalytic reforming unit is split into two fractions: light (C_5, C_6) and heavy (C_{7+}) reformate. The light reformate is sent to a benzene extraction unit to extract benzene present therein and recover near benzene free gasoline. The heavy reformate stream is then sent to a second splitter to recover C_7 and a C_{8+} stream. The C_7 toluene stream is sent to a gasoline pool or other interconversion processes and the C_{8+} stream is sent to a clay tower to remove olefins. The olefin-free effluent is then sent to a xylene re-run splitter/fractionator to send the C_8 stream to a para-xylene extraction unit to recover para-xylene. Other xylenes are also recovered during this latter process and are further sent to a xylene isomerization unit to catalytically convert them to para-xylene. The successfully converted fraction is recycled back to para-xylene extraction unit for distillation. The heavy fraction from the xylene re-run unit is recovered as process reject stream or aromatic bottoms of C_{9+} hydrocarbons.

[0032] Toluene is recovered as a separate fraction, and then may be converted into higher value products, for example benzene in addition to or alternative to xylenes. One toluene conversion process involves the disproportionation of toluene to make benzene and xylenes. Another process involves the hydrodealkylation of toluene to make benzene. Both toluene disproportionation and toluene hydrodealkylation result in the formation of benzene. With the current and continued environmental regulations involving benzene, it is desirable that the toluene conversion not result in the formation of significant quantities of benzene.

[0033] One problem faced by refineries is how to most economically reduce the benzene content in the reformate products sent to the gasoline pool by improving the processes and apparatus of systems described above. In some refineries, the aromatic complex bottoms are added to the gasoline fraction. However, the aromatic complex bottoms deteriorate the gasoline quality and in the long run impact the engine performance negatively.

[0034] The present disclosure concerns the identification that recycling the aromatic bottoms of C_{9+} alkylaromatic compounds generated from the ARC (i.e. at the xylene re-run unit or from a transalkylation unit) back to the catalytic reformer (Figure 3) presents an opportunity to further

generate higher value compounds rather than waste or redistribution to gasoline pools. Particularly, as described herein, the NREF may operate at temperatures of about 490 to about 575 °C and utilize an acidic catalyst. Collectively, these two features provide sufficient energy and opportunity for a carbon-carbon alkyl bond to be severed and to fracture or cleave di- or multi-aromatic compounds in the C_{9+} stream into mono-aromatics. Generating such in the NREF allows higher value aromatics to flow to the aromatics recovery complex and be isolated/recovered therein rather than be discarded as would happen in the first pass through. It should therefore be apparent to one skilled in the art that such recycling or recirculation can continue to exhaustion.

[0035] The aromatic bottoms can be recycled to enter the catalytic reformer at one or multiple points. As identified in Figures 4 and 5, the NREF can possess multiple reactors and multiple furnaces. Accordingly, the C_{9+} stream of aromatic bottoms can enter the NREF at one or multiple points therein. One point of entry is to rejoin the hydrotreated naphtha stream emerging from the NHT prior to entry to the NREF. The only parameter that may be impacted by returning the aromatic bottoms to the NREF is the liquid hourly space velocity ("LHSV") as the added line increases the feed into the respective reforming unit.

[0036] Further, as set forth in Figures 4 and 5, the hydrotreated naphtha stream can flow through three or more reactors, passing through a furnace before entering each reactor. The C_{9+} stream, in addition or in lieu of joining the hydrotreated naphtha at or before entry to the NREF, may be inserted prior to a stream feeding into a furnace within the NREF or upon exit form a reactor with the NREF. As further depicted in Figure 5, the reactors are connected to a regenerator to turn over spent catalyst. There are several types of process configurations which differ how they regenerate the reforming catalyst. Catalyst regeneration, which involves combusting detrimental coke in the presence of oxygen, includes a semi-regenerative process, cyclic regeneration, and continuous regeneration. Semi-regeneration involves the entire unit, including all reactors in the series, to be shut-down for catalyst regeneration. Cyclic configurations utilize an additional “swing” reactor to permit one reactor at a time to be taken off-line for regeneration while the others remain in service. Continuous catalyst regeneration configurations provide for essentially uninterrupted operation by catalyst removal, regeneration and replacement.

[0037] Referring first to Figure 1, a schematic of a conventional system for gasoline and aromatic production is shown. In the embodiment of FIG. 1, a refinery with an aromatic complex

is presented. In a refining system, a crude oil inlet stream **10** is fluidly coupled to atmospheric distillation unit (ADU) **100**, and crude oil from the crude oil inlet stream **10** is separated into naphtha stream **20**, atmospheric residue stream **12**, and diesel stream **11**. Diesel stream **11** proceeds to diesel hydrotreating unit (DHT) (not shown), and naphtha stream **20** proceeds to naphtha hydrotreating unit (NHT) **200**. A hydrotreated naphtha stream **30** exits NHT **200** and enters catalytic naphtha reforming unit (NREF) **300**. A separated hydrogen stream **31** exits NREF **300**, and a reformate stream **40** also exits NREF **300**. A portion of reformate stream **40** enters aromatic complex (ARC) **400**, and another portion of reformate stream **40** is separated by pool stream **41** to a gasoline pool. The ARC **400** separates the reformate into a pool stream **42** (e.g., C_4-C_{10} non-aromatics), an aromatics stream (C_6-C_8 aromatics) **43**, and an aromatic bottoms stream (C_{9+}) **60**.

[0038] The crude oil is distilled in ADU **100** to recover naphtha, which boils in the range of about 36 °C to about 180 °C, and diesel, which boils in the range of about 180 °C to about 370 °C. An atmospheric residue fraction in atmospheric residue stream **12** boils at about 370 °C and higher. Naphtha stream **20** is hydrotreated in NHT **200** to reduce the sulfur and nitrogen content to less than about 0.5 ppmw, and the hydrotreated naphtha stream **30** is sent to NREF **300** to improve its quality, or in other words increase the octane number to produce gasoline blending stream or feedstock for an aromatics recovery unit. Diesel stream **11** is hydrotreated in DHT to desulfurize the diesel oil to obtain a diesel fraction meeting stringent specifications at ultra-low sulfur diesel (ULSD). An atmospheric residue fraction is either used as a fuel oil component or sent to other separation or conversion units to convert low value hydrocarbons to high value products. Reformate stream **40** from NREF **300** can be used as a gasoline blending component or sent to an aromatic complex, such as ARC **400**, to recover high value aromatics, such as benzene, toluene, and xylenes (BTX).

[0039] Referring to Figure 2, an overview of an ARC **400**, is shown. The reformate stream **40** from the NREF **300** of Figure 1 flows initially into a reformate splitter **1** to separate into a light C_5 and C_6 hydrocarbon stream **401** and a heavy C_{7+} stream **410**. The C_5 and C_6 stream **401** feeds to a benzene extraction unit **2** to separate into C_5 and C_6 non-aromatic stream **402** for raffinate motor gasoline (MoGas) and a C6 aromatics stream **403** for benzene products. The C_{7+} stream **410** feeds to a splitter **3** to produce a C7 cut MoGas stream **411** and a C_{8+} hydrocarbon stream **420**.

[0040] The C_{8+} stream **420** is run through a clay treater **4** and then streamed **430** to a xylene re-run unit **5** to separate C_{8+} hydrocarbons into a C_8 hydrocarbon stream **431** and C_{9+} (heavy aromatic MoGas) hydrocarbon stream **60**. The xylene-re-run unit **5** is a distillation column including trays and/or structured packing and/or random packing to fractionate mixed xylenes from heavier aromatics. The C_8 hydrocarbon stream **431** proceeds to a para-xylene extraction unit **6** to recover para-xylene in a para-xylene product stream **433**. The para-xylene extraction unit **6** also produces a C_7 cut MoGas stream **432**, which combines with C_7 cut MoGas stream **411** to produce C_7 cut MoGas stream **412**. Other xylenes are recovered and sent to xylene isomerization unit **7** by stream **434** to convert them to para-xylene. The isomerization unit **7** includes a catalyst, such as a zeolite, that assists in transforming ortho- and meta-xylenes to para-xylene. The isomerized xylenes are sent to a splitter column **8**. The converted fraction is recycled back to para-xylene extraction unit **6** from splitter column **8** by way of streams **452** and **431**. Splitter top stream **451** is recycled back to reformate splitter **1**. The heavy fraction from the xylene rerun unit **5** is recovered as aromatic bottoms (shown as C_{9+} and Hvy Aro MoGas in FIG. 2 at stream **60**).

[0041] Referring to Figure 3, a schematic is shown of one aspect of the present disclosure, in which the aromatic bottoms stream **60** is recycled and fed back into the catalytic reforming unit **300**. Aromatic bottoms relate to C_{9+} aromatics and may be a more complex mixture of compounds including di-aromatics. C_{9+} aromatics boil in the range of about 100 °C to about 450 °C.

[0042] Aromatics bottoms at stream **60** are recycled to the NREF **300** for full extinction or partially if a bleed stream **250** is required. Recycled aromatics bottoms at stream **60** will not substantially change the operating conditions, as the stream **60** enters at a temperature in the naphtha and gasoline boiling range. The liquid hourly space velocity ("LHSV") may be impacted, as there will be increased feed to the respective reforming unit.

[0043] Referring to Figure 4, a more detailed view of the NREF is seen, with the aromatic bottom stream **60** flowing from the ARC back into the NREF. The bottoms stream **60** may enter the NREF at one, two or three points. The NREF features three reactors **310 320 330** and a furnace **350** or multiple furnaces placed in between. The multiple reactors may be used due to the endothermicity of the reaction and catalyst deactivation in each reactor. The effluents are heated to the reaction temperature by the furnace and send to the next reactor. The hydrotreated naphtha **30** enters from the NHT and passes through the heat exchanges **360** furnace **350** and into the first

reactor **310**. The reaction passes back through the furnace **350** and to the second reactor **320**. The reactants passes back through the furnace **350** and into the third reactor **330** and then passes through the heat exchanger **360** and to a splitter **340** to separate light gases **31** and reformate **40**, which flows to the ARC **400**.

[0044] Figure 5 shows a slightly different arrangement of the NREF, with independent furnaces **350** placed between the reactors **310 320 330**. Also depicted are feeds for catalyst regeneration through feeding spent catalyst to a regenerator **360** and then back to each reactor. As with Figure 4, an aromatic bottoms stream of C_{9+} hydrocarbons can enter the NREF prior to entry in the first reactor **310**, the second reactor **320** or the third reactor **330**.

[0045] According to an aspect, either alone or in combination with any other aspect, a method for recovery of benzene, toluene and xylene, includes: supplying to a naphtha reforming unit (NREF) a stream of hydrotreated naphtha; allowing the stream to flow through the NREF to generate reformate and hydrogen gas; supplying at least a portion of reformate from the NREF to an aromatics recovery complex (ARC); flowing the portion of reformate in the ARC through a reformate splitter to generate a C_{7+} stream; flowing the C_{7+} stream through a second splitter to generate a C_{8+} stream; flowing the C_{8+} stream through a clay tower to deolefinate the C_{8+} stream; flowing the deolefinated C_{8+} stream through a xylene re-run splitter to obtain a C_8 stream and a C_{9+} stream; and recycling the C_{9+} stream back to enter the stream of hydrotreated naphtha to thereby reprocess the C_{9+} stream to recover benzene, toluene and xylene.

[0046] According to a second aspect, either alone or in combination with any other aspect, the C_{9+} stream recycles to the stream of hydrotreated naphtha prior to entering the NREF.

[0047] According to a third aspect, either alone or in combination with any other aspect, the C_{9+} stream recycles to the stream of hydrotreated naphtha within the NREF.

[0048] According to a fourth aspect, either alone or in combination with any other aspect, the C_{9+} stream feeds into the NREF equally before each reactor unit contained therein.

[0049] According to a fifth aspect, either alone or in combination with any other aspect, the NREF comprises a temperature and a catalyst suitable to provide sufficient energy to break an alkyl carbon-carbon bond.

[0050] According to a sixth aspect, either alone or in combination with any other aspect, the operating temperature of the NREF is from about 490 °C to about 520 °C.

[0051] According to a seventh aspect, either alone or in combination with any other aspect, the catalyst of the NREF is an acidic catalyst.

[0052] According to an eighth aspect, either alone or in combination with any other aspect, the catalyst is selected from a zeolite, a platinum compound, a palladium compound or combinations thereof.

[0053] According to a ninth aspect, either alone or in combination with any other aspect, the catalyst is a zeolite with a framework selected from Faujasite (FAU) (zeolite Y, USY), Beta (*BEA), Mordenite (MOR), ZSM-5 (MFI) or combinations thereof.

[0054] According to a tenth aspect, either alone or in combination with any other aspect, the method may also include: flowing the C_8 stream to a para-xylene extraction unit to obtain a para-xylene stream and a xylene isomer stream; flowing the xylene isomer stream to a xylene isomerization unit coupled to a further splitter; and recycling the xylene isomer stream to the xylene re-run splitter, wherein further C_{9+} compounds join the C_{9+} stream.

[0055] According to an eleventh aspect, either alone or in combination with any other aspect, the NREF has a hydrogen/oil operating ratio of about 100 to about 2500 L/L.

[0056] According to a twelfth aspect, either alone or in combination with any other aspect, the NREF has a hydrogen/oil operating ratio of about 100 to about 1000 L/L.

[0057] According to a thirteenth aspect, either alone or in combination with any other aspect, the NREF has a hydrogen/oil operating ratio of about 100 to about 750 L/L

[0058] According to a fourteenth aspect, either alone or in combination with any other aspect, the NREF has an operating LHSV of about 0.5 to about 40 h^{-1}.

[0059] According to a fifteenth aspect, either alone or in combination with any other aspect, the NREF has an operating LHSV of about 0.5 to about 10 h^{-1}.

[0060] According to a sixteenth aspect, either alone or in combination with any other aspect, the NREF has an operating LHSV of about 0.5 to about 4 h^{-1}.

[0061] According to a seventeenth aspect, either alone or in combination with any other aspect, the NREF has an operating pressure of about 1 to about 50 bar.

[0062] According to an eighteenth aspect, either alone or in combination with any other aspect, the NREF has an operating pressure of about 1 to about 20 bar.

[0063] According to a nineteenth aspect, either alone or in combination with any other aspect, the NREF has an operating temperature of about 250 to about 560 °C.

[0064] According to a twentieth aspect, either alone or in combination with any other aspect, the NREF has an operating temperature of about 450 to about 560 °C.

[0065] EXAMPLES

[0066] One or more of the previously described features will be further illustrated in the following example simulations using Arab light crude oil. The reformer was arranged as follows:

Hydrogen/Oil	L/L	625
LHSV	h^{-1}	4
Pressure	Bar	3
Temperature	°C	520

with a catalyst of Pt on alumina, that is chlorinated in the process. The naphtha hydrotreater was arranged as follows:

Hydrogen/Oil	L/L	200
LHSV	h^{-1}	6
Pressure	Bar	20
Temperature	°C	300

with a catalyst of Co-Mo on alumina. By recycling, the LHSV for the reformer increased from 4 to 4.5 h^{-1}.

[0067] The difference between the two arrangements depicted in Figures 1 (Comparative Example A) and 3 (Inventive Example 1) were assessed for notable difference obtained by

returning the C_{9+} stream of aromatic bottoms back to the NREF. The details are presented in Table 1 below.

			Comparative Example A	**Inventive Example 1**
Stream	**Name**	**Units**		
10	Crude Oil	KBPSD	400.0	400.0
60	ARC Bottoms	KBPSD	7.9	7.0
20	Naphtha to hydrotreater	KBPSD	67.0	67.0
11	Atmospheric Residue	KBPSD	200.5	200.5
30	Hydrotreated Naphtha	KBPSD	66.2	74.2
11	Diesel	KBPSD	164.2	164.2
40	Reformate	KBPSD	53.0	60.9
43	Aromatics (BTX)	Mtons/D	4.2	4.8

*KBPSD- kilo barrels per stream day; The returning line of the aromatic bottoms to the NREF caused an 11% decline in the amount of ARC bottoms present, while allowing almost a 14% increase in BTX production. This also minimizes C_{9+} production, which in turn minimizes the heavy ends in the gasoline as C_{9+} is no longer available to be added to the gasoline. Further, with this scheme, existing refinery equipment may be used without any further need to install additional process units to process this heavy stream.

[0068] Throughout this disclosure, ranges are provided. It is envisioned that each discrete value encompassed by the ranges are also included. Additionally, the ranges which may be formed by each discrete value encompassed by the explicitly disclosed ranges are equally envisioned.

CLAIMS

1. A method for recovery of benzene, toluene and xylene, the method comprising:

supplying to a naphtha reforming unit (NREF) a stream of hydrotreated naphtha;

allowing the stream to flow through the NREF to generate reformate and hydrogen gas;

supplying at least a portion of reformate from the NREF to an aromatics recovery complex (ARC);

flowing the portion of reformate in the ARC through a reformate splitter to generate a C_{7+} stream;

flowing the C_{7+} stream through a second splitter to generate a C_{8+} stream;

flowing the C_{8+} stream through a clay tower to deolefinate the C_{8+} stream;

flowing the deolefinated C_{8+} stream through a xylene re-run splitter to obtain a C_8 stream and a C_{9+} stream; and

recycling the C_{9+} stream back to enter the stream of hydrotreated naphtha to thereby reprocess the C_{9+} stream to recover benzene, toluene and xylene.

2. The method of claim 1, wherein the C_{9+} stream recycles to the stream of hydrotreated naphtha prior to entering the NREF.

3. The method of claim 1, wherein the C_{9+} stream recycles to the stream of hydrotreated naphtha within the NREF.

4. The method of claim 3, wherein the C_{9+} stream feeds into the NREF equally before each reactor unit contained therein.

5. The method of any one of claims 1 to 4, wherein the NREF comprises a temperature and a catalyst suitable to provide sufficient energy to break an alkyl carbon-carbon bond.

6. The method of claim 5, wherein the temperature of the NREF is from about 490 °C to about 520 °C.

7. The method of claim 5 or 6, wherein the catalyst comprises an acidic catalyst.

8. The method of claim 5 or 6, wherein the catalyst is selected from the group consisting of a zeolite, a platinum compound, a palladium compound or combinations thereof.

9. The method of claim 5 or 6, wherein the catalyst is a zeolite with a framework selected from the group consisting of Faujasite (FAU), Beta (BEA), Mordenite (MOR), ZSM-5 (MFI) or combinations thereof.

10. The method of any one of claims 1 to 9, further comprising:

flowing the C_8 stream to a para-xylene extraction unit to obtain a para-xylene stream and a xylene isomer stream;

flowing the xylene isomer stream to a xylene isomerization unit coupled to a further splitter; and

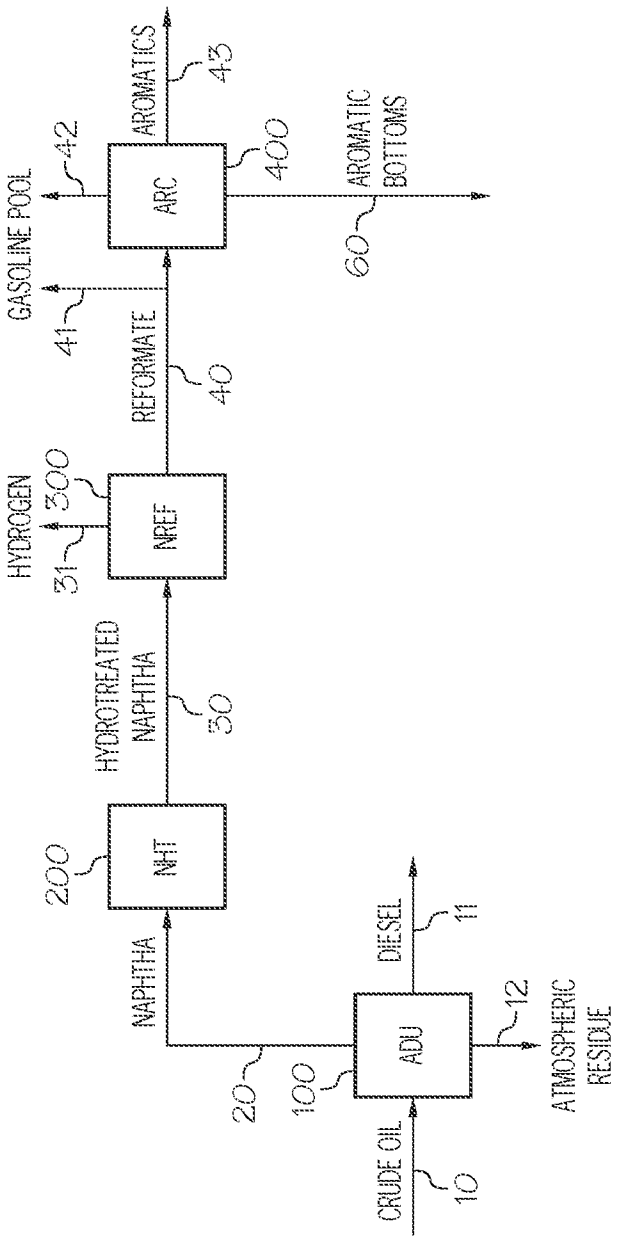
recycling the xylene isomer stream to the xylene re-run splitter, wherein further C_{9+} compounds join the C_{9+} stream.

11. The method of any one of claims 1 to 10, wherein the NREF has a hydrogen/oil operating ratio of about 100 to about 2500 L/L.

12. The method of any one of claims 1 to 11, wherein the NREF has an operating liquid hourly space velocity (LHSV) of about 0.5 to about 40 h^{-1}.

13. The method of any one of claims 1 to 12, wherein the NREF has an operating pressure of about 1 to about 50 bar.

14. The method of any one of claims 1 to 13, wherein the NREF has an operating temperature of about 250 to about 560 °C.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30
NREF
300
HYDROGEN
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ARC
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GASOLINE POOL
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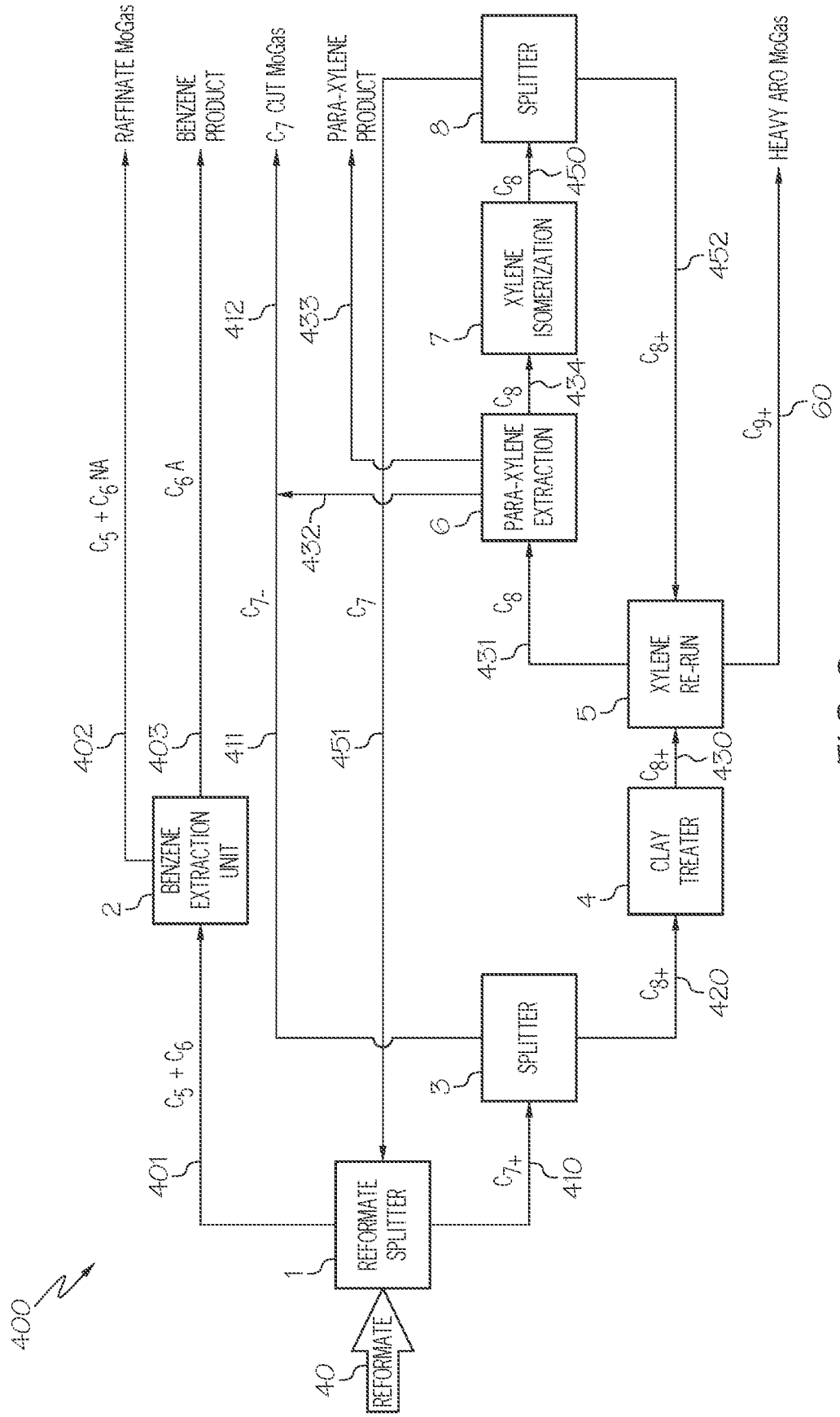
AROMATICS
42
43
AROMATIC BOTTOMS
60

FIG. 1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C_6 A
SPLITTER
3
410
C_{7+}
CLAY TREATER
4
420
C_{8+}
XYLENE RE-RUN
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430
C_{8+}
451
C_8
PARA-XYLENE EXTRACTION
6
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C_8
434
XYLENE ISOMERIZATION
7
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SPLITTER
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C_8
452
C_{8+}
411
C_{7-}
412
C_7 CUT MoGas
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C_7
C_{9+}
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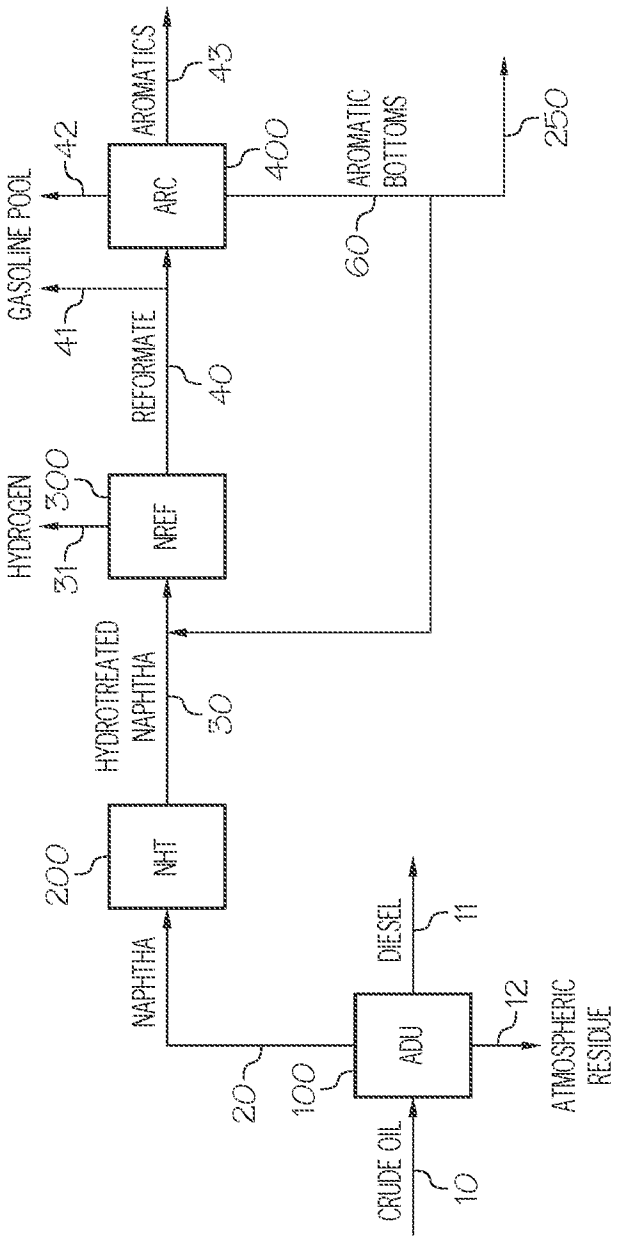
HEAVY ARO MoGas
RAFFINATE MoGas
BENZENE PRODUCT

FIG. 2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50
NREF
300
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ARC
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AROMATICS
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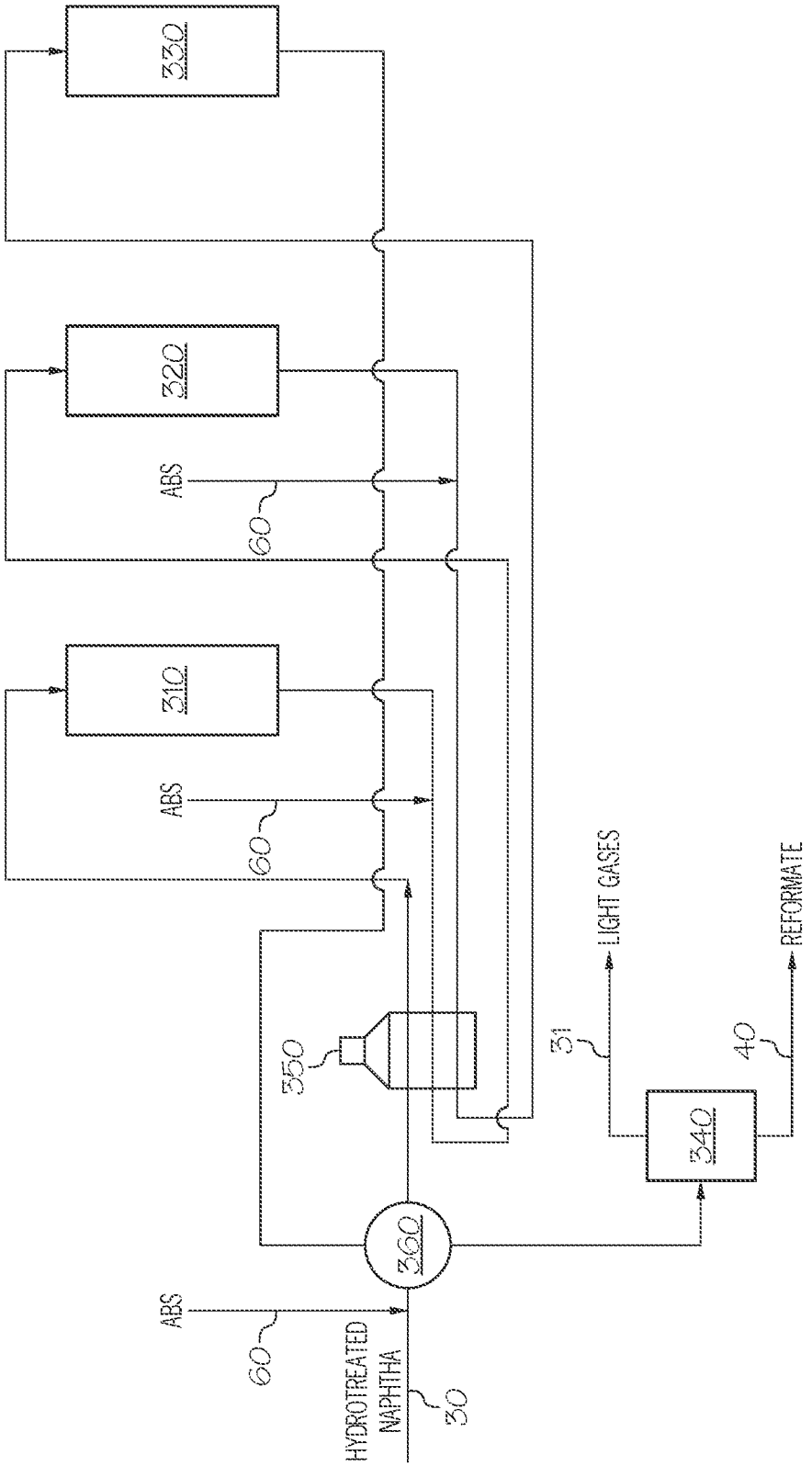
AROMATIC BOTTOMS
60
250

FIG. 3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HYDROTREATED NAPHTHA
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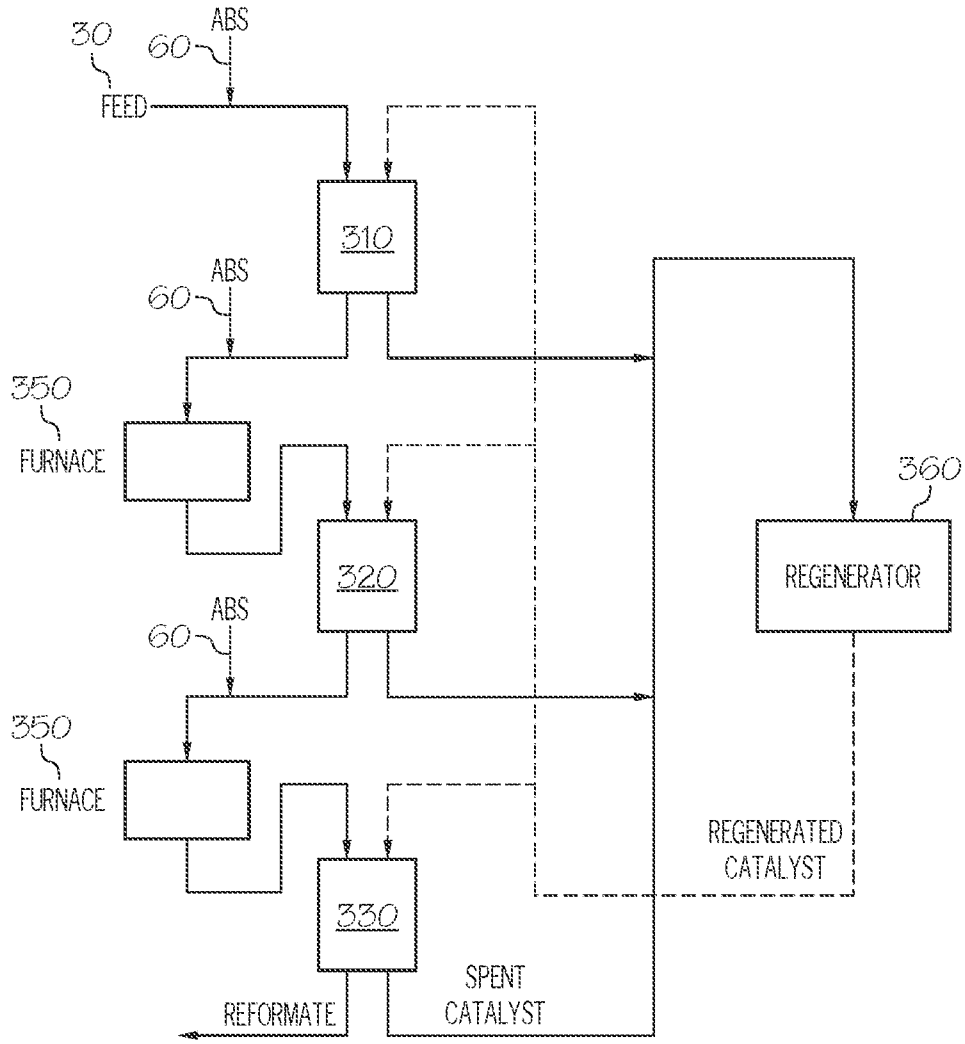
FIG. 4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FURNACE
320
360
REGENERATOR
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ABS
350
FURNACE
REGENERATED
CATALYST
330
REFORMATE
SPENT
CATALYST

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/017378

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G35/095 C10G35/085 C10G45/02 C10G69/08 C10G61/04
C07C5/27 C10G29/00 C10G25/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/079701 A1 (GATTUPALLI RAJESWAR R [US] ET AL) 22 March 2018 (2018-03-22) paragraphs [0016], [0017], [0037] figure 1	1-14
A	US 2018/066197 A1 (KOSEOGLU OMER REFA [SA] ET AL) 8 March 2018 (2018-03-08) figure 2	1-14
A	US 2015/166436 A1 (NOE JASON L [US]) 18 June 2015 (2015-06-18) figure 1	1-14
A	US 2013/144097 A1 (BENDER TIMOTHY P [US] ET AL) 6 June 2013 (2013-06-06) claim 1	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 May 2021	26/05/2021

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Ruiz Martínez, C

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2021/017378

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