(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
03 February 2022 (03.02.2022)

WIPO | PCT

(10) International Publication Number
WO 2022/025958 A1

(51) International Patent Classification:

C10G 47/20 (2006.01)	*C10G 67/06* (2006.01)
C10G 49/04 (2006.01)	*C07C 15/02* (2006.01)
C10G 49/08 (2006.01)	*C07C 15/12* (2006.01)
C10G 35/00 (2006.01)	*B01J 29/14* (2006.01)
C10G 63/04 (2006.01)	*B01J 29/06* (2006.01)
C10G 25/00 (2006.01)	*B01J 23/85* (2006.01)
C10G 61/06 (2006.01)	*B01J 23/883* (2006.01)

(21) International Application Number:
PCT/US2020/062795

(22) International Filing Date:
02 December 2020 (02.12.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
16/944,394 31 July 2020 (31.07.2020) US

(71) Applicant: **SAUDI ARABIAN OIL COMPANY** [SA/SA]; Post Office Box 5000, Dhahran, 31311 (SA).

(71) Applicant *(for AG only)*: **ARAMCO SERVICES COMPANY** [US/US]; 1200 Smith Street, Two Allen Building, Houston, Texas 77002 (US).

(72) Inventors: **KOSEOGLU, Omer Refa**; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA). **HODGKINS, Robert Peter**; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA).

(74) Agent: **DERBYSHIRE, Zachary E.** et al.; Dinsmore & Shohl LLP, One South Main Street, Suite 1300, Dayton, Ohio 45402 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW,

(54) Title: IMPROVED AROMATIC RECOVERY COMPLEX WITH A HYDRODEARYLATION STEP TO PROCESS CLAY TOWER EFFLUENTS

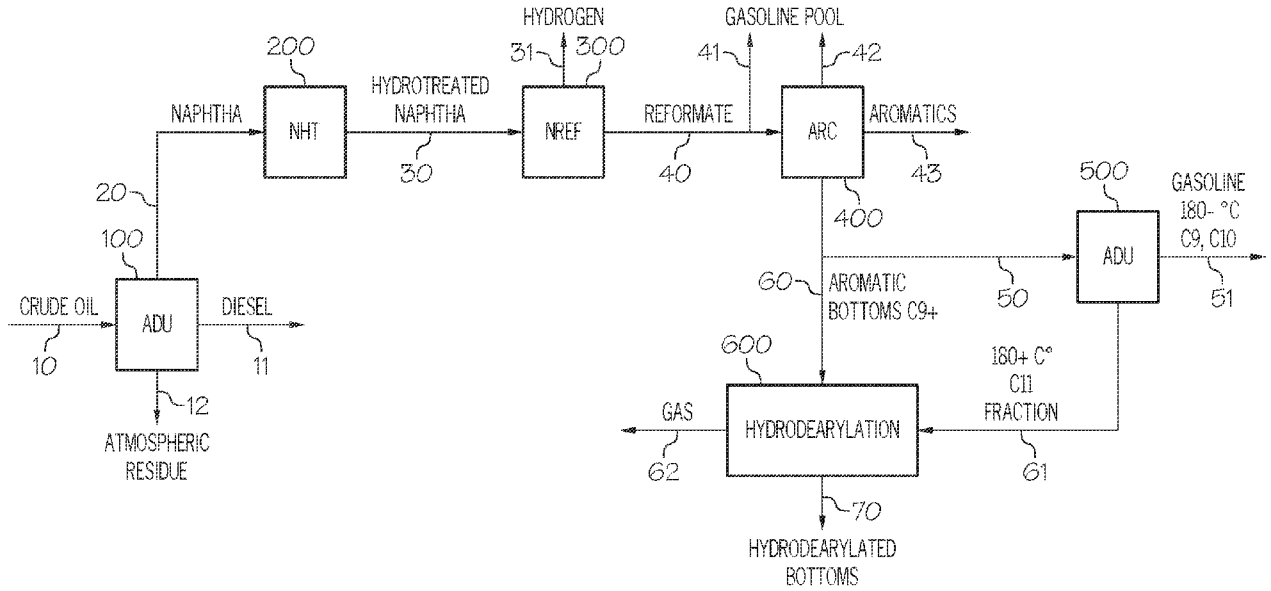


FIG. 3

(57) Abstract: The disclosure provides a process to hydrodearylate the non-condensed alkyl-bridged multi-aromatics at the outlet of the clay tower where such multi-aromatics form rather than performing hydrodearylation on the reject stream of the aromatics complex. Hydrodearylation may feature combining a C8+ hydrocarbon stream from a clay treater with a hydrogen stream over a catalyst bed comprising a support and an acidic component optionally containing Group 8 and/or Group 6 metals.

WO 2022/025958 A1

[Continued on next page]

SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

IMPROVED AROMATIC RECOVERY COMPLEX WITH A HYDRODEARYLATION STEP TO PROCESS CLAY TOWER EFFLUENTS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Application Serial No. 16/944,394 filed on July 31, 2020, the entire disclosure of which is hereby incorporated by reference.

TECHNICAL FIELD

[0002] The present disclosure generally relates to processes for hydrodearylation of the non-condensed alkyl-bridged multi-aromatics from a C_{8+} stream within an aromatic production complex.

BACKGROUND

[0003] A typical refinery starts with a crude oil feed into an atmospheric distiller to roughly separate the components therein by their condensation/evaporation temperatures, where they are fed into further processing units, which in turn can feed in to further processing units, until high purity compounds or classes of compounds are obtained. For example, from an atmospheric distiller, a naphtha stream can run off to a hydrotreater (NHT) and naphtha reforming unit (NREF) to remove sulfur-based contaminants with the resulting reformate split into a gasoline pool and an aromatics recovery complex (ARC).

SUMMARY

[0004] Within the ARC, various further processes can be applied to convert naphtha or pyrolysis gasoline into benzene, toluene, and mixed xylenes (BTX), which are basic petrochemical intermediates used for the production of various other chemical products. To maximize the BTX production, the feed to an ARC is generally limited from C_6 up to C_{11} compounds. In most ARCs, the aromatics present in reformate are usually separated into different fractions by carbon number; such as benzene, toluene, xylenes, and ethylbenzene, etc. The C_8 fraction may then be subjected to a further processing scheme to generate more high value para-xylene. Para-xylene is usually recovered in high purity from the C_8 fraction by separating the para-xylene from the ortho-xylene, meta-xylene, and ethylbenzene using

selective adsorption or crystallization. The remaining ortho-xylene and meta-xylene are isomerized in a further unit to produce an equilibrium mixture of xylenes and recycled back to extract para-xylene. Ethylbenzene is isomerized into xylenes or is dealkylated to benzene and ethane. The para-xylene-depleted-stream is then recycled to extinction through the isomerization unit and then to the para-xylene recovery unit until all of the ortho-xylene and meta-xylene are converted to para-xylene and recovered. The para-xylene can then be processed to produce terephthalic acid, which is then used to make polyesters, such as polyethylene terephthalate.

[0005] To increase the production of benzene and para-xylene, toluene and C_9 and C_{10} aromatics are processed within the complex through a toluene, C_9, C_{10} transalkylation/toluene disproportionation (TA/TDP) process unit to produce benzene and xylenes. Any remaining toluene, C_9, and C_{10} aromatics are recycled to extinction. Compounds heavier than C_{10} are generally not processed in the TA/TDP unit, as they tend to cause rapid deactivation of the catalysts used at the higher temperatures used in these units, often greater than 400 °C.

[0006] Before para-xylene is recovered from the mixed xylenes, the C_{8+} feed to the selective adsorption unit is processed to eliminate olefins and alkenyl aromatics such as styrene in the feed. Olefinic material can react and occlude the pores of the zeolite adsorbent. The olefinic material is removed by passing a C_{8+} stream across a clay or acidic catalyst to react olefins and alkenyl aromatics with another (typically aromatic) molecule, forming heavier compounds (C_{16+}). These heavier compounds are typically removed from the mixed xylenes by fractionation. The heavy compounds are generally removed from the complex as lower value fuels blend stock.

[0007] Also during hydrocarbon processing, compounds composed of an aromatic ring with one or more coupled alkyl groups containing three or more carbon molecules per alkyl group may be formed. Formation of these compounds may be from processes used by petroleum refiners and petrochemical producers to produce aromatic compounds from non-aromatic hydrocarbons, such as catalytic reforming. As many of these heavy alkyl aromatic compounds fractionate with the fractions containing greater than 10 carbon atoms, they are

not typically sent as feedstock to the transalkylation unit, and instead are sent to gasoline blending or used as fuel oil.

[0008] Accordingly, ongoing needs exist for improved methods and systems for producing light aromatics within a refinery system. Disclosed herein are processes to generate light alkyl mono-aromatic compounds from the heavy alkyl aromatic and alkyl-bridged non-condensed alkyl aromatic compounds instead of using such for low-value fuel oil blending or gasoline blending at the expense of the gasoline quality. Due to the desire to produce valuable para-xylene, placement of a hydrodearylation unit within the aromatics recovery complex provides additional materials for the xylene re-run to maximize para-xylene production.

[0009] The present disclosure provides a process to recover or improve the presence of alkyl mono-aromatic compounds. In some instances, the process includes directing a feed stream from a clay treater of an aromatic recovery complex to a hydrodearylation unit. The feed stream includes C_{8+} compounds of one or more heavy alkyl aromatic compounds and alkyl-bridged multi-aromatic compounds. The hydrodearylation unit dearylates alkyl-bridged multi-aromatic compounds through adding a hydrogen stream to the feed stream over a catalyst, resulting in production of an alkyl mono-aromatic compound containing stream, which can then feed into a xylene re-run unit.

[0010] In some aspects, the alkyl-bridged alkyl multi-aromatic compounds in the feed stream include at least two benzene rings connected by an alkyl bridge group of at least two carbons, with the benzene rings being connected to different carbons of the alkyl bridge group.

[0011] In some aspects, the clay treater is operated at a temperature between 160 °C and 220 °C. In further aspects, the clay treater is operated at a range of 1-20 bars. In certain aspects, the clay treater is operated at a liquid hourly space velocity (LHSV) of about 0.5 hr^{-1} to about 10 hr^{-1}. In yet other aspects, the clay treater outlet effluent has a bromine index less than 200. In some aspects, the clay treater outlet effluent is substantially olefin free, such as less than 0.2 weight percent.

[0012] In some instances, the hydrogen stream is combined with the feed stream before being supplied to the hydrodearylation unit. In some aspects, the hydrogen stream may include of a recycled hydrogen stream and a makeup hydrogen stream.

[0013] In some instances, the catalyst is presented as a catalyst bed in the hydrodearylation unit. In certain aspects, a portion of the hydrogen stream is fed to the catalyst bed in the hydrodearylation unit to quench the catalyst bed. The catalyst may include a support of silica, alumina, or combinations thereof, and an acidic component of amorphous silica-alumina, zeolite, or combinations thereof. In some aspects, the catalyst may include an IUPAC Group 8-10 metal of iron, cobalt, and nickel, or combinations thereof and an IUPAC Group 6 metal of molybdenum, tungsten, or combinations thereof. In certain aspects, the IUPAC 8-10 metal may be 2 to 20 percent by weight of the catalyst and the IUPAC Group 6 metal may be 1 to 25 percent by weight of the catalyst. In certain aspects, the catalyst may include nickel, molybdenum, ultrastable Y-type zeolite, and γ-alumina support.

[0014] In some instances, the hydrodearylation unit includes an operating temperature within of about 200 to about 450° C. In certain aspects, the hydrodearylation unit may include a hydrogen partial pressure within of about 5 to about 50 bars. The hydrodearylation unit may include a feed rate of the hydrogen stream of about 100 to about 1000 standard liters per liter of feedstock.

[0015] In some instances, the aromatic recovery complex receives a reformate stream from a catalytic reforming unit. A reformate splitter within the aromatic recovery complex may then split the reformate stream into a C_5+C_6 stream that goes to a benzene extraction unit and a C_{7+} stream that feeds to a splitter. The splitter can then divide the C_{7+} stream into a C_7 stream and a C_{8+} stream that passes through the clay treater and thereafter into the hydrodearylation unit. Further, in some instances, the xylene re-run unit may split the alkyl mono-aromatic compound stream into a C_{9+} stream and a C_8 stream that flows to a para-xylene extraction unit and a xylene isomerization unit which can then recycle back to the xylene re-run unit.

[0016] 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

[0017] Figure 1 shows an overview of a traditional refinery system of processes.

[0018] Figure 2 shows a more detailed overview of the processes of an aromatics recovery complex (ARC).

[0019] Figure 3 shows a hydrodearylation unit placed to receive an aromatic bottoms stream.

[0020] Figure 4 shows a hydrodearylation unit according to the current disclosure that receives a C_{8+} stream from a clay treater feed prior to entry into a xylene re-run system.

[0021] 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 drawings will be more fully apparent and understood in view of the detailed description.

DETAILED DESCRIPTION

[0022] This disclosure describes various processes and systems for feeding a C_{8+} stream in an aromatics recovery complex to a hydrodearylation unit for conversion of alkyl-bridged non-condensed alkyl aromatics to lighter mono-alkyl aromatics for improved para-xylene recovery in a refinery.

[0023] As used herein, the term "hydrodearylation" refers to a reaction or series of steps to cleave alkyl bridges of non-condensed alkyl-bridged multi-aromatics or heavy alkyl aromatic compounds to form alkyl mono-aromatics, in the presence a catalyst and hydrogen. "Alkyl bridged non-condensed alkyl aromatic" compounds refer at least two aromatic (or

benzene) rings connected by an alkyl bridge group with at least two carbons bridging between the rings, where the aromatic or benzene rings are connected to different carbons of the alkyl bridge group.

[0024] As used herein, the term "stream" (and variations thereof) refers to a connected pathway flow of vapors, gases or liquids from one source or system or unit to a second. In many instances, a stream may feature one or more of various hydrocarbon compounds, such as straight chain, branched or cyclical alkanes, alkenes, alkadienes, alkynes, alkyl aromatics, alkenyl aromatics, condensed and non-condensed di-, tri- and tetra-aromatics, and gases such as hydrogen and methane, C_{2+} hydrocarbons and further may include various impurities.

[0025] Heavy aromatics are byproducts formed during various processing steps during refining of crude oil. Heavy aromatics include mono-aromatics with long attached alkyl groups, as well as multi-aromatics of two or more aromatic rings linked with alkyl bridges. US Patent 10,053,401, identified that aromatic bottoms of C_{9+} hydrocarbons can be subjected to hydrodearylation using a hydrogen stream and a catalyst to cleave or sever the alkyl bridges and recover lighter mono-aromatics. Recovered mono-aromatics can then be processed to increase the yield of BTX compounds from refineries.

[0026] The clay treater within an aromatics recovery complex is present to remove olefins prior to xylene purification and recycling. By way of example, the clay treater may be operated at a temperature between 160 °C and 220 °C and at a pressure range of 1-20 bars. In some instances, the connected unit is at an elevated height. The clay treater may be operated at a liquid hourly space velocity (LHSV) of between 0.5 hr^{-1} and 10 hr^{-1} and with an outlet effluent bromine index of 200 or less.

[0027] While the clay treater is effective for reducing olefin content, the acidity of the clay and the temperature of the clay treater provides an opportunity for alkenyl aromatics to react with alkyl aromatics to form non-condensed alkyl-bridged di-aromatics. Some di-aromatics can similarly react to form tri-aromatics and so on, providing a site for multi-aromatics production prior to being received at the xylene re-run column where mono-aromatic C_8 compounds (e.g. xylenes) are to be isolated. As C_8 compounds can be depleted

during the clay treating, it is a function of this disclosure to recover light mono-aromatics prior to xylene purification to improve yields and reduce loss of valuable hydrocarbons. The recovery includes, therefore, not just alkyl aromatics that reacted with alkenyl aromatics, but the alkenyl aromatics now reduced to alkyl aromatics.

[0028] The disclosure therefore relates to introducing a hydrodearylation unit into an aromatics recovery complex within a refinery. In some instances, the hydrodearylation unit is introduced between a clay treater and a xylene re-run unit to increase the alkyl mon-aromatic compounds entering the xylene re-run unit. A hydrodearylation unit assists in the recovery of light alkylated mono-aromatics from streams that contain alkyl-bridged non-condensed alkylated multi-aromatic compounds and heavy alkyl-aromatic compounds. Alkyl-bridged non-condensed alkyl aromatic compounds may be referred to as multi-aromatics or poly-aromatics. A more in-depth description of the hydrodearylation process is found in US Patent 10,053,401, which is hereby incorporated by reference in its entirety.

[0029] Hydrodearylation refers to generating mono-aromatic or alkyl aromatic compounds from multi-aromatics, through a process of dearylation or cleaving of the alkyl bridge(s) between the aromatic rings. As set forth herein, a hydrodearylation unit receives a stream of C_{8+} hydrocarbon compounds that include multi- or poly-aromatic compounds. In some instances, the C_{8+} stream may be from a clay treater in an aromatics recovery complex. Clay treatment (or clay filtration; e.g. using a clay treater) refers to a process by which contaminants, such as olefins and alkenyl aromatics, may be removed in an aromatics recovery complex. Typically, a stream may be passed through or over a clay treater or clay tower, where it comes into contact with a surface of the clay. The olefinic species are composed primarily of alkenyl aromatics, such as styrene and methyl-styrene. Such molecules would be expected to react across clay-containing Lewis-acid sites at temperatures around 200 °C with the alkyl aromatics via a Friedel-Crafts reaction to form molecules with two aromatic rings connected with an alkyl bridge. Analysis of spent clay from a commercial unit found polar solvent (i.e., toluene and tetrahydrofuran) soluble hydrocarbons and solvent insoluble hydrogen deficient hydrocarbons on the clay surface. Solvent soluble hydrocarbons are leftovers from the reformate stream and solvent insoluble hydrogen deficient hydrocarbons are basically coke and removed at temperature 400 °C and above .

[0030] The C_{8+} stream from the clay treater is contacted or combined with a further stream of hydrogen as an initial step in hydrodearylation. The two may be contacted wither before or following entry into the unit, but prior to collectively flowing over any catalyst therein.

[0031] The combined flow of the C_{8+} hydrocarbon stream and hydrogen may then contact a catalyst. Collectively, the combination of hydrogen and the catalyst allows for hydrodearylation to occur. The product stream leaves the unit containing newly generated mono-aromatic compounds. The processes for conversion of multi-aromatics into alkyl aromatics may allow for the use of the alkyl aromatics as feedstock to a benzene, toluene, and xylenes (BTX) petrochemicals processing unit.

[0032] In the hydrodearylation unit, the catalyst may be provided as an exposed bed in a reactor. In some instances, a portion of the hydrogen stream may be fed to the catalyst bed in the reactor to provide quenching to the catalyst bed. In some aspects, the catalyst bed may include two or more catalyst beds. The catalyst may further include a support, such as a support selected from silica, alumina, titania and/or combinations thereof. The catalyst may also include an acidic component(s) selected from amorphous silica-alumina, zeolite, and/or combinations thereof. The catalyst may include a Group 8-10 (per IUPAC grading) metal and/or a Group 6 (IUPAC) metal. The catalyst may be a metal selected from iron, cobalt, nickel, and/or combinations thereof. The catalyst may further include a metal selected from the group consisting of molybdenum, tungsten, and/or combinations thereof. The catalyst, in some instances, may contain an IUPAC Group 8-10 metal at about 2 to 20 percent by weight of the total weight of the catalyst (including 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, and 19%) and an IUPAC Group 6 metal at about 1 to 25 percent by weight of the total weight of the catalyst (including 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, and 24%). The catalyst may include one or more of nickel, molybdenum, ultrastable Y-type zeolite, and γ-alumina support.

[0033] The hydrodearylation unit can be operated at a temperature of about 250 °C to about 400 °C and at a pressure from about 5 bar to about 50 bar. In some instances, the hydrodearylation unit is operated at about 350 °C and at a pressure of 15 bar.

[0034] A typical refinery with an aromatic recovery complex (ARC) is presented in Figure 1 and the details of the ARC are presented in Figure 2. The whole crude oil is distilled in an atmospheric distillation unit (ADU) column 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 hydrotreated in a naphtha hydrotreating unit (NHT) to remove sulfur and nitrogen content down to less than 0.5 ppmw (parts per million per weight) and the hydrotreated naphtha fraction is sent to 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 (not shown) to desulfurize the diesel oil to obtain a diesel fraction meeting stringent specifications of < 10 ppm sulfur. The atmospheric residue fraction is either used as a fuel oil component or sent to other separation/conversion units to convert low value hydrocarbons to various fuel oil products. The reformate fraction emerging from the NREF 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.

[0035] Figure 2 shows a more detailed view of a typical aromatic recovery complex (ARC). The reformate that is produced from the NREF is initially processed through a splitter to separate the reformate into two fractions: light and heavy reformate. The light reformate is sent to a benzene extraction unit to extract the benzene and recover almost benzene free gasoline. The heavy reformate stream is sent to a splitter and then a para-xylene extraction unit to recover para-xylene. Prior to entering the xylene re-run splitter, the heavy reformate passes through a clay treater to remove olefins from the system, which improves the zeolite adsorbent cycle length involved in selective adsorption processes when recovering para-xylene. Other xylenes are recovered after para-xylene extraction and sent to a xylene isomerization unit to convert them to para-xylene. The converted fraction is recycled back to the para-xylene extraction unit for appropriate extraction. The heavy fraction from the xylene re-run splitter is recovered as process reject or aromatic bottoms. Aromatic bottoms relate to C_{9+} aromatics and may be a more complex mixture of compounds including di-aromatics.

[0036] As outlined above, aromatic bottoms can be added to the gasoline pool or hydrodearylated per US patent 10,053,401. The aromatics bottoms fraction from the xylene re-run splitter may then be either: i) fractionated with the 180− °C fraction sent directly to a gasoline pool as blending components and the 180+ °C fraction sent to a hydrodearylation unit; or ii) fractionated such that the C_9 and C_{10} components are sent directly to a transalkylation unit and the C_{11+} components are sent to a hydrodearylation unit or iii) sent directly to a hydrodearylation unit to recover light alkyl mono-aromatic compounds from heavy alkyl aromatic and alkyl-bridged non-condensed alkyl aromatic compounds (see, e.g. Figure 3).

[0037] The present invention, conversely, concerns introducing a hydrodearylation within the ARC itself, particularly at the point of receiving a C_{8+} stream at the outlet of the clay treater. Alkyl-bridged non-condensed di-aromatics (or multi-aromatics) may form in the clay treater or tower as described herein. Typically, the effluent at the outlet of the clay treater is fractionated through the xylene re-run splitter and the resulting C_{9+} feed is sent as aromatic bottoms and potentially either hydrodearylated or the C_9 and C_{10} components are removed and the C_{11+} stream can be hydrodearylated, since the heavy alkyl-bridged non-condensed di-aromatics (or multi-aromatics) are now in these heavier streams.

[0038] It is therefore a distinguishing facet of the present disclosure to introduce the hydrodearylation prior to fractionation at the xylene re-run splitter. Placement of a hydrodearylation unit at this point provides an opportunity to reduce multi-aromatics from being fractioned with C_{9+} hydrocarbons from the xylene re-run and increase the C_8 fraction for para-xylene extraction and isomerization. Hence, the embodiments of this disclosure offer an alternative process configuration for hydrodearylation by expanding hydrodearylation to process to the C_{8+} stream.

[0039] Referring now to Figure 1, a schematic of a typical gasoline refinery system is shown. In the system, a crude oil inlet stream **10** is fed into an atmospheric distillation unit (ADU) **100**, and therein crude oil is separated into a naphtha stream **20**, an atmospheric residue stream **12**, and a diesel stream **11**. 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. The atmospheric residue fraction in the

atmospheric residue stream **12** boils at about 370° C. and higher. The naphtha stream **20** then proceeds to a naphtha hydrotreating unit (NHT) **200**. The naphtha stream **20** is hydrotreated in NHT **200** at between 200-260° C and 25-45 bar to remove sulfur and nitrogen content to less than about 0.5 ppmw. A hydrotreated naphtha stream **30** exits the NHT **200** and enters a catalytic naphtha reforming unit (NREF) **300** to improve its quality by mixing with hydrogen at between 500 to 570° C and 35 to 45 bar. A hydrogen stream **31** and a reformate stream **40** exit the NREF **300**. A portion of the reformate stream **40** is separated by a pool stream **41** to a gasoline pool, with the remaining reformate stream **40** entering an aromatic complex (ARC) **400** to recover high value aromatics, such as benzene, toluene and xylenes. 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**.

[0040] Referring to Figure 2, an overview of a typical 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 reformate stream **401** and a heavy C_{7+} reformate 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 C_6 aromatics stream **403** for benzene products. The C_{7+} stream **410** feeds to a splitter **3** to produce a C_7 cut MoGas stream **411** and a C_{8+} hydrocarbon stream **420**.

[0041] The C_{8+} stream **420** is run through a clay treater **4** and then streamed **430** to a xylene re-run unit **5** to split C_{8+} hydrocarbons into a C_8 hydrocarbon stream **431** and C_{9+} (heavy aromatic MoGas) hydrocarbon stream (aromatic bottoms) **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 the C_7 cut MoGas stream **411** from the earlier splitter **3** to produce a combined C_7 cut MoGas stream **412**. Other xylenes are recovered from the para-xylene extraction unit **6** 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

further splitter column **8** by stream **450**. The converted fraction is recycled back to para-xylene extraction unit **6** from splitter column **8** by way of streams **452** (C_{8+}) and **431** (C_8) and further re-passage through the xylene re-run unit **5**. A top stream of lighter compounds **451** from the further splitter column **8** is recycled back to reformate splitter **1** for possible further benzene extraction. 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**).

[0042] Turning to Figure 3, a schematic of the prior introduction of a hydrodearylation unit is shown. Following from Figure 1, a portion of the C_{9+} heavy aromatic bottoms **60** feeds from the ARC **400** into the hydrodearylation unit **600**, while the other portion streams **50** into an atmospheric distillation unit ADU **500** first to obtain a stream of gasoline and C_9 and C_{10} with the remaining C_{11+} compounds or a 180+ °C fraction feeding into the hydrodearylation unit **600** via a stream **61**. Following hydrodearylation, the hydrodearylated bottoms are removed **70** as well as retrieved gas **62**.

[0043] Turing to Figure 4, a schematic of the present disclosure is depicted. Instead of feeding heavy aromatic bottoms of C_{9+} into a hydrodearylation unit **600**, a C_{8+} stream **430** from a clay treater **4** feeds to a hydrodearylation unit **600**. From the hydrodearylation unit **600**, following flow over the catalyst with a hydrogen gas stream, a vented gas stream **62** and a stream of treated C_{8+} compounds **70** feeds back to the xylene re-run **5** and processed as described with Figure 1.

[0044] According to an aspect, either alone or in combination with any other aspect, a process for the recovery of alkyl mono-aromatic compounds, the process including: (a) directing a feed stream from a clay treater of an aromatic recovery complex to a hydrodearylation unit, wherein the stream comprises C_{8+} compounds of one or more heavy alkyl aromatic compounds and alkyl-bridged multi-aromatic compounds; (b) hydrodearylating alkyl-bridged multi-aromatic compounds in the hydrodearylation unit by adding a hydrogen stream to the feed stream over a catalyst to produce an alkyl mono-aromatic compound containing stream; and (c) directing the alkyl mono-aromatic compound containing stream from (b) to a xylene re-run unit.

[0045] According to a second aspect, either alone or in combination with any other aspect, the alkyl-bridged alkyl multi-aromatic compounds in the feed stream include at least two benzene rings connected by an alkyl bridge group of at least two carbons, wherein the benzene rings are connected to different carbons of the alkyl bridge group,

[0046] According to a third aspect, either alone or in combination with any other aspect, the clay treater is operated at a temperature between 160 °C and 220 °C.

[0047] According to a fourth aspect, either alone or in combination with any other aspect, the clay treater is operated at 1-20 bars pressure.

[0048] According to a fifth aspect, either alone or in combination with any other aspect, the clay treater is operated at a liquid hourly space velocity (LHSV) of about 0.5 hr^{-1} to about 10 hr^{-1}.

[0049] According to a sixth aspect, either alone or in combination with any other aspect, the clay treater outlet effluent is substantially olefin free.

[0050] According to a seventh aspect, either alone or in combination with any other aspect, the clay treater outlet effluent has a bromine index less than 200.

[0051] According to an eighth aspect, either alone or in combination with any other aspect, the hydrogen stream is combined with the feed stream before being supplied to the hydrodearylation unit.

[0052] According to a ninth aspect, either alone or in combination with any other aspect, the hydrogen stream is comprised of a recycled hydrogen stream and a makeup hydrogen stream.

[0053] According to a tenth aspect, either alone or in combination with any other aspect, the hydrogen partial pressure is at least 15 bars

[0054] According to an eleventh aspect, either alone or in combination with any other aspect, the catalyst is presented as a catalyst bed in the hydrodearylation unit.

[0055] According to a twelfth aspect, either alone or in combination with any other aspect, a portion of the hydrogen stream is fed to the catalyst bed in the hydrodearylation unit to quench the catalyst bed.

[0056] According to a thirteenth aspect, either alone or in combination with any other aspect, the catalyst includes a support being at least one member selected from silica, alumina, titania or combinations thereof, and an acidic component selected from the group consisting of amorphous silica-alumina, zeolite, or combinations thereof.

[0057] According to a fourteenth aspect, either alone or in combination with any other aspect, the catalyst includes an IUPAC Group 8-10 metal selected from iron, cobalt, and nickel, or combinations thereof and an IUPAC Group 6 metal selected from the group consisting of molybdenum, tungsten, or combinations thereof.

[0058] According to a fifteenth aspect, either alone or in combination with any other aspect, the IUPAC 8-10 metal is 2 to 20 percent by weight of the catalyst and the IUPAC Group 6 metal is 1 to 25 percent by weight of the catalyst.

[0059] According to a sixteenth aspect, either alone or in combination with any other aspect, the catalyst is of a nickel, molybdenum, ultrastable Y-type zeolite, and γ-alumina support.

[0060] According to a seventeenth aspect, either alone or in combination with any other aspect, the hydrodearylation unit has an operating temperature of about 200 to about 450° C.

[0061] According to an eighteenth aspect, either alone or in combination with any other aspect, the hydrodearylation unit has a hydrogen partial pressure of about 5 to about 50 bars

[0062] According to a nineteenth aspect, either alone or in combination with any other aspect, the hydrodearylation unit has a feed rate of the hydrogen stream of about 100 to about 1000 standard liters per liter of feedstock.

[0063] According to a twentieth aspect, either alone or in combination with any other aspect, the aromatic recovery complex receives a reformate stream from a catalytic reforming unit.

[0064] According to a twenty-first aspect, either alone or in combination with any other aspect, a reformate splitter within the aromatic recovery complex splits the reformate stream into a C_5+C_6 stream that goes to a benzene extraction unit and a C_{7+} stream that feeds to a splitter.

[0065] According to a twenty-second aspect, either alone or in combination with any other aspect, the splitter divides the C_{7+} stream to a C_7 stream and a C_{8+} stream that passes through the clay treater and thereafter into the hydrodearylation unit.

[0066] According to a twenty-third aspect, either alone or in combination with any other aspect, the xylene re-run splits the alkyl mono-aromatic compound stream to a C_{9+} stream and a C_8 stream that flows to a para-xylene extraction unit and a xylene isomerization unit that recycles back to the xylene re-run unit.

[0067] EXAMPLES

[0068] One or more of the previously described features will be further illustrated in the following example simulations.

[0069] Example 1

[0070] Properties and composition of the C_{8+} stream at the outlet of the clay treater tower are shown in Table 1.

Table 1. Feedstock / Product properties and composition

Property/Composition	Units	Feedstock	Product
Density	g/cc	0.743	0.740
Paraffins		0.57	0.57
C7-MonoAromatics	wt.%	0.22	0.22
C8-MonoAromatics	wt.%	52.59	54.59

C9-MonoAromatics	wt.%	23.68	23.68
C10-MonoAromatics	wt.%	20.08	20.08
C11+	wt.%	2.86	0.86
Total	wt.%	100.00	100.00

[0071] The C_{8+} stream was contacted with a catalyst subjected to hydrodearylation conditions as follows: Pressure: 15-30 bars, temperature: 280-350°C, liquid hourly space velocity ("LHSV") 1.7 hr^{-1} (Equivalent LHSV based on di-aromatics in the stream: 140 hr^{-1}).

[0072] The problematic di-aromatics in the hydrodearylated product after being subjected to hydrodearylation (at 350 °C and 15 bar) dropped by 70%. The absolute wt.% difference in di-aromatic content between the feed to the hydrodearylation reactor and the hydrodearylated products is almost entirely at the benefit of mono-aromatic formation. The increased % of high-value mono-aromatics can then be processed upstream for benzene and *para*-xylene formation as shown in Table 1.

[0073] 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 process for the recovery of alkyl mono-aromatic compounds, the process comprising

(a) directing a feed stream from a clay treater of an aromatic recovery complex to a hydrodearylation unit, wherein the stream comprises C_{8+} compounds of one or more heavy alkyl aromatic compounds and alkyl-bridged multi-aromatic compounds;

(b) hydrodearylating alkyl-bridged multi-aromatic compounds in the hydrodearylation unit by adding a hydrogen stream to the feed stream over a catalyst to produce an alkyl mono-aromatic compound containing stream, wherein the catalyst comprises a support being at least one member selected from the group consisting of silica, alumina, titania or combinations thereof, and an acidic component selected from the group consisting of amorphous silica-alumina, zeolite, or combinations thereof, and wherein the catalyst further comprises an IUPAC Group 8-10 metal selected from the group consisting of iron, cobalt, and nickel, or combinations thereof and an IUPAC Group 6 metal selected from the group consisting of molybdenum, tungsten, or combinations thereof; and

(c) directing the alkyl mono-aromatic compound containing stream from (b) to a xylene re-run unit.

2. The process of claim 1, wherein the alkyl-bridged alkyl multi-aromatic compounds in the feed stream comprise at least two benzene rings connected by an alkyl bridge group of at least two carbons, wherein the benzene rings are connected to different carbons of the alkyl bridge group,

3. The process of claim 1 or 2, wherein the clay treater is operated at a temperature between 160 °C and 220 °C, at 1-20 bars pressure.

and at an liquid hourly space velocity (LHSV) of about 0.5 hr^{-1} to about 10 hr^{-1}.

4. The process of claims 1 to 3, wherein outlet effluent from the clay treater is substantially olefin free and has a bromine index less than 200.

5. The process of any one of claims 1 to 4, wherein the hydrogen stream is combined with the feed stream before being supplied to the hydrodearylation unit.

6. The process of any one of claims 1 to 5, wherein the hydrogen stream is comprised of a recycled hydrogen stream and a makeup hydrogen stream.

7. The process of any of claims 1 to 6, wherein the hydrogen partial pressure is at least 15 bars

8. The process of any one of claims 1 to 7, wherein the catalyst is presented as a catalyst bed in the hydrodearylation unitand a portion of the hydrogen stream is fed to the catalyst bed in the hydrodearylation unit to quench the catalyst bed.

9. The process of any one of claims 1 to 8, wherein the IUPAC 8-10 metal is 2 to 20 percent by weight of the catalyst and the IUPAC Group 6 metal is 1 to 25 percent by weight of the catalyst.

10. The process of any one of claims 1 to 9, wherein the catalyst comprises nickel, molybdenum, ultrastable Y-type zeolite, and γ-alumina support.

11. The process of any one of claims 1 to 10, wherein step (b) includes an operating temperature within the hydrodearylation unit of about 200 to about 450° C, a hydrogen partial pressure within the hydrodearylation unit of about 5 to about 50 bars, and a feed rate of the hydrogen stream to the hydrodearylation unit of about 100 to about 1000 standard liters per liter of feedstock.

12. The process of any one of claims 1 to 11, wherein the aromatic recovery complex receives a reformate stream from a catalytic reforming unit.

13. The process of claim 12, wherein a reformate splitter within the aromatic recovery complex splits the reformate stream into a C_5+C_6 stream that goes to a benzene extraction unit and a C_{7+} stream that feeds to a splitter.

14. The process of claim 13, wherein the splitter divides the C_{7+} stream to a C_7 stream and a C_{8+} stream that passes through the clay treater and thereafter into the hydrodearylation unit.

15. The process of any one of claims 1 to 14, wherein the xylene re-run splits the alkyl mono-aromatic compound stream to a C_{9+} stream and a C_8 stream that flows to a para-xylene extraction unit and a xylene isomerization unit that recycles back to the xylene re-run unit.

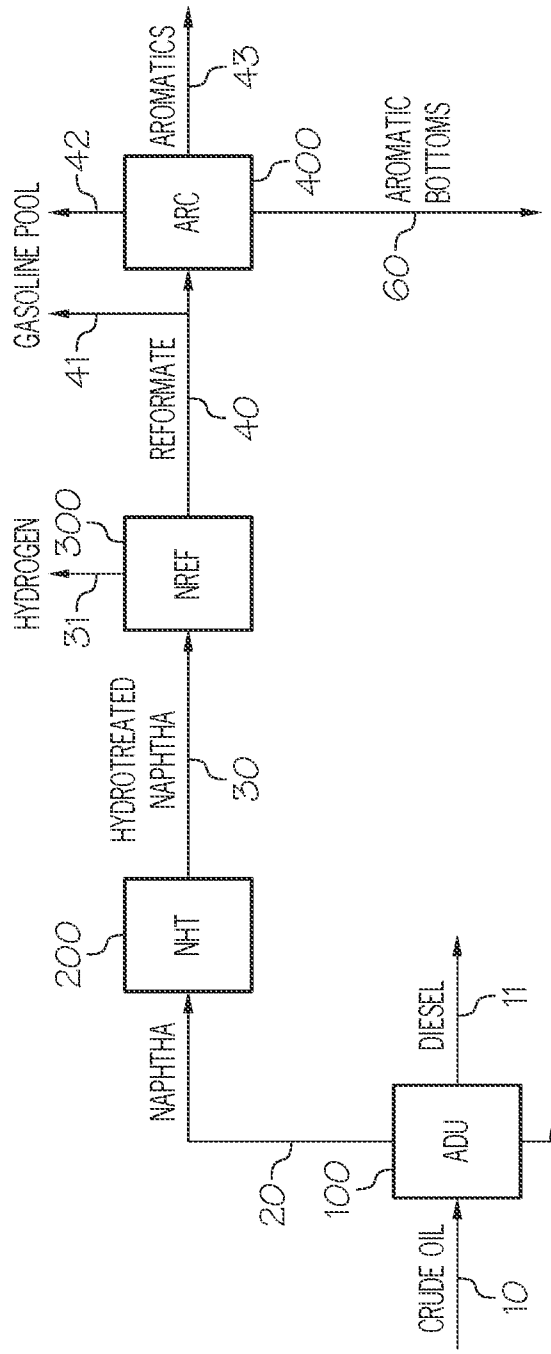

CRUDE OIL
10
ADU
100
ATMOSPHERIC RESIDUE
12
DIESEL
11
20
NAPHTHA
NHT
200
HYDROTREATED NAPHTHA
30
HYDROGEN
31
NREF
300
REFORMATE
40
GASOLINE POOL
41
ARC
42
400
AROMATICS
43
AROMATIC BOTTOMS
60

FIG. 1

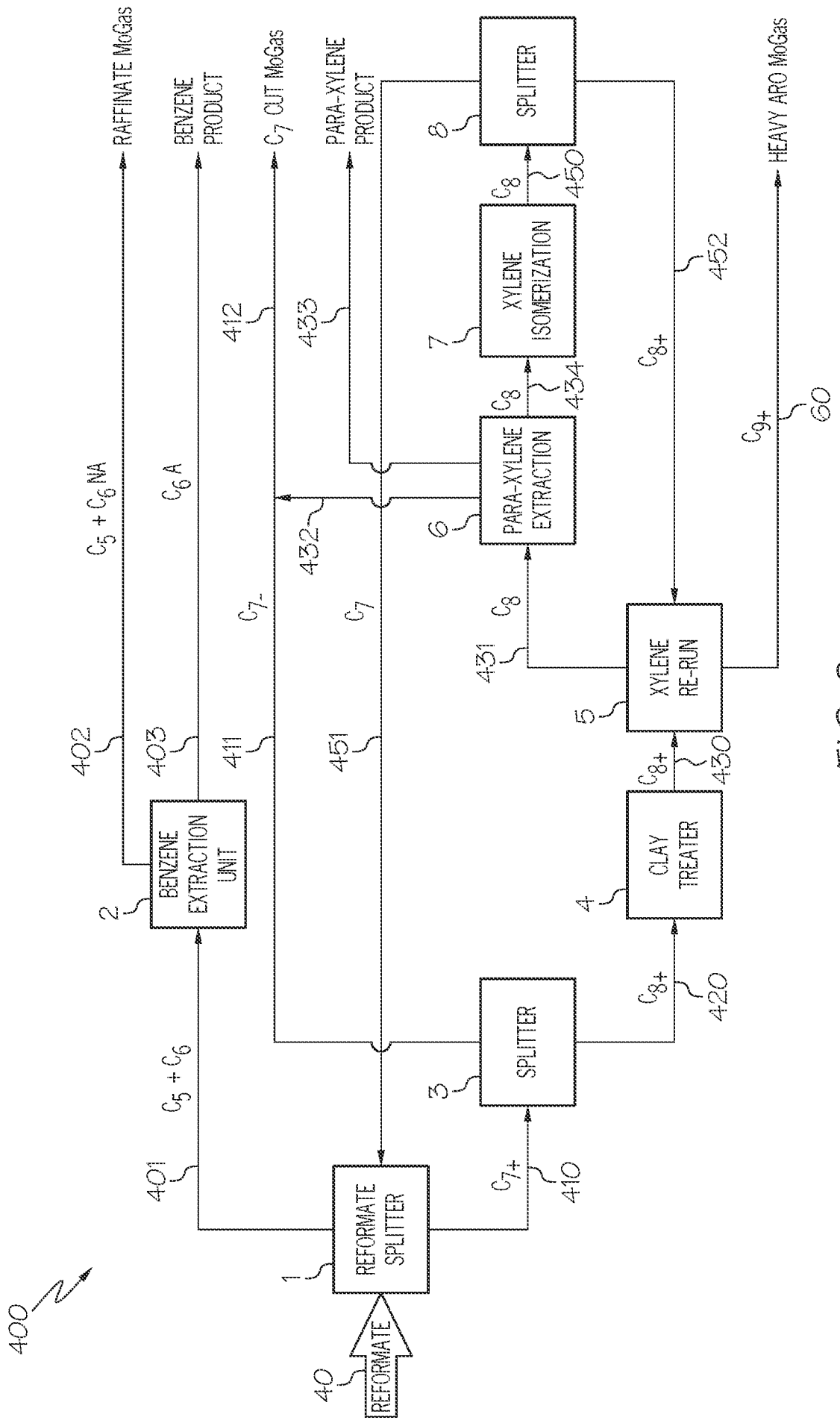

400
REFORMATE
40
REFORMATE SPLITTER
1
401
$C_5 + C_6$
BENZENE EXTRACTION UNIT
2
402
$C_5 + C_6$ NA
403
C_6 A
SPLITTER
3
C_{7+}
410
411
C_{7-}
412
C_7 CUT MoGas
RAFFINATE MoGas
BENZENE PRODUCT
CLAY TREATER
4
C_{8+}
420
XYLENE RE-RUN
5
C_{8+}
430
431
C_8
PARA-XYLENE EXTRACTION
6
C_8
432
C_7
451
433
PARA-XYLENE PRODUCT
XYLENE ISOMERIZATION
7
C_8
434
C_{8+}
452
SPLITTER
8
C_8
450
C_{9+}
60
HEAVY ARO MoGas

FIG. 2

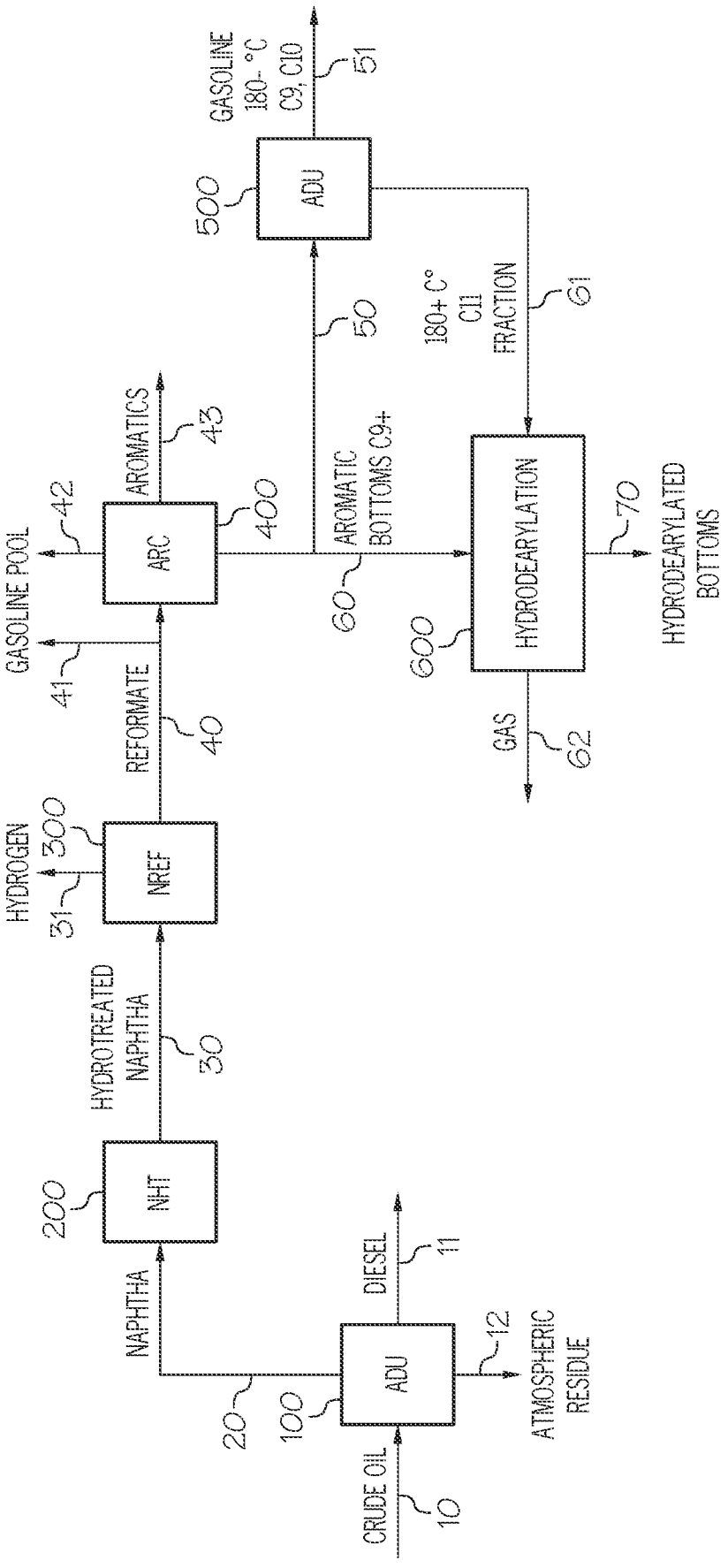

CRUDE OIL
10
ADU
100
ATMOSPHERIC RESIDUE
12
DIESEL
11
NAPHTHA
20
NHT
200
HYDROTREATED NAPHTHA
30
HYDROGEN
31
NREF
300
REFORMATE
40
GASOLINE POOL
41
ARC
400
AROMATICS
42
43
AROMATIC BOTTOMS C9+
60
50
ADU
500
GASOLINE 180- °C C9, C10
51
180+ C° C11 FRACTION
61
HYDRODEARYLATION
600
HYDRODEARYLATED BOTTOMS
70
GAS
62

FIG. 3

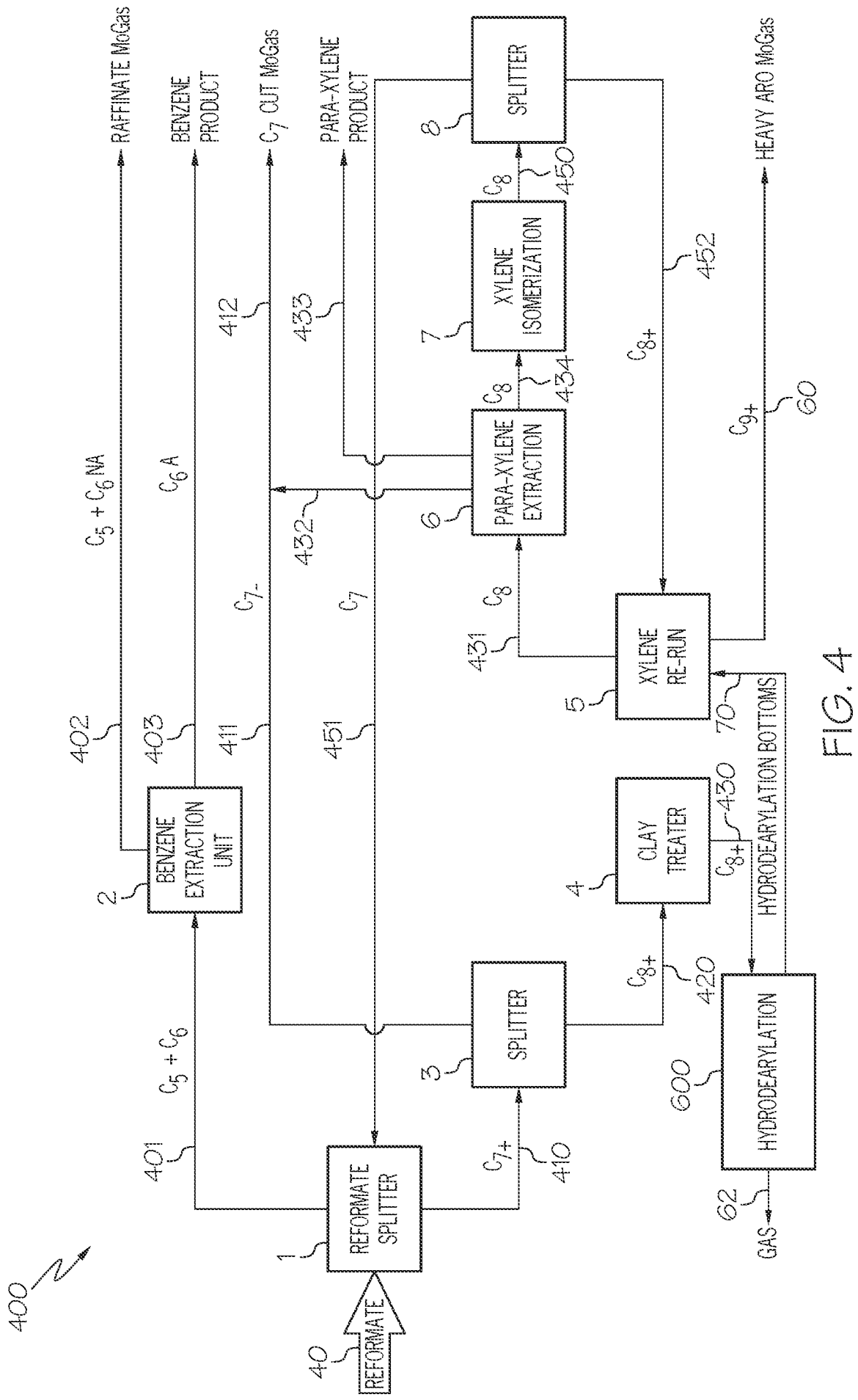

400
REFORMATE
40
REFORMATE SPLITTER
1
401
$C_5 + C_6$
BENZENE EXTRACTION UNIT
2
402
$C_5 + C_6$ NA
403
C_6 A
RAFFINATE MoGas
BENZENE PRODUCT
SPLITTER
3
410
C_{7+}
411
C_{7-}
412
C_7 CUT MoGas
CLAY TREATER
4
420
C_{8+}
430
C_{8+}
HYDRODEARYLATION
600
62
GAS
HYDRODEARYLATION BOTTOMS
XYLENE RE-RUN
5
431
C_8
70
C_{9+}
60
HEAVY ARO MoGas
451
C_7
PARA-XYLENE EXTRACTION
6
432
C_8
433
PARA-XYLENE PRODUCT
XYLENE ISOMERIZATION
7
434
C_8
C_{8+}
452
SPLITTER
8
450
C_8

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/062795

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G47/20 C10G49/04 C10G49/08 C10G35/00 C10G63/04
C10G25/00 C10G61/06 C10G67/06 C07C15/02 C07C15/12
B01J29/14 B01J29/06 B01J23/85 B01J23/883

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 B01J

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 2020/062675 A1 (KOSEOGLU OMER REFA [SA] ET AL) 27 February 2020 (2020-02-27) figures 1-5 paragraph [0022] - paragraph [0046] example 1; tables 1-3 paragraph [0003] - paragraph [0007] -----	1-15
X	US 2014/323788 A1 (RICHMOND DOROTHY M [US]) 30 October 2014 (2014-10-30) figures 1-2 paragraph [0026] - paragraph [0039] -----	1-15
A	EP 0 287 718 A1 (UOP INC [US]) 26 October 1988 (1988-10-26) examples I-IV; tables I-IV page 3, line 47 - page 6, line 10 -----	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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
25 March 2021	06/04/2021

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	Bernet, Olivier

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2020/062795

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2020062675 A1	27-02-2020	NONE	
US 2014323788 A1	30-10-2014	NONE	
EP 0287718 A1	26-10-1988	NONE	