

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

(19) World Intellectual Property Organization
International Bureau



WIPO | PCT

**(43) International Publication Date
3 September 2015 (03.09.2015)**

(10) International Publication Number

WO 2015/128046 A1

(51) **International Patent Classification:**
C10G 9/36 (2006.01) *C10G 65/10* (2006.01)
C10G 69/06 (2006.01)

(21) **International Application Number:**
PCT/EP2014/079242

(22) **International Filing Date:**
23 December 2014 (23.12.2014)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
14156638.0 25 February 2014 (25.02.2014) EP

(71) **Applicants:** SAUDI BASIC INDUSTRIES CORPORATION [SA/SA]; P.O. Box 5101, Riyadh, 11422 (SA).
SABIC GLOBAL TECHNOLOGIES B.V. [NL/NL];
Plasticslaan 1, NL-4612 PX Bergen Op Zoom (NL).

(72) **Inventor; and**

(71) **Applicant (for US only):** OPRINS, Arno Johannes Maria [NL/NL]; c/o SABIC Intellectual Property Group, P.O. Box 3008, NL-6160 GA Geleen (NL).

(74) **Agent:** ALGEMEEN OCTROOI- EN MERKENBURG EAU B.V.; P.O. Box 645, NL-5600 AP Eindhoven (NL).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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).

Published:

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

Published:

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

(54) Title: AN INTEGRATED HYDROCRACKING PROCESS

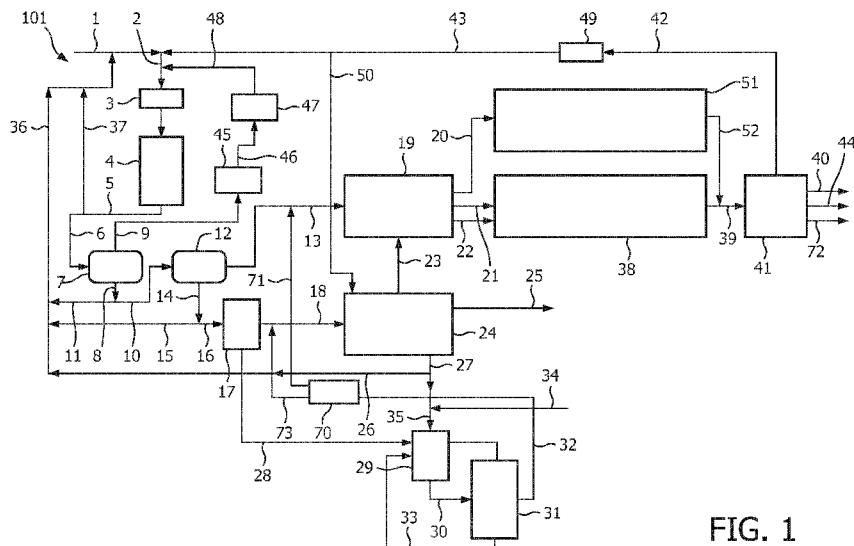


FIG. 1

(57) Abstract: The present invention relates to an integrated hydrocracking process for production of olefinic and aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil. An object of the present invention is to provide an integrated hydrocracking process for production of olefinic and aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil wherein the portion of the crude oil converted to LPG is increased significantly.

Title: An integrated hydrocracking process

The present invention relates to an integrated hydrocracking and steam pyrolysis process for production of olefinic and aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil.

Such a process is known from US Patent Application No. 2013/248417.

This US Patent Application No. 2013/248417 disclose an integrated process for the direct processing of a crude oil wherein crude oil and recycled slurry process product are charged to a hydroprocessing zone operating under conditions effective to produce a hydroprocessed effluent. The hydroprocessed effluent is thermally cracked in the presence of steam to produce a mixed product stream. A residual liquid fraction recovered upstream of the thermal cracking unit or between the convection and pyrolysis steps of the steam cracking operation is thermally cracked in a slurry hydroprocessing zone to produce a slurry intermediate product. Hydrogen from the mixed product stream is purified and recycled to the hydroprocessing zone, and olefins, aromatics and pyrolysis fuel oil are recovered from the separated mixed product stream. Rejected residuals or bottoms from the hydroprocessing zone are upgraded in a slurry hydroprocessing zone in the presence of hydrogen to produce a slurry intermediate product including middle distillates. Slurry intermediate product is only recycled and mixed with the hydrotreated reactor effluent before processing in the steam pyrolysis zone for conversion.

In the process according to US Patent Application No. 2013/248417 the crude oil is hydrocracked to produce a liquid hydrocarbon feed for subsequent processing by means of steam cracking. Steam cracking of heavy liquid feeds results in relatively poor cracker product slate including a relatively small amount of high value chemicals. This is partly compensated by means of sending some of these heavy hydrocarbons together with the heaviest effluent of the first hydrocracking zone to a slurry hydroprocessing zone where this heavy material is further cracked into liquid hydrocarbon steam cracker feed (possibly needing saturation first).

US Patent No. 4,137,147 relates to a process for manufacturing ethylene and propylene from a charge having a distillation point lower than about 360 DEG C. and containing at least normal and iso-paraffins having at least 4 carbon atoms per molecule, wherein: said charge is subjected to a hydrogenolysis reaction in a hydrogenolysis zone, in the presence of a catalyst, (b) the effluents from the

hydrogenolysis reaction are fed to a separation zone from which are discharged (i) from the top, methane and possibly hydrogen, (ii) a fraction consisting essentially of hydrocarbons with 2 and 3 carbon atoms per molecule, and (iii) from the bottom, a fraction consisting essentially of hydrocarbons with at least 4 carbon atoms per molecule, (c) only said fraction consisting essentially of hydrocarbons with 2 and 3 carbon atoms per molecule is fed to a steam-cracking zone, in the presence of steam, to transform at least a portion of the hydrocarbons with 2 and 3 carbon atoms per molecule to monoolefinic hydrocarbons; said fraction consisting essentially of hydrocarbons with at least 4 carbon atoms per molecule, obtained from the bottom of said separation zone, is supplied to a second hydrogenolysis zone where it is treated in the presence of a catalyst, the effluent from the second hydrogenolysis zone is supplied to a separation zone to discharge, on the one hand, hydrocarbons with at least 4 carbon atoms per molecule which are recycled at least partly to the said second hydrogenolysis zone, and, on the other hand, a fraction consisting essentially of a mixture of hydrogen, methane and saturated hydrocarbons with 2 and 3 carbon atoms per molecule; a hydrogen stream and a methane stream are separated from said mixture and there is fed to said steam-cracking zone the hydrocarbons of said mixture with 2 and 3 carbon atoms, together with said fraction consisting essentially of hydrocarbons with 2 and 3 carbon atoms per molecule as recovered from said separation zone following the first hydrogenolysis zone. At the outlet of the steam-cracking zone are thus obtained, in addition to a stream of methane and hydrogen and a stream of paraffinic hydrocarbons with 2 and 3 carbon atoms per molecule, olefins with 2 and 3 carbon atoms per molecule and products with at least 4 carbon atoms per molecule. According to this document the bottom stream of the first hydrogenolysis zone is forwarded to the second hydrogenolysis zone.

US Patent No. 3,842,138 relates to process for thermally cracking a hydrocarbon feedstock to convert it into lower molecular weight products containing large proportions of olefins comprising conducting said process in a heated reactor under superatmospheric pressures, ranging from about 10 bars to about 70 bars read at the reactor outlet, in the presence of hydrogen, at reactor outlet temperatures higher than about 625 C. to about 1100 C. and with residence times within the reaction section shorter than about 0.5 second down to about 0.005 second. Under the operating conditions the molar ratios of ethylene to ethane and of propylene to propane vary between 0.3 and 2 for the first and between 1 and 8 for the second. In

thermal hydrocracking, the temperatures are substantially higher than in the catalytic processes, and under such pyrolytic conditions, the conversion of the charge into gaseous products is higher and may be almost complete, at least as regards the paraffinic hydrocarbons. As for aromatics, due to the more stable structure of the 5 nuclei, only the side chains are affected and are subjected to a more or less intense dealkylation according, to the severity of the operating conditions.

US patent application No. 2006/287561 relates to a process for increasing the production of C2-C4 light olefin hydrocarbons by integrating a process for producing an aromatic hydrocarbon mixture and liquefied petroleum gas (LPG) 10 from a hydrocarbon mixture and a process for producing a hydrocarbon feedstock which is capable of being used as a feedstock in the former process.

US Patent No. 3,839,484 relates to a process for the preparation of unsaturated hydrocarbons by pyrolysis of naphthas boiling in the range of about 80 to 450 F. in a pyrolysis furnace, comprising hydrocracking said naphthas to form a 15 mixture of paraffins and iso paraffins and pyrolyzing the resulting mixture of paraffins and isoparaffins in a pyrolysis furnace.

US patent application No 2007/062848 relates to a process for hydrocracking a feed comprising not less than 20 weight % of one or more aromatic compounds containing at least two fused aromatic rings which compounds are 20 unsubstituted or substituted by up to two C1-4 alkyl radicals to produce a product stream comprising not less than 35 weight % of a mixture of C2-4 alkanes. According to US patent application No 2007/062848 bitumen from the oil sands is fed to a conventional distillation unit, and a naphtha stream from the distillation unit is fed to a naphtha hydrotreater unit. The overhead gas stream is a light gas/light paraffin 25 stream and fed to hydrocarbon cracker. A diesel stream from the distillation unit is fed to a diesel hydrotreater unit, and the gas oil stream from the distillation unit is fed to a vacuum distillation unit, wherein a vacuum gas oil stream from the vacuum distillation unit is fed to a gas oil hydrotreater. A light gas stream from the gas oil hydrotreater is fed to hydrocarbon cracker. The hydrotreated vacuum gas oil from the 30 vacuum gas oil hydrotreater is fed to a catalytic cracker unit. The bottom stream from the vacuum distillation unit is a vacuum (heavy) residue and is sent to a delayed coker producing a number of streams, such as a naphtha stream being sent to a naphtha hydrotreater unit, a diesel stream is sent to diesel hydrotreater unit to produce hydrotreated diesel, and a gas oil stream is fed to a vacuum gas oil

hydrotreater unit resulting in a hydrotreated gas oil stream which is fed to a catalytic cracker unit.

An aspect of such an integrated process is that significant amounts of heavier steam cracking components are recycled over the steam cracker ultimately resulting in increased equipment size and energy demand.

Another aspect is that steam cracking of liquid feeds (and LPG with the exception of ethane) furthermore results in significant amounts of methane being produced to be used as fuel in the steam cracking furnaces. This means that some of the more valuable crude oil is therefore downgraded to methane fuel value. In addition to the carbon atoms representing this efficiency loss there is also a lot of hydrogen lost via this methane as well. As a result more hydrogen than necessary needs to be added to the crude oil making the overall hydrogen balances less favourable.

Another aspect of the integrated process is that any LPG made in the hydrocracking processing steps is sent to the compressor and subsequent steam cracker separation section first. The effect thereof is an increase in the sizing and the energy spend in these downstream separations as the desired steam cracking products are diluted first with this LPG (i.e. adding ethane to the ethylene and propane to propylene product to be separated again).

An object of the present invention is to provide an integrated hydrocracking process for production of olefinic and aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil wherein the aforementioned problems have been overcome.

Another object of the present invention is to provide an integrated hydrocracking process for production of olefinic and aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil wherein the portion of the crude oil converted to LPG is increased significantly.

Another object of the present invention is to provide an integrated hydrocracking process for production of olefinic and aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil wherein efficiency and selectivity of the hydrocracking step is controlled by the severity.

The present invention relates thus to an integrated hydrocracking process for production of olefinic and aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil, the process comprising:

treating the feedstock comprising crude oil and a residual liquid product in a first hydrocracking zone in the presence of hydrogen under conditions effective to produce a first effluent having an increased hydrogen content;

5 separating the first effluent into a LPG comprising stream and a liquid phase stream;

separating said LPG comprising stream into one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising ethane, a stream comprising butanes, a stream comprising propane, a stream comprising C1-minus, a stream comprising C3-minus, 10 a stream comprising C1-C2, a stream comprising C3-C4, a stream comprising C2-C3, a stream comprising C1-C3, a stream comprising C1-C4, a stream comprising C2-C4, a stream comprising C2-minus, a stream comprising C4-minus;

15 further processing one or more of the streams thus obtained in a steam cracker unit and at least one unit, chosen from the group of a butanes dehydrogenation unit, a propane dehydrogenation unit, a combined propane-butanes dehydrogenation unit, or a combination of units thereof to produce mixed product stream(s);

20 feeding the mixed product stream(s) from said steam cracker unit and at least one unit, chosen from the group a butanes dehydrogenation unit, a propane dehydrogenation unit and a combined propane-butanes dehydrogenation unit, or a combination of units thereof, to a second separation section;

thermally cracking the liquid phase stream in a resid hydrocracking zone to produce a slurry intermediate product;

separating the mixed product stream(s).

25 According to the present invention the LPG comprising stream is separated into one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising ethane, a stream comprising butanes, a stream comprising propane, a stream comprising C1-minus, a stream comprising C3-minus, a stream comprising C1-C2, a stream comprising C3-C4, a stream comprising C2-C3, a stream comprising C1-C3, a stream comprising C1-C4, a stream comprising C2-C4, a stream comprising C2-minus, a stream comprising C4-minus using any appropriate separation technology, wherein it is preferred to feed at least one stream chosen from the group of a stream comprising ethane, a stream comprising C1-C2 and a stream comprising C2-minus to a steam

cracker unit. This means that no heavier steam cracking components are recycled over the steam cracker ultimately resulting in decreased equipment size and energy demand. Alternative separation scheme's resulting in a combined propane/butanes stream, possibly also diluted with methane and/or ethane or a propane stream possibly diluted with methane and/or ethane can be used.

5 Please note that streams indicated with the term "a stream" refer to the stream generated within the present process, i.e. these streams are not from "the outside".

10 The present method thus focusses on the optimization of the production of LPG comprising streams, which LPG comprising streams are identified as highly useful feedstock's for steam pyrolysis processes and/or dehydrogenation processes for the production of olefinic and aromatic petrochemicals.

15 As mentioned above, a stream comprising ethane, and/or a stream comprising C1-C2 and/or a stream comprising C2-minus is preferably fed to a gas steam cracking unit, and the propane and butane comprising streams are preferably fed to dehydrogenation units. This processing route results in much higher carbon efficiency and also produces the amounts of hydrogen needed for the high conversion hydrocracking all the way to LPG. A heavy material stream is directly sent as feed to the slurry hydrocracking zone.

20 Thus the present method comprises the combination of a steam cracker unit and at least one unit chosen from the group of a butanes dehydrogenation unit, a propane dehydrogenation unit, a combined propane-butanes dehydrogenation unit, or a combination of units thereof to produce a mixed product stream. This combination of units provides a high yield of the desired products, 25 namely olefinic and aromatic petrochemicals, wherein the portion of the crude oil converted to LPG is increased significantly.

30 According to a preferred embodiment the LPG comprising stream is separated into one or more streams, wherein the stream comprising hydrogen is preferably used as a hydrogen source for hydrocracking purpose, the stream comprising methane is preferably used as a fuel source, the stream comprising ethane is preferably used as a feed for the steam cracking unit, the stream comprising propane is preferably used as a feed for a propane dehydrogenation unit, a stream comprising butanes is preferably used as a feed for a butane dehydrogenation unit, a stream comprising C1-minus is preferably used as a fuel

source and/or as a hydrogen source, a stream comprising C3-minus is preferably used as a feed for a propane dehydrogenation unit but, according to another embodiment, also as a feed for the steam cracking unit, a stream comprising C2-C3 is preferably used as a feed for a propane dehydrogenation unit, but, according to 5 another embodiment, also as a feed for the steam cracking unit, a stream comprising C1-C3 is preferably used as a feed for a propane dehydrogenation unit, but, according to another embodiment, also as a feed for the steam cracking unit, a stream comprising C1-C4 butanes is preferably used as a feed for a butane dehydrogenation unit, a stream comprising C2-C4 butanes is preferably used as a 10 feed for a butane dehydrogenation unit, a stream comprising C2-minus is preferably used as a feed for the steam cracking unit, a stream comprising C3-C4 is preferably used as a feed for a propane or butane dehydrogenation unit, or a combined propane and butane dehydrogenation unit, a stream comprising C4-minus is preferably used as a feed for a butane dehydrogenation unit.

15 As used herein, the term "C# hydrocarbons" or "C#", wherein "#" is a positive integer, is meant to describe all hydrocarbons having # carbon atoms. Moreover, the term "C#+ hydrocarbons" or "C#+" is meant to describe all hydrocarbon molecules having # or more carbon atoms. Accordingly, the term "C5+ hydrocarbons" or "C5+" is meant to describe a mixture of hydrocarbons having 5 or 20 more carbon atoms. The term "C5+ alkanes" accordingly relates to alkanes having 5 or more carbon atoms. Accordingly, the term "C# minus hydrocarbons" or "C# minus" is meant to describe a mixture of hydrocarbons having # or less carbon atoms and including hydrogen. For example, the term "C2-" or "C2 minus" relates to a mixture of ethane, ethylene, acetylene, methane and hydrogen. For example, the term C1-C3 25 refers to a mixture comprising C1, C2 and C3. Finally, the term "C4mix" is meant to describe a mixture of butanes, butenes and butadiene, i.e. n-butane, i-butane, 1-butene, cis- and trans-2-butene, i-butene and butadiene.

The term "olefin" is used herein having its well-established meaning. Accordingly, olefin relates to an unsaturated hydrocarbon compound containing at 30 least one carbon–carbon double bond. Preferably, the term "olefins" relates to a mixture comprising two or more of ethylene, propylene, butadiene, butylene-1, isobutylene, isoprene and cyclopentadiene.

The term "LPG" as used herein refers to the well-established acronym for the term "liquefied petroleum gas". LPG generally consists of a blend of C3-C4 hydrocarbons i.e. a mixture of C3 and C4 hydrocarbons.

The one of the petrochemical products produced in the process of the 5 present invention is BTX. The term "BTX" as used herein relates to a mixture of benzene, toluene and xylenes. Preferably, the product produced in the process of the present invention comprises further useful aromatic hydrocarbons such as ethyl benzene. Accordingly, the present invention preferably provides a process for producing a mixture of benzene, toluene xylenes and ethyl benzene ("BTXE"). The 10 product as produced may be a physical mixture of the different aromatic hydrocarbons or may be directly subjected to further separation, e.g. by distillation, to provide different purified product streams. Such purified product stream may include a benzene product stream, a toluene product stream, a xylene product stream and/or an ethyl benzene product stream.

15 According to the present method a small amount of methane is produced and the methane can be used as fuel for the steam cracking and dehydrogenation furnaces. Any heavier material can be recycled to the different stages of the described process.

According to a preferred embodiment the process further comprises 20 feeding at least one stream chosen from the group of a stream comprising propane, a stream comprising C3-C4, a stream comprising C3-minus, a stream comprising butanes, a stream comprising C4-minus, a stream comprising C2-C3, a stream comprising C1-C3, a stream comprising C1-C4 and a stream comprising C2-C4 to at least one dehydrogenation unit chosen from the group of a butanes dehydrogenation 25 unit, a propane dehydrogenation unit, a combined propane-butanes dehydrogenation unit, or a combination of units thereof.

Please note that streams mentioned here with the term "a stream" refer to the stream generated within the present process, i.e. these streams are not from "the outside".

30 According to another preferred embodiment the process further comprises recovering olefins and aromatics from the separated mixed product stream.

According to a preferred embodiment the process further comprises treating said liquid phase feed in a second hydrocracking zone in the

presence of hydrogen under conditions effective to produce a second effluent having an increased hydrogen content;

recovering from the second effluent from said second hydrocracking zone a BTXE comprising stream, a LPG comprising stream and a residual liquid stream. One of the advantages of a second hydrocracking zone is that it gives more control over the efficiency and selectivity of the hydrocracking steps by controlling the severity.

According to a preferred embodiment the process further comprises thermally cracking said residual liquid stream together with said liquid phase stream in a resid hydrocracking zone to produce a slurry intermediate product. In the resid hydrocracking zone all remaining heavy hydrocarbon fractions are converted to lighter feed that can be converted to LPG in one of the hydrocracking zones. And these LPG comprising streams will be sent to any one of steam cracker unit and dehydrogenation units.

According to a preferred embodiment the process further comprises combining the LPG comprising stream originating from said first hydrocracking zone with the LPG comprising stream originating from said second hydrocracking zone.

According to a preferred embodiment the process further comprises recovering vapour products from the slurry intermediate product and combining the vapour products thus recovered with the LPG comprising stream(s).

According to a preferred embodiment the process further comprises separating from the first and second effluents residual liquid fractions and recycling said residual liquid fractions to inlet of the first hydrocracking zone and/or second hydrocracking zone. In another embodiment the gas/liquid effluent of the slurry hydrocracking zone can be recycled to any of the process units that best matches the composition and pressure of the respective streams similar as to the effluent (heavier than LPG) of the second hydrocracking zone. These two recycles can be either mixed together or can be kept separate so they can go to different feed locations in the present integrated process.

It is preferred to recover olefins and aromatics from the separated mixed product stream(s).

According to a preferred embodiment the process further comprises recovering methane from the separated mixed product stream and recycling said methane to the steam cracker to be used as fuel for burners and/or heaters.

According to a preferred embodiment the process further comprises recovering and purifying hydrogen from the separated mixed product stream(s) and recycling it to the inlet of the first and/or second hydrocracking zone.

According to a preferred embodiment the process further comprises 5 recovering pyrolysis fuel oil from the separated mixed product stream(s) and recycling said pyrolysis fuel oil to the inlet of said first and/or second hydrocracking zone, or even to the inlet of the resid hydrocracking zone.

A very common process for the conversion of alkanes to olefins involves "steam cracking". As used herein, the term "steam cracking" relates to a 10 petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons such as ethylene and propylene. In steam cracking gaseous hydrocarbon feeds like ethane, propane and butanes, or mixtures thereof, (gas cracking) or liquid hydrocarbon feeds like naphtha or gasoil (liquid cracking) is diluted with steam and briefly heated in a furnace without the presence 15 of oxygen. Typically, the reaction temperature is very high, at around 850°C, but the reaction is only allowed to take place very briefly, usually with residence times of 50-500 milliseconds. Preferably, the hydrocarbon compounds ethane, propane and butanes are separately cracked in accordingly specialized furnaces to ensure cracking at optimal conditions. After the cracking temperature has been reached, the 20 gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil. Steam cracking results in the slow deposition of coke, a form of carbon, on the reactor walls. Decoking requires the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer 25 to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace is returned to service. The products produced by steam cracking depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time. Light hydrocarbon feeds such as ethane, propane, butanes or light naphtha give product streams rich in the lighter polymer 30 grade olefins, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphtha and gas oil fractions) also give products rich in aromatic hydrocarbons.

To separate the different hydrocarbon compounds produced by steam cracking the cracked gas is subjected to fractionation unit. Such fractionation units

are well known in the art and may comprise a so-called gasoline fractionator where the heavy-distillate ("carbon black oil") and the middle-distillate ("cracked distillate") are separated from the light-distillate and the gases. In the subsequent quench tower, most of the light-distillate produced by steam cracking ("pyrolysis gasoline" or 5 "pygas") may be separated from the gases by condensing the light-distillate. Subsequently, the gases may be subjected to multiple compression stages wherein the remainder of the light distillate may be separated from the gases between the compression stages. Also acid gases (CO₂ and H₂S) may be removed between compression stages. In a following step, the gases produced by pyrolysis may be 10 partially condensed over stages of a cascade refrigeration system to about where only the hydrogen remains in the gaseous phase. The different hydrocarbon compounds may subsequently be separated by simple distillation, wherein the ethylene, propylene and C₄ olefins are the most important high-value chemicals produced by steam cracking. The methane produced by steam cracking is generally 15 used as fuel gas, the hydrogen may be separated and recycled to processes that consume hydrogen, such as hydrocracking processes. The acetylene produced by steam cracking preferably is selectively hydrogenated to ethylene. The alkanes comprised in the cracked gas may be recycled to the process for converting alkanes to olefins.

20 The term "propane dehydrogenation unit" as used herein relates to a petrochemical process unit wherein a propane feedstream is converted into a product comprising propylene and hydrogen. Accordingly, the term "butane dehydrogenation unit" relates to a process unit for converting a butane feedstream into C₄ olefins. Together, processes for the dehydrogenation of lower alkanes such 25 as propane and butanes are described as lower alkane dehydrogenation process. Processes for the dehydrogenation of lower alkanes are well-known in the art and include oxidative hydrogenation processes and non-oxidative dehydrogenation processes. In an oxidative dehydrogenation process, the process heat is provided by partial oxidation of the lower alkane(s) in the feed. In a non-oxidative 30 dehydrogenation process, which is preferred in the context of the present invention, the process heat for the endothermic dehydrogenation reaction is provided by external heat sources such as hot flue gases obtained by burning of fuel gas or steam. For instance, the UOP Oleflex process allows for the dehydrogenation of propane to form propylene and of (iso)butane to form (iso)butylene (or mixtures

thereof) in the presence of a catalyst containing platinum supported on alumina in a moving bed reactor; see e.g. US 4,827,072. The Uhde STAR process allows for the dehydrogenation of propane to form propylene or of butane to form butylene in the presence of a promoted platinum catalyst supported on a zinc-alumina spinel; see 5 e.g. US 4,926,005. The STAR process has been recently improved by applying the principle of oxydehydrogenation. In a secondary adiabatic zone in the reactor part of the hydrogen from the intermediate product is selectively converted with added oxygen to form water. This shifts the thermodynamic equilibrium to higher conversion and achieve higher yield. Also the external heat required for the endothermic 10 dehydrogenation reaction is partly supplied by the exothermic hydrogen conversion. The Lummus Catofin process employs a number of fixed bed reactors operating on a cyclical basis. The catalyst is activated alumina impregnated with 18-20 wt-% chromium; see e.g. EP 0 192 059 A1 and GB 2 162 082 A. The Catofin process is reported to be robust and capable of handling impurities which would poison a 15 platinum catalyst. The products produced by a butane dehydrogenation process depends on the nature of the butane feed and the butane dehydrogenation process used. Also the Catofin process allows for the dehydrogenation of butane to form butylene; see e.g. US 7,622,623.

Other aspects, embodiments, and advantages of the process of the 20 present invention are discussed in detail below. Moreover, it is to be understood that both the foregoing information and the following detailed description are merely illustrative examples of various aspects and embodiments, and are intended to provide an overview or framework for understanding the nature and character of the claimed features and embodiments. The accompanying drawing is illustrative and is 25 provided to further the understanding of the various aspects and embodiments of the process of the invention.

A process flow diagram including an integrated hydroprocessing 30 process and system as indicated by reference number 101 is shown in FIG. 1. The integrated system 101 generally includes a selective hydroprocessing zone, a steam pyrolysis zone, a product separation zone and a resid hydrocracking zone.

The selective hydroprocessing zone includes a hydroprocessing reaction zone 4, i.e. a first hydrocracking zone unit, having an inlet for receiving a mixture 3 containing a crude oil feed 1, a residual liquid product stream 36, 37, hydrogen 48, 43 and make-up hydrogen as necessary (not shown). Hydroprocessing

reaction zone 4 further includes an outlet for discharging a hydroprocessed effluent 5. Hydroprocessed effluent 5 can be partly recycled as stream 37 to the inlet of hydroprocessing reaction zone 5, i.e. a first hydrocracking zone unit.

The remainder part 6 of reactor effluents 5 from the hydroprocessing reaction zone 4 is sent to a high pressure separator 7. The separator tops 9 are cleaned in an amine unit 45 and a resulting hydrogen rich gas stream 46 is passed to a recycling compressor 47 to be used as a recycle gas 48 in the first hydroprocessing reactor 4. A bottoms stream 8 from the high pressure separator 7, which is in a substantially liquid phase, is cooled and introduced as stream 10 to a low pressure cold separator 12, where it is separated into a gas stream 13, i.e. a LPG comprising stream, and a liquid stream 14. A residual liquid phase 11 from high pressure separator 7 and a residual liquid phase 15 from low pressure cold separator 12 can be recycled to the inlet of hydroprocessing reaction zone 4, i.e. a first hydrocracking zone unit. Gases 13 from low pressure cold separator 12 include hydrogen, H₂S, NH₃ and any light hydrocarbons such as C₁-C₄ hydrocarbons.

LPG comprising stream 13 is further separated in unit 19 into individual streams 20, 21, 22 such one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising ethane, a stream comprising butanes, a stream comprising propane, a stream comprising C₁-minus, a stream comprising C₃-minus, a stream comprising C₁-C₂, a stream comprising C₃-C₄, a stream comprising C₂-C₃, a stream comprising C₁-C₃, a stream comprising C₁-C₄, a stream comprising C₂-C₄, a stream comprising C₂-minus, a stream comprising C₄-minus. Although a restricted number of into individual streams 20, 21, 22 have been shown, it is clear that the invention is not restricted to a specific number of individual streams. Stream 20, i.e. a lights fraction originating from separation unit 19 is preferably sent to a gas steam cracker unit 51. The effluent stream 52 from gas steam cracker unit 51 is sent to a separation section 41. These individual steams 21, 22 are further processed in unit 38, wherein unit 38 is to be understood as a group of units, chosen from a butanes dehydrogenation unit, a propane dehydrogenation unit a combined propane-butanes dehydrogenation unit, or a combination of units thereof to produce a mixed product stream 39. Unit 38 also comprises a separation section 41 for separating the mixed product stream(s) 39 and recovering for example several streams 40, 44, 72, including olefins and aromatics, from the separated mixed product stream 39. Although a restricted number of into

individual streams 40, 44, 72 has been shown, it is clear that the invention is not restricted to a specific number of individual streams. Stream 42 mainly comprises hydrogen. Separation section 41 may comprise several separation units. A stream comprising methane part is separated in unit 41 and recycled to the steam cracker 5 and/or the dehydrogenation units of unit 38 to be used there as fuel for burners and/or heaters. Hydrogen comprising stream 42 is then passed to a hydrogen purification unit 49, such as a pressure swing adsorption (PSA) unit to obtain a hydrogen stream 43 having a purity of 99.9%+, or a membrane separation units to obtain a hydrogen stream 43 with a purity of about 95%, or any other hydrogen 10 purification technology to reach the desired hydrogen purity. The purified hydrogen stream 43 is then recycled back to serve as a major portion of the requisite hydrogen for the hydroprocessing reaction zone 4, or a part 50 thereof is recycled back to serve as a major portion of the requisite hydrogen for the second hydrocracking zone 24. All or a portion of liquid stream 16 serves as the feed to the second 15 hydrocracking zone 24. Second hydrocracking zone 24 produces a second effluent, comprising a BTXE comprising stream 25, a LPG comprising stream 23 and a liquid residual stream 27. Stream 27 can be divided into a stream to be sent to the slurry hydroprocessing zone 31 and a stream to be recycled to the inlet of the first hydrocracking zone 4.

20 In additional embodiments, a separation zone 17 is included upstream of sections 24. Stream 16 is fractioned, for example by distillation or flashing, into a residual liquid phase 28 (to be sent to unit 29) and a liquid phase 18 (to be sent to second hydrocracking zone 24).

25 Although second hydrocracking zone 24 has been shown here as a single box, in the present description reference number 24 is to be understood as a hydrocracking zone, i.e. a hydrocracking zone comprising one or more units chosen from the group of Feed Hydrocracking (FHC), Gasoline Hydrocracking (GHC), Aromatic Ringopening, Hydrocracking (gas oil) and Resid Hydrocracking (vacuum resid), including separation sections.

30 In a process employing the arrangement shown in FIG. 1, a crude oil feedstock 1 and residual heavy liquid products 36, 37 are admixed with an effective amount of hydrogen 48, 43 (and optionally make-up hydrogen, not shown), and the mixture is charged to the inlet of selective hydroprocessing reaction zone 4 at a temperature in the range of from 200[deg.] C. to 600[deg.] C.

Hydroprocessing reaction zone 4 operates under parameters effective to hydrodemetallicize, hydrodearomatize, hydrodenitrogenate, hydrodesulfurize and/or hydrocrack the oil feedstock, which in certain embodiments is crude oil. In certain embodiments, hydroprocessing is carried out using the following conditions:

5 operating temperature in the range of from 200[deg.] C. to 600[deg.] C.; operating pressure in the range of from 0,2 – 20 MPa; and a liquid hour space velocity (LHSV) in the range of from 0.1 h<-1> to 10 h<-1>.

The feed to the resid hydrocracking zone includes combinations of streams 34, originating from the recovery of valuable products from mixed product stream 39, stream 27 coming from second hydrocracking zone 24, stream 28 comprising residual heavy liquid. This combined feed is processed in slurry hydroprocessing zone 31, optionally via a blending zone 29. In the blending zone 29, the residual liquid fraction(s) is/are mixed with a slurry unconverted residue 33 that include the catalyst active particles to form the feed of the slurry hydroprocessing zone 31. This feed 30 is then upgraded in the slurry hydroprocessing zone 31 in the presence of hydrogen (not shown) to produce a slurry intermediate product 32 including middle distillates. In certain embodiments the slurry hydroprocessing zone 31 is under a common high pressure loop with one or more reactors in hydroprocessing zone 4 and/or second hydrocracking zone 24. Slurry intermediate product 32 is recycled, via separation unit 70, and preferably separated into a gaseous stream 71 and a stream 73 but can also enter directly in any of the feeds to the individual hydrocrackers in second hydrocracking zone 24 best matching in feed composition. Such a stream 71 can be combined with other LPG comprising streams 13, 23. Stream 73 is preferably mixed with the effluent from unit 17 before processing in the second hydrocracking zone 24 for conversion.

In an embodiment wherein second hydrocracking zone 24 is not present, liquid stream 16 (now as stream 28) is thermally cracked in a resid hydrocracking or slurry hydroprocessing zone 31 to produce a slurry intermediate product 32.

30 As mentioned above, second hydrocracking zone 24 is a hydrocracking zone comprising one or more units chosen from the group of Feed Hydrocracking (FHC), Gasoline Hydrocracking (GHC), Aromatic Ringopening, Hydrocracking (gas oil) and Resid Hydrocracking (vacuum resid). The preferred FHC conditions include a temperature of 300-550 °C, a pressure of 300-5000 kPa gauge and a Weight

Hourly Space Velocity of 0.1-10 h-1. More preferred feed hydrocracking conditions (FHC) include a temperature of 300-450 °C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-10 h-1. Even more preferred FHC conditions optimized to the ring-opening of aromatic hydrocarbons include a temperature of 5 300-400 °C, a pressure of 600-3000 kPa gauge and a Weight Hourly Space Velocity of 0.2-2 h-1. The preferred gasoline hydrocracking conditions (GHC) include a temperature of 300-580 °C, more preferably of 400-580 °C and even more preferably of 430-530 °C, a pressure of 0.3-5 MPa gauge, more preferably at a pressure of 0.6-3 MPa gauge, particularly preferably at a pressure of 1-2 MPa gauge and most 10 preferably at a pressure of 1.2-1.6 MPa gauge, and a Weight Hourly Space Velocity (WHSV) of 0.1-20 h-1, more preferably at a Weight Hourly Space Velocity of 0.2-15 h-1 and most preferably at a Weight Hourly Space Velocity of 0.4-10 h-1. The aromatic ring opening process (ARO process, see for example US 7,513,988) may comprise aromatic ring saturation at a temperature of 100-500 °C, preferably 200-15 500 °C, more preferably 300-500 °C, a pressure of 2-10 MPa together with 1-30 wt.-%, preferably 5-30 wt.-% of hydrogen (in relation to the hydrocarbon feedstock) in the presence of an aromatic hydrogenation catalyst and ring cleavage at a temperature of 200-600 °C, preferably 300-400 °C, a pressure of 1-12 MPa together with 1-20 wt.-% of hydrogen (in relation to the hydrocarbon feedstock) in the 20 presence of a ring cleavage catalyst, wherein said aromatic ring saturation and ring cleavage may be performed in one reactor or in two consecutive reactors. The process conditions used for hydrocracking generally includes a process temperature of 200-600 °C, elevated pressures of 0.2-20 MPa, space velocities between 0.1-20 h-1.

CLAIMS

1. An integrated hydrocracking process for production of olefinic and
5 aromatic petrochemicals from a hydrocarbon feedstock comprising crude oil, the
process comprising:

treating the feedstock comprising crude oil and a residual liquid product in a first hydrocracking zone in the presence of hydrogen under conditions effective to produce a first effluent having an increased hydrogen content;

10 separating the first effluent into a LPG comprising stream and a liquid phase stream;

separating said LPG comprising stream into one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising ethane, a stream comprising butanes, a stream 15 comprising propane, a stream comprising C1-minus, a stream comprising C3-minus, a stream comprising C1-C2, a stream comprising C3-C4, a stream comprising C2-C3, a stream comprising C1-C3, a stream comprising C1-C4, a stream comprising C2-C4, a stream comprising C2-minus, a stream comprising C4-minus;

20 further processing one or more of the streams thus obtained in a steam cracker unit and at least one unit chosen from the group of, a butanes dehydrogenation unit, a propane dehydrogenation unit, a combined propane-butanes dehydrogenation unit, or a combination of units thereof to produce mixed product stream(s);

25 feeding the mixed product stream(s) from said steam cracker unit and at least one unit, chosen from the group of said butanes dehydrogenation unit, said propane dehydrogenation unit and said combined propane-butanes dehydrogenation unit, or a combination of units thereof, to a second separation section;

thermally cracking the liquid phase stream in a resid hydrocracking zone to produce a slurry intermediate product;

30 separating the mixed product stream(s).

2. The process according to claim 1, further comprising feeding at least one stream chosen from the group of said stream comprising ethane, said stream comprising C1-C2 and said stream comprising C2-minus to said steam cracker unit.

3. The process according to any one of claims 1-2, further comprising feeding at least one stream chosen from the group of said stream comprising propane, said stream comprising C3-C4, said stream comprising C3-minus, said stream comprising butanes, said stream comprising C4-minus, said stream comprising C2-C3, said stream comprising C1-C3, said stream comprising C1-C4 and said stream comprising C2-C4 to at least one dehydrogenation unit chosen from the group of said butanes dehydrogenation unit, said propane dehydrogenation unit, said combined propane-butanes dehydrogenation unit, or a combination of units thereof.

10 4. The process of any one or more of the preceding claims, further comprising recovering olefins and aromatics from the separated mixed product stream(s).

5. The process of claim 1, further comprising:

15 treating said liquid phase feed in a second hydrocracking zone in the presence of hydrogen under conditions effective to produce a second effluent having an increased hydrogen content;

recovering from the second effluent from said second hydrocracking zone a BTXE comprising stream, a LPG comprising stream and said residual liquid stream.

20 6. The process according to claim 5, further comprising thermally cracking said residual liquid stream together with said liquid phase stream in a resid hydrocracking zone to produce a slurry intermediate product.

7. The process according to claim 5, further comprising combining the LPG comprising stream originating from said first hydrocracking zone with the LPG comprising stream originating from said second hydrocracking zone.

25 8. The process of any one or more of the preceding claims, further comprising recovering vapour products from the slurry intermediate product and combining the vapour products thus recovered with the LPG comprising stream(s).

9. The process according to any one or more of the preceding claims, 30 further comprising separating from the first effluent originating from said first hydrocracking zone and the second effluent originating from said second hydrocracking zone residual liquid fractions and recycling said residual liquid fractions to inlet of the first hydrocracking zone and/or second hydrocracking zone.

10. The process of any one or more of the preceding claims, further comprising recovering methane from the separated mixed product stream(s) and recycling said methane to the steam cracker to be used as fuel for burners and/or heaters.

5 11. The process of any one or more of the preceding claims, further comprising recovering and purifying hydrogen from the separated mixed product stream(s) and recycling it to the inlet of the first and/or second hydrocracking zone.

12. The process of any one or more of the preceding claims, further comprising recovering pyrolysis fuel oil from the separated mixed product stream(s)
10 and recycling said pyrolysis fuel oil to the inlet of said first and/or second hydrocracking zone.

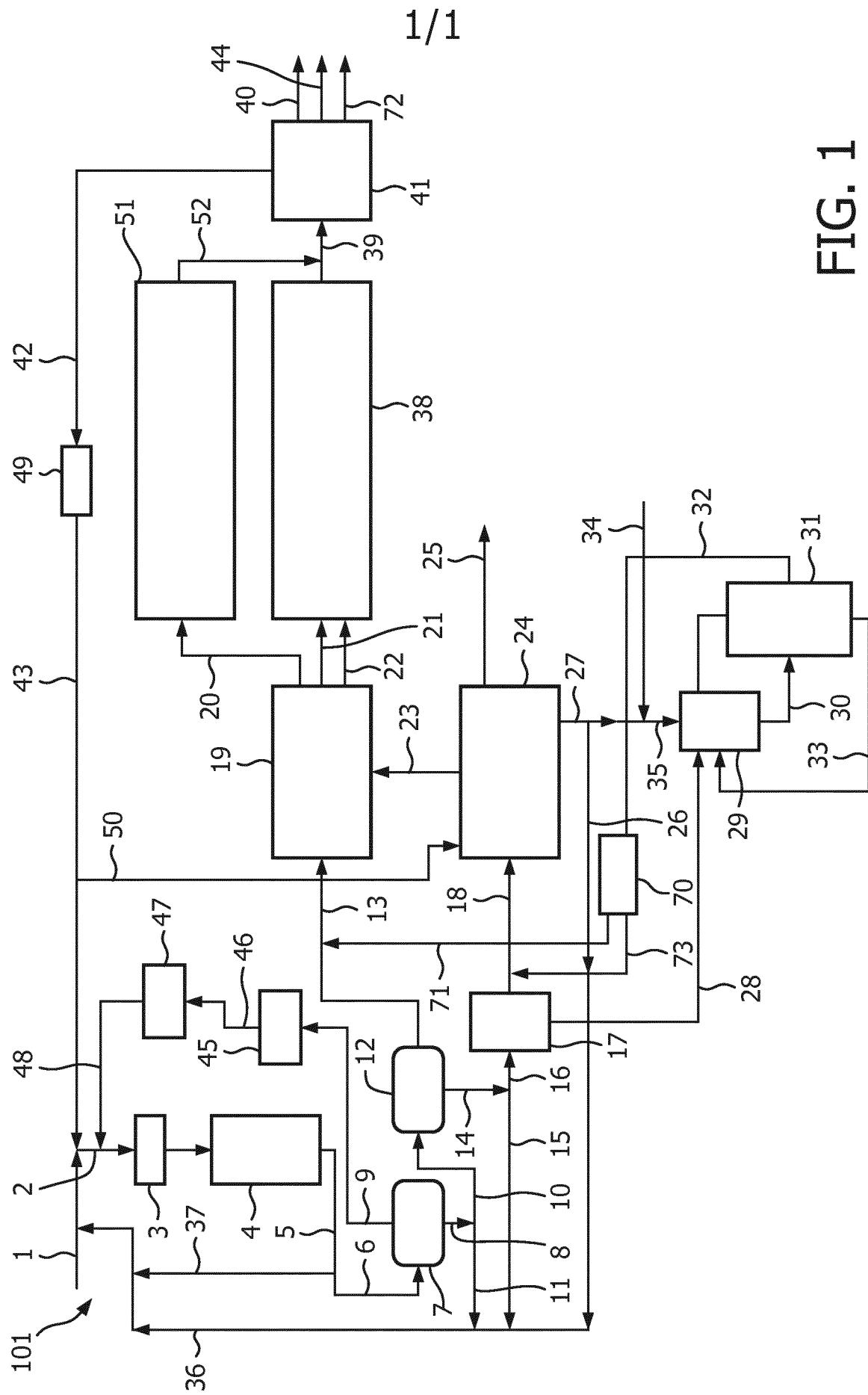


FIG.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/079242

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G9/36 C10G69/06 C10G65/10
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

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.
Y	US 2013/248417 A1 (SAYED ESAM [SA] ET AL) 26 September 2013 (2013-09-26) cited in the application paragraph [0003]; figure 1 paragraphs [0022], [0038]; claim 1.a. paragraph [0023] paragraphs [0026] - [0028] paragraphs [0030] - [0031] ----- -/-/	1-12

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
19 March 2015	30/03/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Vaz, Miguel

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/079242

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 137 147 A (FRANCK JEAN-PIERRE ET AL) 30 January 1979 (1979-01-30) column 1, lines 63-64; figure 1 column 1, line 68 - column 2, lines 1-2 column 2, lines 54-59 - column 4, lines 55-62 column 6, lines 41-60 column 5, lines 24-32, 64-68 column 5, lines 32-57 column 6, lines 66-68 - column 7, lines 1-7 column 9, lines 13-15, 26-27; figure 2 column 5, lines 32-35, 53-57 column 5, lines 58-60 ----- US 2007/062848 A1 (OBALLA MICHAEL C [CA] ET AL) 22 March 2007 (2007-03-22) paragraphs [0045] - [0049]; figure 3 paragraph [0041] ----- US 3 839 484 A (ZIMMERMAN C ET AL) 1 October 1974 (1974-10-01) drawing column 1, lines 65-67 - column 2, lines 1-17 column 3, lines 40-75 - column 4, lines 1-27 claims 5, 6 -----	1-12
Y		1-12
A		1,10,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/079242

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 2013248417	A1	26-09-2013	CN 104245890 A		24-12-2014
			EP 2834325 A1		11-02-2015
			KR 20150008385 A		22-01-2015
			US 2013248417 A1		26-09-2013
			WO 2013142617 A1		26-09-2013
<hr/>					
US 4137147	A	30-01-1979	NONE		
<hr/>					
US 2007062848	A1	22-03-2007	BR PI0616317 A2		14-06-2011
			CA 2541051 A1		20-03-2007
			CN 101268170 A		17-09-2008
			EP 1945739 A1		23-07-2008
			JP 2009508881 A		05-03-2009
			KR 20080047560 A		29-05-2008
			US 2007062848 A1		22-03-2007
			WO 2007033467 A1		29-03-2007
<hr/>					
US 3839484	A	01-10-1974	DE 2115117 A1		03-02-1972
			US 3839484 A		01-10-1974
<hr/>					