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(54) PROCESS FOR UPGRADING REFINERY HEAVY HYDROCARBONS TO PETROCHEMICALS

VERFAHREN ZUR AUFWERTUNG VON SCHWEREN RAFFINERIEKOHLENWASSERSTOFFEN IN PETROCHEMIKALIEN

PROCÉDÉ DE VALORISATION D'HYDROCARBURES LOURDS DE RAFFINERIE EN PRODUITS PÉTROCHIMIQUES

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Description

[0001] The present invention relates to a process for upgrading refinery heavy hydrocarbons to petrochemicals.

[0002] EP 1 779 929 relates to a process for the conversion of sulphur containing hydrocarbon feedstocks into a form suitable for use in automotive diesel.

[0003] US patent application No 2012/000819 relates to a method for producing an alkyl benzene with a high added value, and a catalyst used therefor, wherein the method allows a minimum naphthene ring-opening reaction to occur by causing an appropriate hydrocracking reaction without causing unnecessary nuclear hydrogenation.

[0004] US Patent No 4,943,366 relates to the production of high octane gasoline by hydrocracking highly aromatic fractions obtained from catalytic cracking operations, wherein a gas oil or resid feed is cracked in an FCC unit and the cracking products are fractionated in the cracker fractionator and in a distillation tower. The lower boiling fraction is then passed to hydrotreater which forms the first stage of the hydrocracking unit. The hydrotreated cycle oil then passes to another hydrocracker which forms the second stage of the unit in which the saturation of the aromatics continues and ring opening and cracking take place to form a hydrocracked product. After hydrogen separation in a separator, the hydrocracker effluent is fractionated in a distillation tower to form the products including dry gas, gasoline, middle distillate and a bottoms fraction.

[0005] WO2007/055488 relates to a method of preparing aromatic hydrocarbons and liquefied petroleum gas (LPG) from a hydrocarbon mixture, comprising the following steps of: (a) introducing a hydrocarbon feedstock mixture and hydrogen into at least one reaction zone; (b) converting the hydrocarbon feedstock mixture in the presence of a catalyst to (i) a non-aromatic hydrocarbon compound through hydrocracking and to (ii) an aromatic hydrocarbon compound which is abundant in benzene, toluene and xylene (BTX) through dealkylation/transalkylation within the reaction zone; and (c) recovering the LPG and aromatic hydrocarbon compound, respectively from the reaction products of step (b) through gas-liquid separation and distillation.

[0006] WO99/22577 relates to a low pressure hydrocracking, the process comprising the following steps: (a) mixing a liquid feed with hydrogen gas, (b) hydrocracking said mixture in a fixed bed hydrocracker which possesses at least two beds of packed catalyst particles, producing a lighter fraction and a heavier fraction, c) passing a portion of the heavier fraction through an extinction recycle process comprising the following steps:(1) passing the material to be recycled to a hydrocracker and (2) recycling the heavier fraction of the effluent.

[0007] US patent application No 2012/205285 relates to a process for hydroprocessing a hydrocarbon feed, which comprises (a) contacting the feed with (i) a diluent and (ii) hydrogen, to produce a liquid feed; (b) contacting the liquid feed with a first catalyst in a first treatment zone, to produce a first product effluent; (c) contacting the first product effluent with a second catalyst in a second treatment zone, to produce a second product effluent; and (d) recycling a portion of the second product effluent as a recycle product stream for use in the diluent in step (a), wherein the first treatment zone comprises at least two stages, wherein the first catalysts is a hydrotreating catalyst and the second catalyst is a ring opening catalyst, the first and second treatment zones are liquid-full reaction zones.

[0008] US patent application No 2012/083639 relates to process for maximizing high-value aromatics production utilizing stabilized crude benzene withdrawal, the process comprising the steps of: separating aromatic reactor effluent comprising a C5- fraction and a C6 to C10 fraction into a benzene-rich stream and at least one liquid stream and at least one vapor stream depleted in benzene, one of the liquid streams depleted in benzene comprising a benzene-depleted C6- fraction; and removing at least a portion of the C5- fraction from the benzene-rich stream.

[0009] 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) 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.

[0010] 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 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 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 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.

[0011] 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.

[0012] EP 0 219 195 relates to process for the conversion of a feed comprised of hydrocarbon compounds to lower boiling, higher octane hydrocarbons by contacting said feed, in the presence of hydrogen, over a catalyst to selectively hydrogenate and hydrocrack fused two-ring hydroaromatic hydrocarbon compound, to produce a lower molecular weight, higher octane product.

[0013] WO2012/071137 relates to a process for preparing a gas cracker feedstock, comprising contacting a feed containing one or more paraffins comprising 4 to 12 carbon atoms with a catalyst in the presence of hydrogen at elevated temperatures and elevated pressures and converting at least 40wt% of the paraffins comprising 4 to 12 carbon atoms based on the total weight of paraffins comprising 4 to 12 carbon atoms in the feed to ethane and/or propane to obtain a hydrocracked gas cracker feedstock comprising ethane and/or propane.

[0014] US Patent No. 6,187,984 relates to a method for the dehydrogenation of n-butane to butenes comprising contacting a feedstock containing n-butane under reaction conditions suitable for the conversion of n-butane to butenes in the presence of a catalyst.

[0015] US patent application No. 2003/232720 relates to a method of dehydrogenating a dehydrogenatable hydrocarbon comprising contacting the dehydrogenatable hydrocarbon with a dehydrogenation catalyst composite to provide a dehydrogenated hydrocarbon.

[0016] Conventionally, crude oil is processed, via distillation, into a number of cuts such as naphtha, gas oils and residua. Each of these cuts has a number of potential uses such as for producing transportation fuels such as gasoline, diesel and kerosene or as feeds to some petrochemicals and other processing units.

[0017] Light crude oil cuts such as naphthas and some gas oils can be used for producing light olefins and single ring aromatic compounds via processes such as steam cracking in which the hydrocarbon feed stream is evaporated and diluted with steam and then exposed to a very high temperature (750°C to 900°C) in short residence time (<1 second) furnace (reactor) tubes. In such a process the hydrocarbon molecules in the feed are transformed into (on average) shorter molecules and molecules with lower hydrogen to carbon ratios (such as olefins) when compared to the feed molecules. This process also generates hydrogen as a useful by-product and significant quantities of lower value co-products such as methane and C9+ Aromatics and condensed aromatic species (containing more aromatic rings which share edges).

[0018] Typically, the heavier (or higher boiling point) aromatic species, such as residua are further processed in a crude oil refinery to maximize the yields of lighter (distillable) products from the crude oil. This processing can be carried out by processes such as hydro-cracking (whereby the hydro-cracker feed is exposed to a suitable catalyst under conditions which result in some fraction of the feed molecules being broken into shorter hydrocarbon molecules with the simultaneous addition of hydrogen). Heavy refinery stream hydrocracking is typically carried out at high pressures and temperatures and thus has a high capital cost.

[0019] Heavier crude oil cuts are relatively rich in substituted aromatic species and especially substituted condensed aromatic species (containing two or more aromatic rings which share edges) and under steam cracking conditions these materials yield substantial quantities of heavy by products such as C9+ aromatics and condensed aromatics. Hence, a consequence of the conventional combination of crude oil distillation and steam cracking is that a substantial fraction of the crude oil is preferably not processed via the steam cracker as the cracking yield of valuable products from heavier cuts is not considered to be sufficiently high, compared to the alternative refinery fuel value.

[0020] Another aspect of the technology discussed above is that even when only light crude oil cuts (such as naphtha) are processed via steam cracking a significant fraction of the feed stream is converted into low value heavy by-products such as C9+ aromatics and condensed aromatics. With typical naphthas and gas oils these heavy by-products might constitute 2 to 25% of the total product yield (Table VI, Page 295, Pyrolysis: Theory and Industrial Practice by Lyle F. Albright et al, Academic Press, 1983). Whilst this represents a significant financial downgrade of expensive naphtha and/or gas oil in lower value material on the scale of a conventional steam cracker the yield of these heavy by-products does not typically justify the capital investment required to up-grade these materials (e.g. by hydrocracking) into streams that might produce significant quantities of higher value chemicals. This is partly because hydrocracking plants have high capital costs and, as with most petrochemicals processes, the capital cost of these units typically scales with throughput raised to the power of 0.6 or 0.7. Consequently, the capital costs of a small scale hydro-cracking unit are normally considered to be too high to justify such an investment to process steam cracker heavy by-products.

[0021] Another aspect of the conventional hydrocracking of heavy refinery streams such as residua is that these are typically carried out under compromise conditions chosen to achieve the desired overall conversion. As the feed streams contain a mixture of species with a range of ease of cracking this result in some fraction of the distillable products formed by hydrocracking of relatively easily hydrocracked species being further converted under the conditions necessary to hydrocrack species more difficult to hydrocrack. This increases the hydrogen consumption and heat management difficulties associated with the process and also increase the yield of light molecules such as methane at the expense of more valuable species.

[0022] A result of such a combination of crude oil distillation and steam cracking of the lighter distillation cuts is that steam cracking furnaces are typically unsuitable for the processing of cuts which contain significant quantities of material with a boiling point greater than ~350°C as it is difficult to ensure complete evaporation of these cuts prior to exposing the mixed hydrocarbon and steam stream to the high temperatures required to promote thermal cracking. If droplets of liquid hydrocarbon are present in the hot sections of cracking tubes coke is rapidly deposited on the tube surface which reduces heat transfer and increases pressure drop and ultimately curtails the operation of the cracking tube necessitating a shutdown of the furnace to allow for decoking. Due to this difficulty a significant portion of the original crude oil cannot be processed into light olefins and aromatic species via a steam cracker.

[0023] US2009/173665 relates to a catalyst and process for increasing the monoaromatics content of hydrocarbon feedstocks that include polynuclear aromatics, wherein the increase in monoaromatics can be achieved with an increase in gasoline/diesel yields and while reducing unwanted compounds thereby providing a route for upgrading hydrocarbons that include significant quantities of polynuclear aromatics.

[0024] The LCO Unicracking or LCO-X process of UOP as disclosed in WO2009/008878 uses partial conversion hydrocracking to produce high quality gasoline and diesel stocks in a simple once-through flow scheme. The feedstock is processed over a pre-treatment catalyst and then hydrocracked in the same stage. The products are subsequently separated without the need for liquid recycle. The LCO Unicracking process can be designed for lower pressure operation meaning that the pressure requirement will be somewhat higher than high severity hydrotreating but significantly lower than a conventional partial conversion and full conversion hydrocracking unit design. The upgraded middle distillate product makes a suitable ultra-low sulphur diesel (ULSD) blending component. The naphtha product from low-pressure hydrocracking of LCO-X has ultra-low sulphur and high octane and can be directly blended into the ultra-low sulphur gasoline (ULSG) pool.

[0025] US 7,513,988 relates to a process to treat compounds comprising two or more fused aromatic rings to saturate at least one ring and then cleave the resulting saturated ring from the aromatic portion of the compound to produce a C2-C4 alkane stream and an aromatic stream. Such a process may be integrated with a hydrocarbon (e.g. ethylene) (steam) cracker so that hydrogen from the cracker may be used to saturate and cleave the compounds comprising two or more aromatic rings and the C2-C4 alkane stream may be fed to the hydrocarbon cracker, or may be integrated with a hydrocarbon cracker (e.g. steam cracker) and an ethyl benzene unit, that is to treat the heavy residues from processing oil sands, tar sands, shale oils or any oil having a high content of fused ring aromatic compounds to produce a stream suitable for petrochemical production.

[0026] US2005/0101814 relates to a process for improving the paraffin content of a feedstock to a steam cracking unit, comprising: passing a feedstream comprising C5 through C9 hydrocarbons including C5 through C9 normal paraffins into a ring opening reactor, the ring opening reactor comprising a catalyst operated at conditions to convert aromatic hydrocarbons to naphtenes and a catalyst operated at conditions to convert naphtenes to paraffins, and producing a second feedstream; and passing at least a portion of the second feedstream to a steam cracking unit.

[0027] US 7,067,448 relates to a process for the manufacture of n-alkanes from mineral oil fractions and fractions from thermal or catalytic conversion plants containing cyclic alkanes, alkenes, cyclic alkenes and/or aromatic compounds. More in detail, this publication refers to a process for processing mineral oil fractions rich in aromatic compounds, in which the cyclic alkanes obtained after the hydrogenation of the aromatic compounds are converted to n-alkanes of a chain length which as far as possible is less than that of the charged carbons.

[0028] The LCO-process as discussed above relates to full conversion hydrocracking of LCO to naphtha, in which

LCO is a mono-aromatics and di-aromatics containing stream. A consequence of the full conversion hydrocracking is that a highly naphthenic, low octane naphtha is obtained that must be reformed to produce the octane required for product blending.

[0029] WO2006/122275 relates to a process for upgrading a heavy hydrocarbon crude oil feedstock into an oil that is less dense or lighter and contains lower sulphur than the original heavy hydrocarbon crude oil feedstock while making value added materials such as olefins and aromatics, which process comprises, inter alia, the steps of: combining a portion of the heavy hydrocarbon crude oil with an oil soluble catalyst to form a reactant mixture, reacting the pre-treated feedstock under relatively low hydrogen pressure to form a product stream, wherein a first portion of the product stream includes a light oil and a second portion of the product stream includes a heavy crude oil residue, and a third portion of the product stream includes a light hydrocarbon gas, and injecting a portion of the light hydrocarbon gas stream in a cracking unit to produce streams containing hydrogen and at least one olefin.

[0030] WO2011005476 relates to a process for the treatment of heavy oils, including crude oils, vacuum residue, tar sands, bitumen and vacuum gas oils using a catalytic hydrotreating pre-treatment process, specifically the use of hydrodemetallization (HDM) and hydrodesulphurization (HDS) catalysts in series in order to improve the efficiency of a subsequent coker refinery.

[0031] US2008/194900 relates to an olefins process for steam cracking an aromatics-containing naphtha stream comprising: recovering olefins and pyrolysis gasoline streams from a steam cracking furnace effluent, hydrogenating the pyrolysis gasoline stream and recovering a C6-C8 stream therefrom, hydrotreating an aromatics-containing naphtha stream to obtain a naphtha feed, dearomatizing the C6-C8 stream with the naphtha feed stream in a common aromatics extraction unit to obtain a raffinate stream; and feeding the raffinate stream to the steam cracking furnace.

[0032] WO2008/092232 relates to a process for extraction of chemical components from a feedstock, such as a petroleum, natural gas condensate, or petrochemical feedstock, such as a whole range naphtha feedstock comprising the steps of: subjecting the whole range naphtha feedstock to a desulphurizing process, separating from the desulphurized whole range naphtha feedstock a C6 to C11 hydrocarbon fraction, recovering from the C6 to C11 hydrocarbon fraction an aromatics fraction, an aromatics precursors fraction and a raffinate fraction in an aromatics extraction unit, converting aromatics precursors in the aromatics precursors fraction to aromatics, and recovering aromatics from step in the aromatics extraction unit.

[0033] An object of the present invention is to provide a method for upgrading heavy hydrocarbon feedstock to aromatics (BTXE) and LPG.

[0034] Another object of the present invention is to provide a process for the production of light olefins and aromatics from a heavy hydrocarbon feedstock in which a high yield of aromatics can be attained.

[0035] Another object of the present invention is to provide a process for upgrading of a crude oil feedstock to petrochemicals with a high carbon efficiency and hydrogen integration.

[0036] The present invention relates thus to a process for upgrading refinery heavy hydrocarbons to petrochemicals, comprising the following steps of:

(a) feeding a hydrocarbon feedstock to a ring opening reaction area;
(b) feeding the effluent from (a) to a separation unit for producing a gaseous stream comprising light boiling hydrocarbons, a liquid stream comprising naphtha boiling range hydrocarbons and a liquid stream comprising diesel boiling range hydrocarbons;
(c) feeding said liquid stream comprising naphtha boiling range hydrocarbons to a hydrocracking unit,
(d) separating reaction products of said hydrocracking unit of step (c) into an overhead gas stream, comprising light boiling hydrocarbons, and a BTX (a mixture of benzene, toluene and xylenes) comprising bottom stream,
(e) feeding the overhead gas stream from the hydrocracking unit of step (d) and the gaseous stream from the separation unit of step (b) to a steam cracking unit and at least one or more units chosen from the group of propane dehydrogenation unit, butane dehydrogenation and combined propane-butane dehydrogenation unit, preferably after separating a hydrogen containing stream from said gas streams.

[0037] The present inventors assume that by combining a ring-opening process with a hydrocracking unit, i.e. a so called gasoline hydrocracking unit/feed hydrocracking unit ("GHC/FHC") the overall process no longer produces fuels in addition to LPG and BTXE but only LPG and BTXE. The latter may also obtained directly as a purified stream as all co-boilers of BTXE are cracked. The LPG can be used in steam cracking and/or PDH/BDH. The hydrogen produced there can be used to feed these hydro processing steps. If needed hydrodesulphurization (HDS), hydrodenitrogenation (HDN) can be applied according to the catalyst/process requirements. The term "hydrocracking" is used herein in its generally accepted sense and thus may be defined as catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen; see e.g. Alfke et al. (2007). The products of this process are saturated hydrocarbons and, depending on the reaction conditions such as temperature, pressure and space velocity and catalyst activity, aromatic hydrocarbons including BTX.

[0038] 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.

[0039] The one of the petrochemical products produced in the process of the 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 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. The terms "naphthenic hydrocarbons" or "naphthenes" or "cycloalkanes" is used herein having its established meaning and accordingly relates types of alkanes that have one or more rings of carbon atoms in the chemical structure of their molecules.

[0040] The liquid effluent from the ring opening process, after separating out a heavier recycle stream containing multi ring components, is fed to the hydrocracking unit ("GHC/FHC"). This greatly simplifies the ring-opening process and reduces redundancies in separating units required. Please note that in another embodiment the liquid effluent is vaporized before entering the hydrocracking unit. Thus the feed to the hydrocracking unit can be liquid phase, vapour phase or mixed vapour-liquid phase. The hydrogen loop can be applied around both units, i.e. the ring opening reaction area and the hydrocracking unit ("GHC/FHC"), with multiple addition and injection points of hydrogen. The naphtha stream or a portion thereof is sent to the FHC/GHC reaction section and possibly all heavier material is recycled to be further converted thus simplifying the flowchart.

[0041] The present process further comprises separating reaction products of said hydrocracking unit of step (c) into an overhead gas stream, comprising light boiling hydrocarbons and a BTX comprising bottom stream. The hydrogen containing gaseous stream may be separated from the overhead gas stream comprising light boiling hydrocarbons.

[0042] The present process further preferably comprises feeding the overhead gas stream from the hydrocracking unit of step (d) and the gaseous stream from the separation unit of step (b) to another separation unit and feeding the thus separated streams to said steam cracking unit and said dehydrogenation unit(s).

[0043] According to the present invention the dehydrogenation process is a catalytic process and the steam cracking process is a thermal cracking process.

[0044] The process further comprises feeding the overhead stream from the hydrocracking unit and the gaseous stream from the separation unit to a steam cracking unit and one or more units chosen from the group of propane dehydrogenation unit, butane dehydrogenation and combined propane-butane dehydrogenation unit, preferably after separating a hydrogen containing stream from the gas streams.

[0045] By means of adding ring-opening it is possible to process a heavier feed than would be possible to send directly to a FHC/GHC unit. Furthermore, the addition of a separation unit upfront of the ring opening process allows the FHC/GHC unit to convert any naphthenics in the feed stream boiling in the naphtha range into aromatics/BTX. This way a higher BTX yield can be obtained when compared to ring-opening only because these naphthenics would otherwise be cracked in the ring-opening process to produce LPG rather than BTX.

[0046] According to a preferred embodiment the present process further comprises pre-treating the hydrocarbon feedstock in a splitter unit, from which splitter unit the naphtha boiling range hydrocarbons are fed directly into the hydrocracking unit and its heavier fraction is fed into the ring opening reaction area.

[0047] The present process further comprises preferably pre-treating the hydrocarbon feedstock in an aromatics extraction unit, from which aromatics extraction unit its aromatic rich stream is fed into the reaction area for ringopening, wherein the aromatics extraction unit is chosen from the group of the type of a distillation unit, the molecular sieve type and the type of a solvent extraction unit.

[0048] In addition to the splitter as mentioned above yields towards BTX can be further improved by "pre-cracking" the feed using hydrocracking technology. Such a preferred process can produce a highly naphthenic and aromatic naphtha range material based on the type of feed material that can be processed in the FHC/GHC section to produce a maximum BTX as again even more naphthenics are converted to BTX when compared to feeding directly into a ring-opening process.

[0049] The hydrogen loop for the three reaction sections can be optimized with respect to purity, cascading, pressure levels. Heavy unconverted material at the outlet of the ring-opening reactor can be recycled to either the ring-opening process or to the first hydrocracking step.

[0050] Thus, the present process further comprises preferably pre-treating the hydrocarbon feedstock in a pre-hydrocracking unit, from which pre-hydrocracking unit the gaseous stream comprising LPG is fed to a steam cracking unit and at least one or more units chosen from the group of propane dehydrogenation unit, butane dehydrogenation unit and combined propane-butane dehydrogenation unit, its heavier hydrocarbon fraction is fed to the ring opening reaction area and a stream comprising naphtha boiling range hydrocarbons is fed directly to the hydrocracking unit.

[0051] The present inventors found that in another embodiment the first pre-hydrocracking step can be replaced by a hydrodealkylation/reforming process, resulting in a high purity BTXE stream. As a result even more BTX can be produced compared to the embodiment of the pre-hydrocracking step because of the 'active' additional aromatics production in the reforming type of first reactor, which means that not only naphtenes are aromatized but also some additional ring formation must occur.

[0052] Thus, the present process further comprises preferably pre-treating the hydrocarbon feedstock in a hydrodealkylation/reforming type unit, from which hydrodealkylation/reforming type unit a BTXE stream is obtained, the gaseous stream comprising LPG is fed to one or more units chosen from the group of steam cracking unit, propane dehydrogenation unit, butane dehydrogenation unit and combined propane-butane dehydrogenation unit, and its heavier hydrocarbon fraction is fed into the ring opening reaction area.

[0053] The present process further comprises preferably feeding a bottom stream, e.g. the BTX rich stream of the hydrocracking unit to a transalkylation unit.

[0054] In addition, the present process further comprises preferably feeding the liquid stream comprising diesel boiling range hydrocarbons from the separation unit to an aromatics saturation unit.

[0055] The present process further comprises preferably feeding at least one of the gaseous stream from the separation unit, the gaseous stream from the hydrodealkylation/reforming type unit and the gaseous stream from the pre-hydrocracking unit to the hydrocracking unit. According to another embodiment at least one of a stream from the hydrodealkylation/reforming type unit and a stream from the pre-hydrocracking unit is sent to the reaction area for ringopening. Such a stream can be a gaseous stream.

[0056] The overhead stream from the hydrocracking unit, the gaseous stream from the separation unit, and possibly the gaseous streams from the pre-hydrocracking unit and the hydrodealkylation/reforming type unit can be separated into individual streams, each stream predominantly comprising C2 paraffins, C3 paraffins and C4 paraffins, respectively, and feeding each individual stream to a specific furnace section of the steam cracker unit, wherein a hydrogen containing stream is sent to one or more hydrogen consuming process units, such as the hydrocracking unit and the reaction area for ring opening.

[0057] According to a preferred embodiment the gaseous stream, sent to the steam cracker unit, is partly sent to a dehydrogenation unit, wherein it is preferred to send only the C3-C4 fraction to the dehydrogenation unit, especially as separate C3 and C4 streams, more preferably as a combined C3 + C4 stream.

[0058] 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, namely olefinic and aromatic petrochemicals, wherein the portion of the crude oil converted to LPG is increased significantly.

[0059] According to a preferred embodiment the gaseous streams, for example the overhead gas stream from the hydrocracking unit of step (d) and the gaseous stream from the separation unit of step (b), are 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 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 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.

[0060] The present process further comprises recovering hydrogen from the reaction products of one or more units chosen from the group of steam cracking unit, propane dehydrogenation unit, butane dehydrogenation unit and combined propane-butane dehydrogenation unit, and feeding the hydrogen thus recovered to the hydrocracking unit and the reaction area for ring opening, especially further comprising recovering hydrogen from the dehydrogenation unit and feeding the hydrogen thus recovered to any hydrogen consuming unit, such as the hydrocracking unit and the reaction area for ring opening.

[0061] The process conditions prevailing in the reaction area for ring opening include a temperature from 100[deg.] C. to 500[deg.] C. and a pressure from 2 to 10 MPa together with from 50 to 300 kg of hydrogen per 1,000 kg of feedstock over an aromatic hydrogenation catalyst and passing the resulting stream to a ring cleavage unit at a temperature from 200[deg.] C. to 600[deg.] C. and a pressure from 1 to 12 MPa together with from 50 to 200 kg of hydrogen per 1,000 kg of the resulting stream over a ring cleavage catalyst.

[0062] The term "(aromatic) ring opening unit" refers to a refinery unit for performing a hydrocracking process suitable for converting a feed that is relatively rich in aromatic hydrocarbon having a boiling point in the kerosene and gasoil boiling point range to produce LPG and, depending on the process conditions, a light-distillate (ARO-derived gasoline). Such an aromatic ring opening process (ARO process) is for instance described in US 7,513,988. Accordingly, the ARO process may comprise aromatic ring saturation at a temperature of 300-500 °C, a pressure of 2-10 MPa together with 10-30 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, a pressure of 1-12 MPa together with 5-20 wt-% of hydrogen (in relation to the hydrocarbon feedstock) in the presence of an ring cleavage catalyst, wherein said aromatic ring saturation and ring cleavage may be performed in one reactor or in two consecutive reactors. The aromatic hydrogenation catalyst may be a conventional hydrogenation/hydrotreating catalyst such as a catalyst comprising a mixture of Ni, W and Mo on a refractory support, typically alumina. The ring cleavage catalyst comprises a metallic component and a support, preferably one or more metals selected from the group consisting of Pd, Rh, Ru, Ir, Os, Cu, Co, Ni, Pt, Fe, Zn, Ga, In, Mo, W and V. By adapting the residence time under aromatic ring saturation conditions, the process can be steered towards full saturation and subsequent cleavage of all rings (relatively long residence time under aromatic ring saturation conditions) or towards keeping one aromatic ring unsaturated and subsequently cleavage of all but one ring (relatively short residence time under aromatic ring saturation conditions). In the latter case, the ARO process produces a light-distillate ("ARO-gasoline") which is relatively rich in hydrocarbon compounds having one aromatic ring.

[0063] The process conditions prevailing in the separation unit include preferably a temperature from 149[deg.]C to 288[deg.]C and a pressure from 1 MPa to 17.3 Mpa.

[0064] The process conditions prevailing in the hydrocracking unit include a reaction temperature of 300-580 °C, preferable of 450-580 °C, more preferable of 470-550 °C, a pressure of 0.3-5 MPa gauge, preferably at a pressure of 0.6-3 MPa gauge, particularly preferable at a pressure of 1000-2000 kPa gauge most preferable at a pressure of 1-2 MPa gauge, most preferable at a pressure of 1.2-1 .6 Mpa gauge, a Weight Hourly Space Velocity (WHSV) of 0.1-10 h-1, preferable of 0.2-6 h-1, more preferable of 0.4-2 h-1.

[0065] The process conditions prevailing in the steam cracking unit include preferably are a reaction temperature around 750-900 °C, residence times of 50-1000 milliseconds and a pressure selected of atmospheric up to 175 kPa gauge.

[0066] A very common process for the conversion of alkanes to olefins involves "steam cracking" As used herein, the term "steam cracking" relates to a 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 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 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 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 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.

[0067] 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 "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 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 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.

[0068] 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 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 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 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 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 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.

[0069] The hydrocarbon feedstock of step (a) is chosen form the group of shale oil, crude oil, kerosene, diesel, atmospheric gas oil (AGO), gas condensates, waxes, crude contaminated naphtha, vacuum gas oil (VGO), vacuum residue, atmospheric residue, naphtha and pre-treated naphtha, or a combination thereof. Other preferred feed stocks are light cycle oil/heavy cycle oil (LCO/HCO), coker naphtha and diesel, FCC naphtha and diesel and even slurry oil.

[0070] The invention will be described in further detail below and in conjunction with the attached drawings in which the same or similar elements are referred to by the same number, and where:

Figure 1 is a schematic illustration of an embodiment of the process of the invention.
Figure 2 is another embodiment of the process of the invention.
Figure 3 is another embodiment of the process of the invention.
Figure 4 is another embodiment of the process of the invention.
Figure 5 is another embodiment of the process of the invention.
Figure 6 is another embodiment of the process of the invention.

[0071] Referring now to the process and apparatus schematically depicted in Figure 1, there is shown a process 101 for upgrading refinery heavy hydrocarbons to petrochemicals. Hydrocarbon feedstock 5 is sent to a ring opening reaction area 1 and its effluent 17 is sent to a separation unit 2 producing a gaseous stream 4 comprising LPG, liquid stream 18 comprising naphtha boiling range hydrocarbons and a liquid stream 15 comprising diesel boiling range hydrocarbons. Stream 15, comprising diesel boiling range hydrocarbons, is preferably recycled to the inlet of ringopening reaction area 1. Stream 18 comprising naphtha boiling range hydrocarbons is sent to a hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising aromatic hydrocarbons, such as BTX. Stream 4 and stream 9 are combined as stream 10 and further processed in a steam cracker unit and a dehydrogenation unit, chosen from the group of a propane dehydrogenation unit, a butane dehydrogenation unit and a combined propane/butane dehydrogenation unit. In this embodiment gaseous stream 10 is first separated in a separation unit 20 into individual streams 24, 25, 26. However, the number of streams is not limited. The light hydrocarbons fraction 24 is sent to a gas steam cracker unit 22 and its effluent is sent to a further separation section 23, which section 23 may comprise several separation units. Streams 25, 26 are processed in a dehydrogenation section 21, this section 21 may comprise several dehydrogenation units, such as a propane dehydrogenation unit, a butane dehydrogenation unit and a combined propane/butane dehydrogenation unit. The dehydrogenated effluent 28 is sent to separation unit 23 and separated into individual streams 29, 30, for example olefins comprising streams. However, the number of streams is not limited. According to another embodiment stream 4 can be (partly) sent to hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising aromatic hydrocarbons, such as BTX.

[0072] According to process 201 (see figure 2) a hydrocarbon feedstock 5 is pre-treated in a splitter unit 5 producing stream 16, comprising naphtha boiling range hydrocarbons. Stream 16 is directly sent to hydrocracking unit 3. The effluent of splitter unit 5, comprising heavy hydrocarbons, is sent to a ringopening reaction area 1. Ringopening reaction area 1 produces an effluent stream 17. Stream 17 is sent to a separation unit 2 producing a gaseous stream 4 comprising LPG, liquid stream 18 comprising naphtha boiling range hydrocarbons and a stream 15 comprising diesel boiling range hydrocarbons. Stream 15 comprising diesel boiling range hydrocarbons is preferably recycled to the inlet of ringopening reaction area 1. Stream 18 is further converted in hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG and a bottom stream 11 comprising BTX. Stream 4 and stream 9 are combined as stream 10 and can be further processed as mentioned in the discussion of Figure 1 above. According to another embodiment stream 4 can be (partly) sent to hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising aromatic hydrocarbons, such as BTX.

[0073] In addition to splitter unit 5 as discussed above in Figure 2 yields towards BTX can be further improved by providing a pre-hydrocracking unit 6. According to the process 301 of Figure 3 hydrocarbon feedstock 5 is pre-hydrocracked in pre-hydrocracking unit 6 producing a gaseous stream 13 and a bottom stream 8, comprising naphtha. Stream 8 is sent directly to hydrocracking unit 3. The heavy fraction coming from the pre-hydrocracking unit 6 is sent to a ringopening reaction area 1. In ringopening reaction area 1 the hydrocarbons coming from preheat hydrocracking unit 6 are converted in effluent 17. Effluent 17 is sent to a separation unit 2 producing a gaseous stream 4 comprising LPG, liquid stream 18 comprising naphtha boiling range hydrocarbons and a stream 15 comprising diesel boiling range hydrocarbons. Stream 15 comprising diesel boiling range hydrocarbons is recycled to the inlet of pre-hydrocracking unit 6. Stream 18 is fed to a hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising BTX. Gaseous streams 4 and 9 are combined as stream 10, which stream 10 can be further processed as discussed above in Figure 1. According to another embodiment stream 4 and stream 13 can be (partly) sent to hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising aromatic hydrocarbons, such as BTX. In addition stream 13 can be (partly) sent to ringopening reaction area 1.

[0074] According to another embodiment, now process 401 in Figure 4, the first hydrocracking step as discussed above in Figure 3 can be replaced by a hydrodealkylation unit 7, from which unit 7 a BTXE stream 12 is obtained and a gaseous stream 14 comprising LPG. The heavier fraction coming from unit 7 is sent to a ringopening reaction area 1 and results in an effluent 17. Effluent 17 coming from ringopening reaction area 1 is sent to a separation unit 2 producing a gaseous stream 4 comprising LPG, liquid stream 18 comprising naphtha boiling range hydrocarbons and a stream 15 comprising diesel boiling range hydrocarbons. Stream 15 comprising diesel boiling range hydrocarbons is recycled to the inlet of hydrodealkylation unit 7. Stream 18 is sent to a hydrocracking unit 3, producing an overhead gas stream 9, comprising LPG and a bottom stream 11, comprising BTX. The BTXE rich stream produced in unit 7 can be further treated in hydrocracking unit 3. The gaseous streams 14, 4 and 9 are combined as stream 10, which stream can be further processed as discussed in Figure 1 above. According to another embodiment (not shown) stream 4 and stream 14 can be (partly) sent to hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising aromatic hydrocarbons, such as BTX. In addition stream 14 can be (partly) sent to ringopening reaction area 1.

[0075] In a preferred embodiment, as shown in Figure 5, according to process 501 for upgrading refinery heavy hydrocarbons to petrochemicals a hydrocarbon feedstock 5 is sent to a ring opening reaction area 1 and its effluent 17 is sent to a separation unit 2 producing a gaseous stream 4 comprising LPG, a liquid stream 18 comprising naphtha boiling range hydrocarbons and a liquid stream 15 comprising diesel boiling range hydrocarbons. Stream 15 comprising diesel boiling range hydrocarbons can be (partly) recycled to the inlet of ringopening reaction area 1. Figure 5 also shows that stream 15 comprising diesel boiling range hydrocarbons is sent as stream 49 to an aromatics saturation unit 50 producing stream 51. The remaining process units and streams are similar to those mentioned in Figure 1 above. According to another embodiment stream 4 can be (partly) sent to hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising aromatic hydrocarbons, such as BTX.

[0076] According to another preferred embodiment, at least a portion of the benzene and toluene, and the 9 and 10 carbon number aromatic compounds are introduced into a transalkylation zone. According to this embodiment, shown in Figure 6 as process 601, stream 11 is introduced into a transalkylation zone 60 to enhance the production of xylene compounds resulting in a stream 62. A once through hydrogen-rich gaseous stream 61 is also introduced into the transalkylation zone 60. This gaseous stream 61 can be obtained from other hydrogen producing units, such as hydrogen recovered from the reaction products of steam cracking unit and dehydrogenation unit. Operating conditions preferably employed in the transalkylation zone include a temperature from 177[deg.]C to 525[deg.]C and a liquid hourly space velocity in the range from 0.2 to 10 hr. Any suitable transalkylation catalyst may be utilized in the transalkylation zone. Preferred transalkylation catalysts contain a molecular sieve, a refractory inorganic oxide and a reduced non-framework weak metal. The preferred molecular sieves are zeolitic aluminosilicates, such as MFI types of zeolites, which may be any of those which have a silica to alumina ratio greater than 10 and a pore diameter of 5 to 8 angstroms. According to another embodiment stream 4 can be (partly) sent to hydrocracking unit 3 producing an overhead gas stream 9, comprising LPG, and a bottom stream 11, comprising aromatic hydrocarbons, such as BTX.

Examples

[0077] The process scheme used here is in accordance with the one shown in Figure 1. A hydrocarbon feedstock 5 is fed into a reaction area for ring opening 1 and its reaction products 17, which are generated from the reaction area, are separated by unit 2 into an overhead stream 4, a side stream 18 and a bottom stream 15. The side stream 18 is fed into a gasoline hydrocracker (GHC) unit 3, wherein the reaction products of the GHC unit 3 are separated into an overhead gas stream 9, comprising light components such C2-C4 paraffins, hydrogen and methane, and a stream 11 comprising predominantly aromatic hydrocarbon compounds and non-aromatic hydrocarbon compounds. The overhead gas stream 9 from the gasoline hydrocracker (GHC) unit 3 is combined with stream 4 originating from unit 2.

[0078] According to case 1 (example according to the invention) kerosene as feedstock is sent to a reaction area for ring opening and the side stream thereof is sent to a gasoline hydrocracker (GHC) unit, the LPG fraction is separated from the overhead of unit 2.

[0079] According to case 2 (example according to the invention) light vacuum gasoil (LVGO) as feedstock is sent to a reaction area for ring opening and the side stream thereof is sent to a gasoline hydrocracker (GHC) unit, the LPG fraction is separated from overhead of unit 2.

[0080] The characteristics of kerosene and LVGO can be found in Table 1. Table 2 shows the distribution of monoaromatics and aromatic molecules with more than one ring (Di+ aromatics) in the feeds. Table 3 shows the battery limit product slate (wt. % of feedstock).

Table 1: characteristics of kerosene and LVGO

		Kerosene	LVGO
n-paraffins	wt.-%	23.7	18.3
i-paraffins	wt.-%	17.9	13.8
Naphthenes	wt.-%	37.4	35.8
Aromatics	wt.-%	21.0	32.0
Density 60F	Kg/L	0.810	0.913
IBP	°C	174	306
BP10	°C	196	345
BP30	°C	206	367
BP50	°C	216	384
BP70	°C	226	404
BP90	°C	242	441
FBP	°C	266	493

Table 2: Classification of aromatic molecules as function of number of aromatic rings in kerosene and LVGO

		Kerosene	LVGO
Total Aromatics	wt.-% of feed	21.0	32.0
Monoaromatics	wt.-% of feed	12.5	9.0
Di+ aromatics	wt.-% of feed	8.5	23.0

Table 3: Battery limit product slate (wt. % of feedstock)

COMPONENT	Case 1: KEROSENE	Case 2: LVGO
LPG	87.8	89.4
Ethane	24.8	25.3
Propane	54.1	55.1
n-butane	7.1	7.2
Iso-butane	1.8	1.8
BTX	12.2	10.6
Benzene	3.3	2.9
Toluene	5.9	5.1
Xylenes	3.0	2.6

[0081] The data presented above show that the presence of a reaction area for ring opening and gasoline hydrocracking (GHC) of the feeds converts multi-ring aromatic molecules into more valuable single-ring aromatics and LPG. Additionally, BTX is also obtained from the dehydrogenation of naphthenes into mono-ring aromatics.

Claims

1. A process for upgrading refinery heavy hydrocarbons to petrochemicals, comprising the following steps of:

   (a) feeding a hydrocarbon feedstock to a ring opening reaction area, wherein the process conditions prevailing in said reaction area for ring opening are a temperature from 100 °C to 500 °C and a pressure from 2 to 10 MPa together with from 50 to 300 kg of hydrogen per 1,000 kg of feedstock over an aromatic hydrogenation catalyst and passing the resulting stream to a ring cleavage unit at a temperature from 200 °C to 600 °C and a pressure from 1 to 12 MPa together with from 50 to 200 kg of hydrogen per 1000 kg of said resulting stream over a ring cleavage catalyst;
   (b) feeding the effluent from (a) to a separation unit for producing a gaseous stream comprising light boiling hydrocarbons, a liquid stream comprising naphtha boiling range hydrocarbons and a liquid stream comprising diesel boiling range hydrocarbons;
   (c) feeding said liquid stream comprising naphtha boiling range hydrocarbons to a hydrocracking unit, wherein the process conditions prevailing in said hydrocracking unit are a reaction temperature of 300-580 °C, a pressure of 0.3-5 MPa gauge, and a Weight Hourly Space Velocity (WHSV) of 0.1-10 h-1;
   (d) separating reaction products of said hydrocracking unit of step (c) into an overhead gas stream, comprising light boiling hydrocarbons, and a BTX (a mixture of benzene, toluene and xylenes) comprising bottom stream,
   (e) feeding the overhead gas stream from the hydrocracking unit of step (d) and the gaseous stream from the separation unit of step (b) to a steam cracking unit and at least one or more units chosen from the group of propane dehydrogenation unit, butane dehydrogenation and combined propane-butane dehydrogenation unit, preferably after separating a hydrogen containing stream from said gas streams.

2. The process as set forth in claim 1, further comprising feeding the overhead gas stream from the hydrocracking unit of step (d) and the gaseous stream from the separation unit of step (b) to another separation unit and feeding the thus separated streams to said steam cracking unit and said dehydrogenation unit(s).

3. The process as set forth in any one of claims 1-2, wherein said dehydrogenation process is a catalytic process and said steam cracking process is a thermal cracking process.

4. The process according to any one or more of the preceding claims,
   further comprising pretreating said hydrocarbon feedstock in an aromatics extraction unit, from which aromatics extraction unit its aromatics rich stream is fed into said reaction area for ringopening, especially wherein said aromatics extraction unit is chosen from the group of the type of a distillation unit, the molecular sieve type and the type of a solvent extraction unit, especially
   further comprising pretreating said hydrocarbon feedstock in a splitter unit, from which splitter unit the naphtha boiling range hydrocarbons fraction is fed directly into said hydrocracking unit and its heavier fraction is fed into said ring opening reaction area, especially
   further comprising pretreating said hydrocarbon feedstock in a pre-hydrocracking unit, from which pre-hydrocracking unit a heavy hydrocarbons fraction is fed to said ring opening reaction area, a stream comprising naphtha boiling range hydrocarbons is fed directly to said hydrocracking unit and a gaseous stream comprising LPG is fed to a steam cracking unit and one or more units chosen from the group of propane dehydrogenation unit, butane dehydrogenation unit and combined propane-butane dehydrogenation unit, especially
   further comprising pretreating said hydrocarbon feedstock in a hydrodealkylation/reforming type unit, from which hydrodealkylation/reforming type unit a BTXE type stream is obtained, a heavy hydrocarbons fraction is fed to said ring opening reaction area and a gaseous stream comprising LPG is fed to a steam cracking unit and one or more units chosen from the group of, propane dehydrogenation unit, butane dehydrogenation unit and combined propane-butane dehydrogenation unit.

5. The process according to any one or more of the preceding claims, further comprising feeding at least one of said gaseous stream from said separation unit of step (b), said gaseous stream from said hydrodealkylation/reforming type unit and said gaseous stream from said pre-hydrocracking unit to said hydrocracking unit.

6. The process according to any one or more of the claims 2-5, further comprising feeding said bottom stream from said hydrocracking unit to a transalkylation unit.

7. The process according to any one or more of the preceding claims, further comprising feeding said liquid stream comprising diesel boiling range hydrocarbons from said separation unit to an aromatics saturation unit.

8. The process according to any one or more of the preceding claims, further comprising separating the overhead gas stream from said hydrocracking unit, the gaseous stream from said separation unit of step (b), and possibly the gaseous streams from said pre-hydrocracking unit and said hydrodealkylation/reforming type unit, into individual streams, each stream predominantly comprising C2 paraffins, C3 paraffins and C4 paraffins, respectively, and feeding each individual stream to a specific furnace section of said steam cracker unit, wherein a hydrogen containing stream is sent to one or more hydrogen consuming process units, such as said (pre)-hydrocracking unit and said reaction area for ring opening,
further comprising feeding only the C3-C4 fraction to at least one of said dehydrogenation units, especially as separate C3 and C4 streams, more preferably as a combined C3 + C4 stream.

9. The process as set forth in any one of claims 1-8, wherein the process conditions prevailing in said separation unit are a temperature from 149[deg.] C to 288[deg.] C and a pressure from 1 MPa to 17.3 Mpa.

10. The process as set forth in any one of claims 1-9, wherein the process conditions prevailing in said hydrocracking unit are a reaction temperature of 450-580 °C, preferable of 470-550 °C, a pressure of 0.6-3 MPa gauge, preferable at a pressure of 1000-2000 kPa gauge, most preferable at a pressure of 1-2 MPa gauge, even most preferable at a pressure of 1.2-1.6 MPa gauge, a Weight Hourly Space Velocity (WHSV) of 0.2-6 h-1, preferable of 0.4-2 h-1.

11. The process as set forth in any one of claims 1-10, wherein the process conditions prevailing in said steam cracking unit are a reaction temperature around 750-900 °C, residence times of 50-1000 milliseconds and a pressure selected of atmospheric up to 175 kPa gauge.

12. The process as set forth in any one of claims 1-11, wherein the hydrocarbon feedstock of step (a) is chosen from the group of shale oil, crude oil, kerosene, diesel, atmospheric gas oil (AGO), gas condensates, waxes, crude contaminated naphtha, vacuum gas oil (VGO), vacuum residue, atmospheric residue, naphtha and pretreated naphtha, light cycle oil/heavy cycle oil (LCO/HCO), coker naphtha and diesel, FCC naphtha and diesel, and slurry oil, or a combination thereof.

Patentansprüche

1. Prozess zum Veredeln von raffinierten schweren Kohlenwasserstoffen zu Petrochemikalien, umfassend die folgenden Schritte:

(a) Zuführen eines Kohlenwasserstoff-Rohstoffs zu einem Ringöffnungsreaktionsbereich, wobei die Prozessbedingungen, die in diesem Bereich für die Ringöffnung vorherrschen, eine Temperatur von 100 °C bis 500 °C und ein Druck von 2 bis 10 MPa sind, zusammen mit 50 bis 300 kg Wasserstoff pro 1.000 kg Rohstoff über einem aromatischen Hydrierkatalysator sind, und Weiterführen des sich daraus ergebenden Stroms zu einer Ringspaltungseinheit bei einer Temperatur von 200 °C bis 600 °C und einem Druck von 1 bis 12 MPa, zusammen mit 50 bis 200 kg Wasserstoff pro 1000 kg des sich daraus ergebenden Stroms über einem Ringspaltungskatalysator;
(b) Zuführen des Ablaufs aus (a) zu einer Trenneinheit zum Herstellen eines gasförmigen Stroms, der niedrig siedende Kohlenwasserstoffe umfasst, eines flüssigen Stroms, der Kohlenwasserstoffe im Siedebereich von Naphtha umfasst, und eines flüssigen Stroms, der Kohlenwasserstoffe im Siedebereich von Diesel umfasst;
(c) Zuführen des flüssigen Stroms, der Kohlenwasserstoffe im Siedebereich von Naphtha umfasst, zu einer Hydrocrackeinheit, wobei die Prozessbedingungen, die in der Hydrocrackeinheit vorherrschen, eine Reaktionstemperatur von 300 - 580 °C, ein Druck von 0,3 - 5 MPa Überdruck und eine Katalysatorbelastung (WHSV) von 0,1 - 10 h-1 sind;
(d) Trennen von Reaktionsprodukten der Hydrocrackeinheit aus Schritt (c) in einen oberen Gasstrom, der niedrig siedende Kohlenwasserstoffe umfasst, und einen BTX (ein Gemisch aus Benzol, Toluol und Xylolen) umfassenden unteren Strom,
(e) Zuführen des oberen Gasstroms aus der Hydrocrackeinheit aus Schritt (d) und des gasförmigen Stroms

aus der Trenneinheit aus Schritt (b) zu einer Dampfcrackeinheit und mindestens einer oder mehrerer Einheit(en), die ausgewählt ist (sind) aus der Gruppe bestehend aus einer Propandehydrierungseinheit, einer Butandehydrierungs- und einer kombinierten Propan-Butandehydrierungseinheit, bevorzugt nach dem Trennen eines Wasserstoff enthaltenden Stroms von den Gasströmen.

2. Prozess nach Anspruch 1, ferner umfassend das Zuführen des oberen Gasstroms aus der Hydrocrackeinheit aus Schritt (d) und des gasförmigen Stroms aus der Trenneinheit aus Schritt (b) zu einer weiteren Trenneinheit und das Zuführen der so getrennten Ströme zu der Dampfcrackeinheit und der (den) Dehydrierungseinheit(en).

3. Prozess nach einem der Ansprüche 1 - 2, wobei der Dehydrierungsprozess ein katalytischer Prozess ist und der Dampfcrackingprozess ein thermischer Crackingprozess ist.

4. Verfahren nach einem oder mehreren der vorstehenden Ansprüche,
ferner umfassend das Vorbehandeln des Kohlenwasserstoff-Rohstoffs in einer Aromatenextraktionseinheit, wobei von dieser Aromatenextraktionseinheit der aromatenreiche Strom in den Reaktionsbereich zur Ringöffnung eingeführt wird, wobei insbesondere die Aromatenextraktionseinheit ausgewählt ist aus der Gruppe des Typs einer Destilliereinheit, des Typs eines Molekularsiebs und des Typs einer Lösungsmittelextraktionseinheit, insbesondere
ferner umfassend das Vorbehandeln des Kohlenwasserstoff-Rohstoffs in einer Splittereinheit, wobei von dieser Splittereinheit der Anteil der Kohlenwasserstoffe im Siedebereich von Naphtha direkt der Hydrocrackeinheit zugeführt wird, und der schwerere Anteil in den Ringöffnungsreaktionsbereich eingeführt wird, insbesondere
ferner umfassend das Vorbehandeln des Kohlenwasserstoff-Rohstoffs in einer Hydrocrack-Vorbehandlungseinheit, wobei von dieser Hydrocrack-Vorbehandlungseinheit ein Anteil schwerer Kohlenwasserstoffe dem Ringöffnungsreaktionsbereich zugeführt wird, ein Strom, der Kohlenwasserstoffe im Siedebereich von Naphtha umfasst, direkt der Hydrocrackeinheit zugeführt wird, und ein gasförmiger Strom, der LPG umfasst, einer Dampfcrackeinheit und einer oder mehreren Einheit(en) zugeführt wird, die ausgewählt ist (sind) aus der Gruppe bestehend aus einer Propandehydrierungseinheit, einer Butandehydrierungseinheit und einer kombinierten Propan-Butandehydrierungseinheit, insbesondere
ferner umfassend das Vorbehandeln des Kohlenwasserstoff-Rohstoffs in einer Einheit des Hydrodealkylierungs-/Reformationstyps, wobei von dieser Einheit des Hydrodealkylierungs-/Reformationstyps ein Strom des BTXE-Typs erhalten wird, ein Anteil schwerer Kohlenwasserstoffe dem Ringöffnungsreaktionsbereich zugeführt wird, und ein gasförmiger Strom, der LPG umfasst, einer Dampfcrackeinheit oder einer oder mehreren Einheit(en) zugeführt wird, die ausgewählt ist (sind) aus der Gruppe bestehend aus einer Propandehydrierungseinheit, einer Butandehydrierungseinheit und einer kombinierten Propan-Butandehydrierungseinheit.

5. Verfahren nach einem oder mehreren der vorstehenden Ansprüche, ferner umfassend das Zuführen mindestens eines des gasförmigen Stroms aus der Trenneinheit aus Schritt (b), des gasförmigen Stroms aus der Einheit des Hydrodealkylierungs-Reformationstyps und des gasförmigen Stroms von der Hydrocrack-Vorbehandlungseinheit zu der Hydrocrackeinheit.

6. Verfahren nach einem oder mehreren der Ansprüche 2 - 5, ferner umfassend das Zuführen des unteren Stroms aus der Hydrocrackeinheit zu einer Transalkylierungseinheit.

7. Verfahren nach einem oder mehreren der vorstehenden Ansprüche, ferner umfassend das Zuführen des flüssigen Stroms, der Kohlenwasserstoffe im Siedebereich von Diesel umfasst, zu einer Aromatensättigungseinheit.

8. Verfahren nach einem oder mehreren der vorstehenden Ansprüche, ferner umfassend das Trennen des oberen Gasstroms von der Hydrocrackeinheit, des gasförmigen Stroms aus der Trenneinheit aus Schritt (b) und möglicherweise der gasförmigen Ströme aus der Hydrocrack-Vorbehandlungseinheit und der Einheit des Hydrodealkylierungs-/Reformationstyps in einzelne Ströme, wobei jeder Strom hauptsächlich jeweils C2-Paraffine, C3-Paraffine und C4-Paraffine umfasst, und das Zuführen jedes einzelnen Stroms zu einem spezifischen Ofenbereich der Dampfcrackeinheit, wobei ein Wasserstoff enthaltender Strom zu einer oder mehreren Wasserstoff verbrauchender (verbrauchenden) Prozesseinheit(en) geleitet wird, wie der Hydrocrack(-Vorbehandlungs)einheit und dem Reaktionsbereich für die Ringöffnung,
ferner umfassend das Zuführen nur des C3-C4-Anteils zu mindestens einer der Dehydrierungseinheiten, insbesondere als getrennte C3- und C4-Ströme, mehr bevorzugt als kombinierter C3+C4-Strom.

9. Verfahren nach einem oder mehreren der Ansprüche 1 - 8, wobei die Prozessbedingungen, die in der Trenneinheit vorherrschen, eine Temperatur von 149 [Grad] C bis 288 [Grad] C und ein Druck von 1 MPa bis 17,3 MPa sind.

10. Verfahren nach einem oder mehreren der Ansprüche 1 - 9, wobei die Prozessbedingungen, die in der Hydrocrackeinheit vorherrschen, eine Reaktionstemperatur von 450 - 580 °C, bevorzugt von 470 - 550 °C, ein Druck von 0,6 - 3 MPa Überdruck, bevorzugt bei einem Druck von 1000 - 2000 kPa Überdruck, am meisten bevorzugt bei einem Druck von 1 - 2 MPa Überdruck, und noch mehr bevorzugt bei einem Druck von 1,2 - 1,6 MPa Überdruck, eine Katalysatorbelastung (WHSV) von 0,2 - 6 h-1, bevorzugt von 0,4 - 2 h-1 sind.

11. Verfahren nach einem oder mehreren der Ansprüche 1 - 10, wobei die Prozessbedingungen, die in der Dampfcrackeinheit vorherrschen, eine Reaktionstemperatur um 750 - 900 °C, Verweilzeiten von 50 - 1000 Millisekunden und ein Druck sind, der von Atmosphärendruck bis zu 175 kPa Überdruck ausgewählt ist.

12. Verfahren nach einem oder mehreren der Ansprüche 1 - 11, wobei der Kohlenwasserstoff-Rohstoff aus Schritt (a) ausgewählt ist aus der Gruppe bestehend aus Schieferöl, Rohöl, Kerosin, Diesel, atmosphärischem Gasöl (AGO), Gaskondensaten, Wachsen, rohem kontaminiertem Naphtha, Vakuumgasöl (VGO), Vakuumrückstand, Atmosphärenrückstand, Naphtha und vorbehandeltem Naphtha, Leichtöl/Schweröl (LCO/HCO), Cokernaphtha und Diesel, FCC-Naphtha und Diesel, und Schlammöl oder einer Kombination daraus.

Revendications

1. Procédé de valorisation d'hydrocarbures lourds de raffinerie en produits pétrochimiques, comprenant les étapes suivantes de :

(a) alimentation d'une matière première d'hydrocarbures dans une zone de réaction d'ouverture de cycle, dans lequel les conditions de procédé appliquées dans ladite zone de réaction pour l'ouverture de cycle sont une température de 100 °C à 500 °C et une pression de 2 à 10 MPa conjointement avec 50 à 300 kg d'hydrogène par 1 000 kg de matière première sur un catalyseur d'hydrogénation d'aromatique et le passage du flux résultant vers une unité de clivage de cycle à une température de 200 °C à 600 °C et une pression de 1 à 12 MPa conjointement avec 50 à 200 kg d'hydrogène par 1000 kg dudit flux résultant sur un catalyseur de clivage de cycle ;
(b) alimentation de l'effluent provenant de (a) vers une unité de séparation pour produire un flux gazeux comprenant des hydrocarbures à ébullition basse, un flux liquide comprenant des hydrocarbures à plage d'ébullition de naphta et un flux liquide comprenant des hydrocarbures à plage d'ébullition de diesel ;
(c) alimentation dudit flux liquide comprenant des hydrocarbures à plage d'ébullition de naphta vers une unité d'hydrocraquage, dans lequel les conditions de procédé appliquées dans ladite unité d'hydrocraquage sont une température de réaction de 300 à 580 °C, une pression manométrique de 0,3 à 5 MPa, et une vitesse spatiale horaire en poids (VSHP) de 0,1 à 10 h^{-1} ;
(d) séparation des produits de réaction de ladite unité d'hydrocraquage de l'étape (c) en un flux de gaz de tête, comprenant les hydrocarbures à ébullition basse, et un BTX (un mélange de benzène, de toluène et de xylènes) constituant un flux de résidu,
(e) alimentation du flux de gaz de tête provenant de l'unité d'hydrocraquage de l'étape (d) et du flux gazeux provenant de l'unité de séparation de l'étape (b) vers une unité de vapocraquage et au moins une ou plusieurs unités choisies dans le groupe de l'unité de déshydrogénation de propane, l'unité de déshydrogénation de butane et l'unité de déshydrogénation de propane-butane combinée, de préférence après la séparation d'un flux contenant de l'hydrogène à partir desdits flux de gaz.

2. Procédé selon la revendication 1, comprenant en outre l'alimentation du flux de gaz de tête provenant de l'unité d'hydrocraquage de l'étape (d) et du flux gazeux provenant de l'unité de séparation de l'étape (b) vers une autre unité de séparation et l'alimentation des flux séparés ainsi vers ladite unité de vapocraquage et ladite/lesdites unité(s) de déshydrogénation.

3. Procédé selon l'une quelconque des revendications 1 à 2, dans lequel ledit procédé de déshydrogénation est un procédé catalytique et ledit procédé de vapocraquage est un procédé de craquage thermique.

4. Procédé selon l'une un ou plusieurs quelconques des revendications précédentes,
comprenant en outre le prétraitement de ladite matière première d'hydrocarbures dans une unité d'extraction d'aromatiques, le flux riche en aromatiques provenant de l'unité d'extraction d'aromatiques étant alimenté dans ladite zone de réaction pour ouverture de cycle, en particulier dans lequel ladite unité d'extraction d'aromatiques est choisie dans le groupe du type d'une unité de distillation, du type de tamis moléculaire et du type d'une unité

d'extraction par solvant, en particulier
comprenant en outre le prétraitement de ladite matière première d'hydrocarbures dans une unité de séparateur, dans lequel, depuis ladite unité de séparateur, la fraction d'hydrocarbures à plage d'ébullition de naphta est alimentée directement dans ladite unité d'hydrocraquage et sa fraction la plus lourde est alimentée dans ladite zone de réaction d'ouverture de cycle, en particulier
comprenant en outre le prétraitement de ladite matière première d'hydrocarbures dans une unité de préhydrocraquage, où, depuis l'unité de préhydrocraquage, une fraction d'hydrocarbures lourds est alimentée vers ladite zone de réaction d'ouverture de cycle, un flux comprenant des hydrocarbures à plage d'ébullition de naphta est alimenté directement vers ladite unité d'hydrocraquage et un flux gazeux comprenant du GPL est alimenté vers une unité de vapocraquage et une ou plusieurs unités choisies dans le groupe d'une unité de déshydrogénation de propane, une unité de déshydrogénation de butane et une unité de déshydrogénation de propane-butane combinée, en particulier
comprenant en outre le prétraitement de ladite matière première d'hydrocarbures dans une unité de type hydrodésalkylation/reformage, où, depuis l'unité de type hydrodésalkylation/reformage, un flux de type BTXE est obtenu, une fraction d'hydrocarbures lourds est alimentée vers ladite zone de réaction d'ouverture de cycle et un flux gazeux comprenant du GPL est alimenté vers une unité de vapocraquage et une ou plusieurs unités choisies dans le groupe de, une unité de déshydrogénation de propane, une unité de déshydrogénation de butane et une unité de déshydrogénation de propane-butane combinée.

5. Procédé selon l'une un ou plusieurs quelconques des revendications précédentes, comprenant en outre l'alimentation d'au moins l'un parmi ledit flux gazeux provenant de ladite unité de séparation de l'étape (b), ledit flux gazeux provenant de ladite unité de type hydrodésalkylation/reformage et ledit flux gazeux provenant de ladite unité de préhydrocraquage vers ladite unité d'hydrocraquage.

6. Procédé selon l'une ou plusieurs quelconques des revendications 2 à 5, comprenant en outre l'alimentation dudit flux de résidu depuis ladite unité d'hydrocraquage vers une unité de transalkylation.

7. Procédé selon l'une ou plusieurs quelconques des revendications précédentes, comprenant en outre l'alimentation dudit flux de liquide comprenant des hydrocarbures de plage d'ébullition de diesel depuis ladite unité de séparation vers une unité de saturation d'aromatiques.

8. Procédé selon l'une un ou plusieurs quelconques des revendications précédentes, comprenant en outre la séparation du flux de gaz de tête provenant de ladite unité d'hydrocraquage, du flux gazeux provenant de ladite unité de séparation de l'étape (b), et éventuellement des flux gazeux provenant de ladite unité de préhydrocraquage et de ladite unité de type hydrodésalkylation/reformage, en flux individuels, chaque flux comprenant principalement des paraffines en C2, des paraffines en C3 et des paraffines en C4, respectivement, et l'alimentation de chaque flux individuel vers une section de four spécifique de ladite unité de vapocraquage, dans lequel un flux contenant de l'hydrogène est envoyé à une ou plusieurs unités de traitement consommant de l'hydrogène, telles que ladite unité de (pré)-hydrocraquage et ladite zone de réaction pour ouverture de cycle,
comprenant en outre l'alimentation uniquement de la fraction en C3-C4 vers au moins l'une desdites unités de déshydrogénation, en particulier sous la forme de flux en C3 et C4 séparés, plus préférablement sous la forme d'un flux combiné C3 + C4.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel les conditions de procédé appliquées dans ladite unité de séparation sont une température de 149 °C à 288 °C et une pression de 1 MPa à 17,3 MPa.

10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel les conditions de procédé appliquées dans ladite unité d'hydrocraquage sont une température de réaction de 450 à 580 °C, de préférence de 470 à 550 °C, une pression manométrique de 0,6 à 3 MPa, de préférence à une pression manométrique de 1000 à 2000 kPa, de manière préférée entre toutes à une pression manométrique de 1 à 2 MPa, encore plus préférablement à une pression manométrique de 1,2 à 1,6 MPa, une vitesse spatiale horaire en poids (VSHP) de 0,2 à 6 h^{-1}, de préférence de 0,4 à 2 h^{-1}.

11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel les conditions de procédé appliquées dans ladite unité de vapocraquage sont une température de réaction d'environ 750 à 900 °C, des temps de séjour de 50 à 1000 millisecondes et une pression sélectionnée de la pression atmosphérique à une pression manométrique de 175 kPa.

12. Procédé selon l’une quelconque des revendications 1 à 11, dans lequel la matière première d’hydrocarbures de l’étape (a) est choisie dans le groupe des pétrole de schiste, pétrole brut, kérosène, diesel, gazole atmosphérique (AGO), condensats de gaz, cires, naphta brut contaminé, gazole sous vide (VGO), résidu sous vide, résidu atmosphérique, naphta et naphta prétraité, huile pour cycle légère/huile pour cycle lourde (LCO/HCO), naphta et diesel de cokéfaction, naphta et diesel FCC, et boue de pétrole, ou une combinaison de ceux-ci.

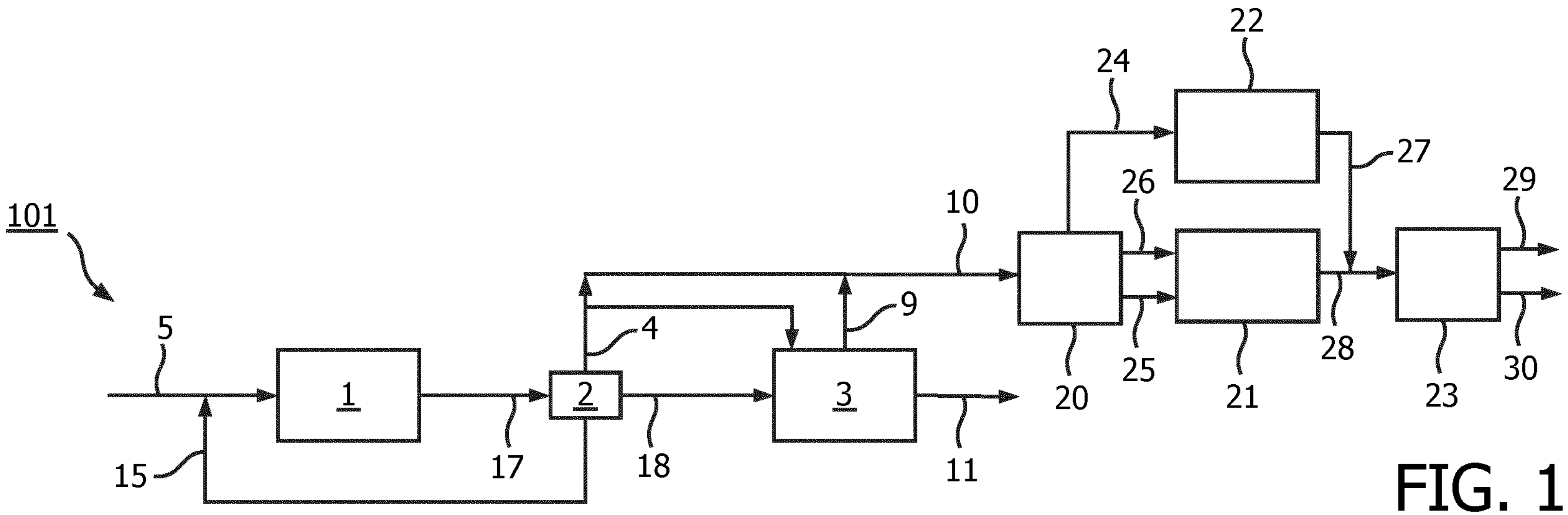
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FIG. 1

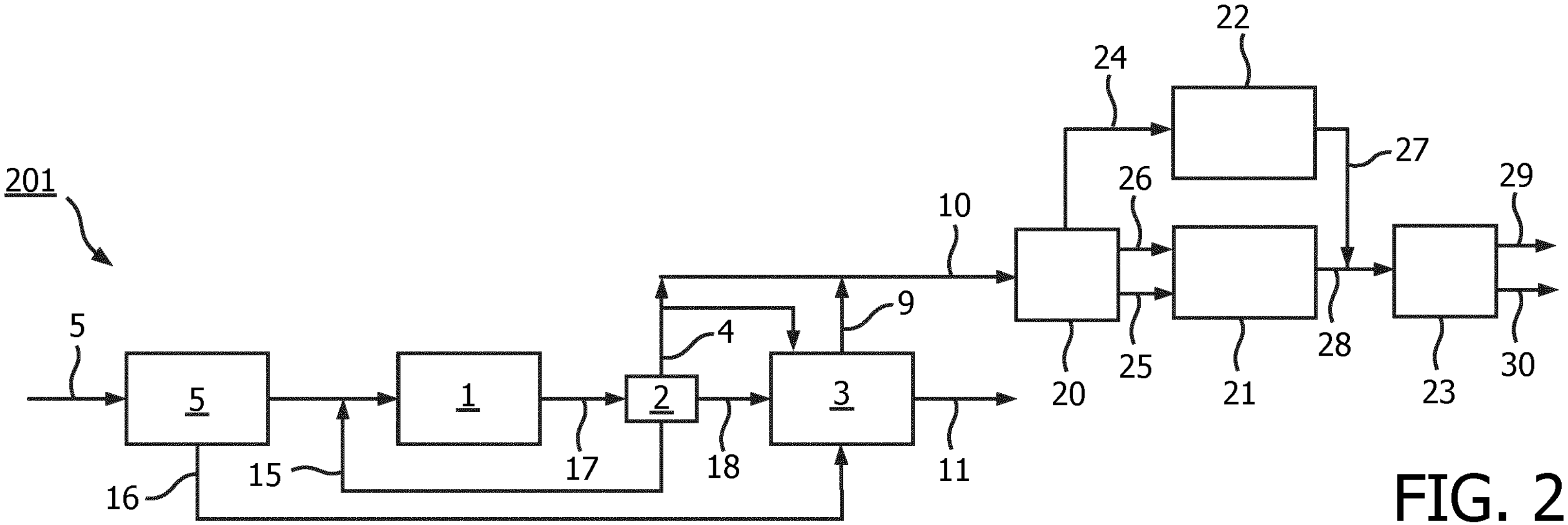
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FIG. 2

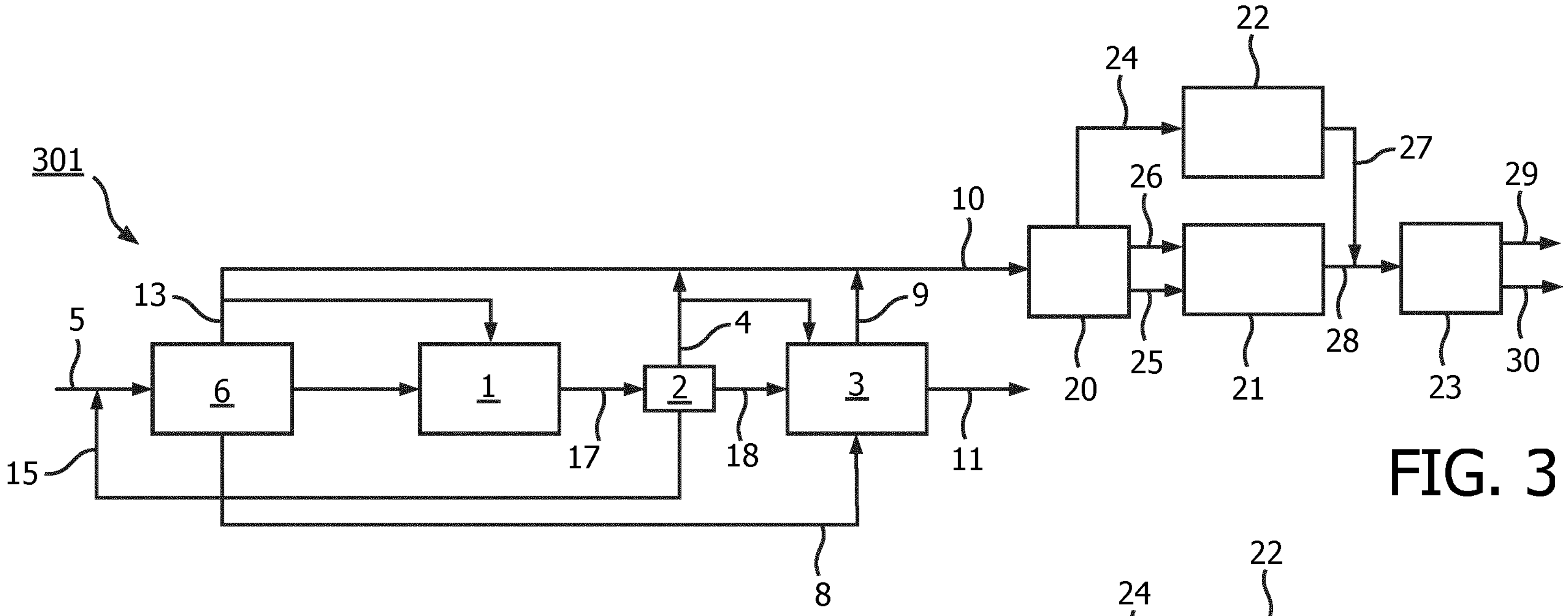
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FIG. 3

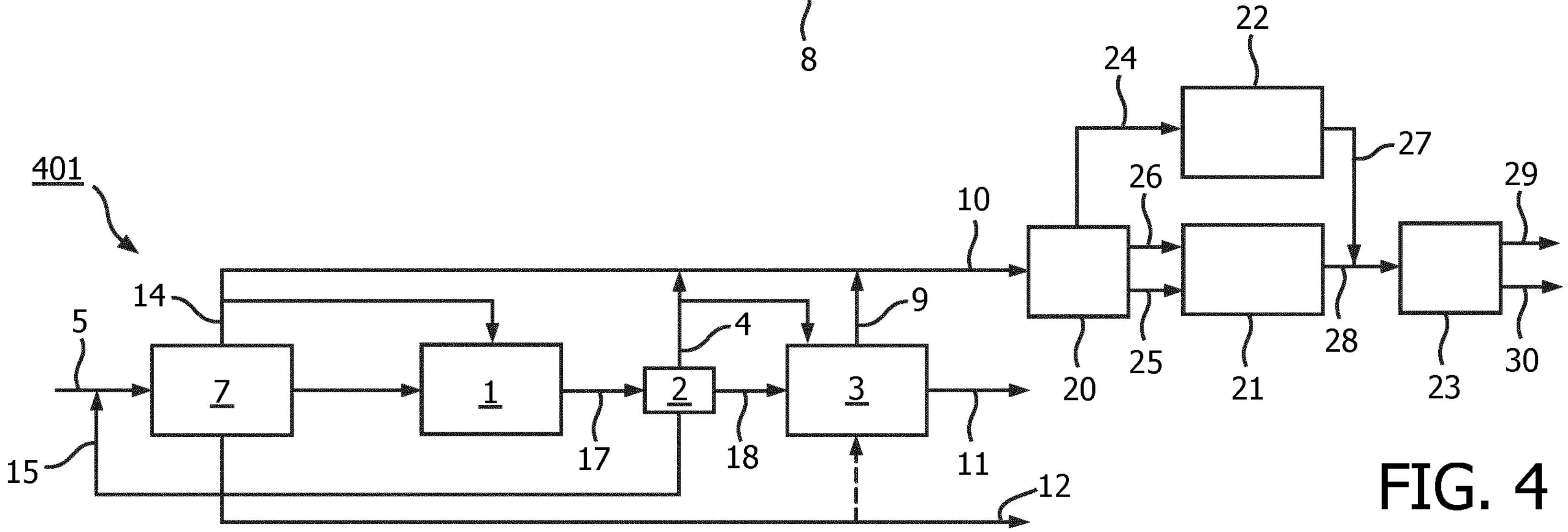
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FIG. 4

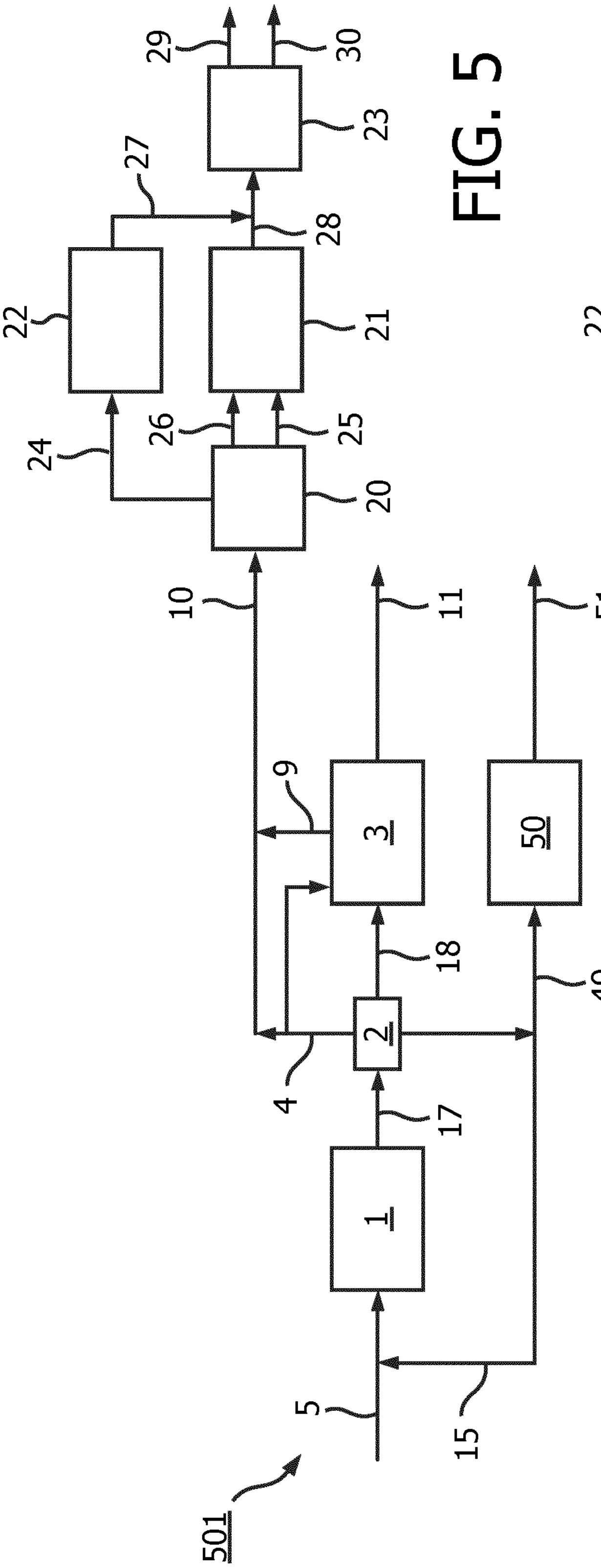
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FIG. 5

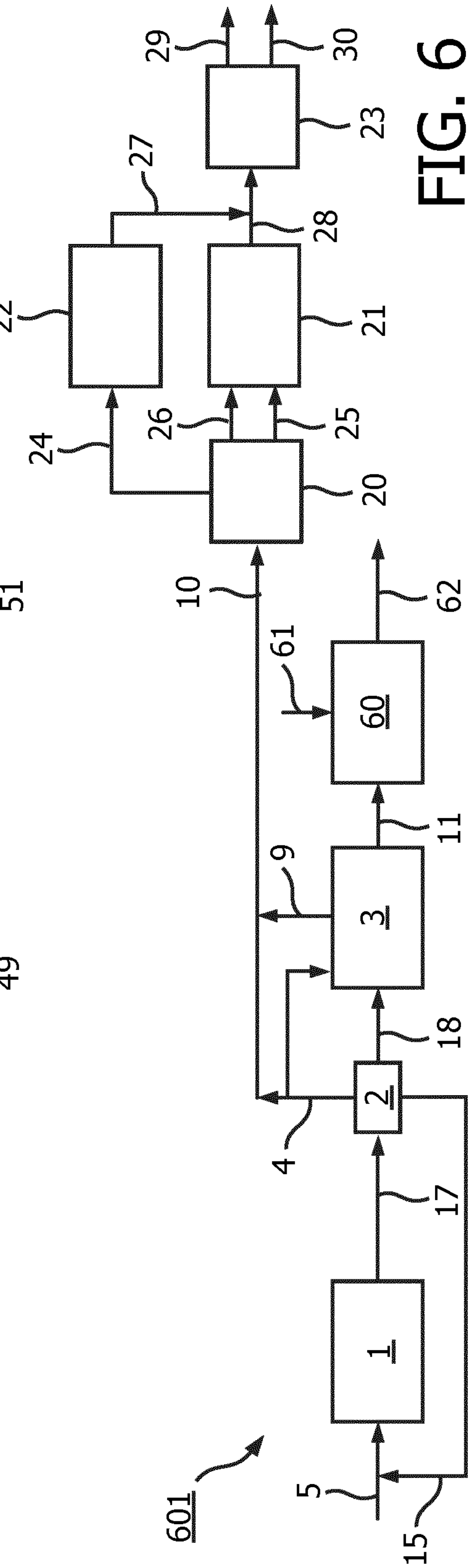
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FIG. 6

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