

PROCESS FOR PRODUCING LPG AND BTX

The invention is directed to a process for producing LPG and BTX from a mixed hydrocarbon feedstream and a system for performing such process.

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It is known that liquid petroleum gas (LPG) can be produced by converting naphtha or like materials by cracking, such as hydrocracking. Known processes to convert naphtha like material to LPG all suffer from either producing an LPG quality that has an undesirably high ratio of C4 hydrocarbons (hereinafter C# hydrocarbons are sometimes referred as C#, wherein # is a positive integer) to C3 hydrocarbons or an excessive production of methane. The undesirably high ratio of C4 hydrocarbons to C3 hydrocarbons results in an unbalance in the volumes of C3 and C4 derivatives/products obtained compared to petrochemical demand. The excessive production of methane is caused when the severity of the hydrocracking is increased to shift the products slate to ethane and propane as desired products.

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In the prior art, such as in published patent applications WO2012/071137 and GB1148967, focus has been on maximizing C2. This results in high methane production as well. Alternatively, published US patents numbers US6379533, US3718575, US3579434 and others focus on LPG production including C4. This LPG does not constitute a desired feed for steam cracking for producing particularly useful products such as ethylene and propylene.

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For application of LPG as fuel, the C3/C4 ratio is not very relevant, explaining the limited amount of development in this area. WO2012/071137 and GB1148967 describe recycling of C4+ material to maximize ethane production. To limit the size of the recycle stream, this implies a rather high severity in the (single) hydrocracking reactor provided, resulting in excessive methane production. Furthermore, WO2012/071137 and GB1148967 describe no equivalent of a hydrocracking process which results in benzene, toluene, xylene (BTX) product.

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Among others, US6379533 and US3718575 describe a (integrated) multi-stage hydrocracking approach but solely aim at producing LPG with no control over the C3 to C4 ratio or the total amount of C4's being produced. As indicated above, this is a problem when not producing LPG fuels but petrochemicals derived from the C3 and C4 contained in the LPG.

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With the demand for C4 derivatives possibly being smaller than for C3 derivatives, it would be desirable to control the amount of C4 produced. It is further desirable to control the composition of the C4 product (normal versus iso-butanenes) as this will determine the ratio between the different C4 derivatives that will be produced.

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There is a need in the industry for a process for producing LPG and BTX where the C2-C3 yield is increased relative to the C4 yield.

Accordingly, the invention provides a process for producing LPG and BTX, comprising

- 10 a) subjecting a mixed hydrocarbon feedstream to first hydrocracking in the presence of a first hydrocracking catalyst to produce a first hydrocracking product stream;
- b) separating the first hydrocracking product stream to provide at least
- a light hydrocarbon stream comprising at least C2 and C3 hydrocarbons,
- a middle hydrocarbon stream comprising C4 and/or C5 hydrocarbons and
- 15 a heavy hydrocarbon stream comprising at least C6+ hydrocarbons and
- c) subjecting the heavy hydrocarbon stream to second hydrocracking in the presence of a second hydrocracking catalyst to produce a second hydrocracking product stream comprising BTX, wherein the second hydrocracking is more severe than the first hydrocracking, wherein at least part of the middle hydrocarbon stream is recycled back to the first
- 20 hydrocracking in step a).

In another aspect, the invention provides a process for producing C2 and C3 hydrocarbons and BTX, comprising

- 25 a) subjecting a mixed hydrocarbon feedstream to first hydrocracking in the presence of a first hydrocracking catalyst to produce a first hydrocracking product stream;
- b) separating the first hydrocracking product stream to provide at least
- a light hydrocarbon stream comprising at least C2 and C3 hydrocarbons,
- a middle hydrocarbon stream comprising C4 and/or C5 hydrocarbons and
- a heavy hydrocarbon stream comprising at least C6+ hydrocarbons and
- 30 c) subjecting the heavy hydrocarbon stream to second hydrocracking in the presence of a second hydrocracking catalyst to produce a second hydrocracking product stream comprising BTX, wherein the second hydrocracking is more severe than the first hydrocracking, wherein at least part of the middle hydrocarbon stream is recycled back to the first hydrocracking in step a).

According to the process of the invention, at least part of the C4 and/or C5 in the first hydrocracking product stream is recycled back to the first hydrocracking instead of being subjected to the second hydrocracking for producing BTX.

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The second hydrocracking is more severe than the first cracking in the process of the present invention. A severe hydrocracking is herein meant that more cracking of the hydrocarbons occurs. The feature 'the second hydrocracking is more severe than the first hydrocracking' is herein understood to mean that the catalyst and/or the conditions (temperature, pressure and WHSV) of the second hydrocracking are chosen such that the stream produced by the second hydrocracking comprises a higher proportion of C1 than the stream produced by the first hydrocracking for a given hydrocarbon feed stream. For example, the second hydrocracking may be performed at a higher temperature and/or a lower WHSV and/or using a hydrocracking catalyst with a higher hydrocracking ability.

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The second hydrocracking step is optimized for producing BTX preferably substantially free of BTX coboilers. Subjecting C4 and/or C5 to the second hydrocracking together with C6+ as in prior art processes results in a larger amount of C1 due to more severe conditions required to produce on-spec BTX, particularly when larger amounts of C4 and/or C5 are present in the feed.

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Instead of subjecting C4 and/or C5 to the second hydrocracking together with C6+, at least part of C4 and/or C5 in the first hydrocracking product stream is subjected again to the less severe first hydrocracking in the process according to the invention. Part of the recycled C4 and/or C5 is then converted to a relatively high amount of C2-C3 and a relatively low amount of C1. This increases the proportion of the more valuable C2-C3 and decreases the proportion of the less valuable C1, C4 and C5 in the final product compared to a process in which a mixed hydrocarbon feedstream is directly subjected to a second hydrocracking or a process in which all of the product stream from the first hydrocracking is subjected to the second hydrocracking.

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US3928174 describes processing of reformate product of catalyst reforming. In US3928174, C5+ reformate is separated to recover toluene enriched C6+ reformate material from the bottom of the stabilizer (Fig. 1, (8), (12)) and C5 and lower boiling components from the top of the stabilizer (10). The C6+ from the bottom is separated into an overhead fraction comprising

some toluene and lower boiling components (16) and a bottom fraction of C7+ toluene-xylene rich fraction (18). The overhead fraction and the bottom fraction are each passed to a catalyst zone. In US3928174, C5 and lower boiling components are separated out as a whole and no separation is made to separate C3- and C4+. The overhead fraction (16) is formed from a portion which does not contain C5- (12), and therefore its overhead fraction (16) does not comprise C4 and/or C5. Accordingly, US3928174 at least does not disclose providing a middle hydrocarbon as required in step b) of the process of the invention.

Unlike the prior art processes, the process according to the invention controls the composition of the LPG. The prior art processes produce LPG without controlling its composition, whereas the process according to the invention produces increased amounts of C2-C3 hydrocarbons and decreased amounts of C4 hydrocarbons. Further the C1 production is limited.

In a process where a mixed hydrocarbon feedstream is subjected to a first hydrocracking and (a part of) the first hydrocracking product stream is subjected to a more severe second hydrocracking, the compositions of the second hydrocracking product stream are influenced by the conditions of the second hydrocracking as well as the feed for the second hydrocracking. The present inventors have realized that: when C4/C5 is subjected to the second hydrocracking together with C6+, severe conditions lead to large amounts of C2-C3 in combination with a large amount of C1 (conditions for conversion of C4/C5 into C2-C3 would result in a large amount of C6+ being converted to C1) and less severe conditions lead to small amounts of C2-C3 in combination with a small amount of C1. The present inventors have realized that desired compositions can be obtained by treating C4/C5 separately from C6+ hydrocarbons. The composition of the obtained LPG can be controlled (increased amounts of C2-C3 and decreased amounts of C4) while limiting the amount of C1 by separating out C4/C5 and recycling it to the first hydrocracking. Only the heavy hydrocarbon stream is sent to the second hydrocracking, which can be converted to desired composition without producing a large amount of C1.

Hydrocracking

As used herein, the term "hydrocracking unit" or "hydrocracker" relates to a unit in which a hydrocracking process is performed i.e. a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen; see e.g. Alfke et al. (2007) loc.cit. The products of this process are saturated hydrocarbons and, depending on the reaction conditions such as temperature, pressure and space velocity and catalyst activity, naphthenic (cycloalkane)

hydrocarbons and aromatic hydrocarbons including BTX. Hydrocracking reactions proceed through a bifunctional mechanism which requires an acid function, which provides for the cracking and isomerization and which provides breaking and/or rearrangement of the carbon-carbon bonds comprised in the hydrocarbon compounds comprised in the feed, and a

5 hydrogenation function. Many catalysts used for the hydrocracking process are formed by combining various transition metals, or metal sulfides with the solid support such as alumina, silica, alumina-silica, magnesia and zeolites. The catalysts may be a physical mixture of two catalysts with different metals or supports. Hydrocracking reactions can also proceed via the so-called mono-molecular or Haag-Dessau cracking mechanism which only requires the presence

10 of acid sites. This is usually important at higher temperatures (i.e. >500 °C) but can also play a role at lower temperatures.

Second hydrocracking

The second hydrocracking process is a hydrocracking process suitable for converting a complex

15 hydrocarbon feed that is relatively rich in aromatic hydrocarbon compounds with one ring to LPG and BTX, wherein said process is optimized to keep the aromatic ring intact of the aromatics comprised in the feedstream, but to remove most of the longer side-chains from said aromatic ring. A significant portion of 6-ring naphthenes can be converted to aromatics. Substantially all co-boilers of aromatic C6+ hydrocarbons are hydrocracked. The second

20 hydrocracking product stream is hence preferably substantially free from non-aromatic C6+ hydrocarbons. As meant herein, the term "stream substantially free from non-aromatic C6+ hydrocarbons" means that said stream comprises less than 1 wt-% non-aromatic C6+ hydrocarbons, preferably less than 0.7 wt-% non-aromatic C6+ hydrocarbons, more preferably less than 0.6 wt-% non-aromatic C6+ hydrocarbons and most preferably less than 0.5 wt-%

25 non-aromatic C6+ hydrocarbons.

In the second hydrocracking in the process according to the invention, the heavy hydrocarbon stream is contacted in the presence of hydrogen with a second hydrocracking catalyst.

30 Catalysts having hydrocracking activity are described on pages 13-14 and 174 of Hydrocracking Science and Technology (1996) Ed. Julius Scherzer, A.J. Gruia, Pub. Taylor and Francis. Hydrocracking reactions generally proceed through a bifunctional mechanism which requires a relatively strong acid function, which provides for the cracking and isomerization and a metal function, which provides for the olefin hydrogenation. Many catalysts used for the hydrocracking

process are formed by composting various transition metals with the solid support such as alumina, silica, alumina-silica, magnesia and zeolites.

In preferred embodiments of the invention, the second hydrocracking catalyst is a hydrocracking catalyst comprising 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and a silica (SiO_2) to alumina (Al_2O_3) molar ratio of 5-200.

The process conditions comprise a temperature of 300-580 °C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-15 h^{-1} .

Preferably, the catalyst is a hydrocracking catalyst comprising 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and a silica (SiO_2) to alumina (Al_2O_3) molar ratio of 5-200 and the process conditions comprise a temperature of 425-580 °C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-15 h^{-1} . In these embodiments, the obtained second hydrocracking product stream is advantageously substantially free from non-aromatic C6+ hydrocarbons due to the catalyst and the conditions employed. Hence, chemical grade BTX can easily be separated from the hydrocracking product stream.

Preferably, the second hydrocracking is performed at a temperature of 425-580 °C, more preferably 450-550 °C.

Preferably, the second hydrocracking is performed at a pressure of 300-5000 kPa gauge, more preferably at a pressure of 1200-4000 kPa gauge. By increasing reactor pressure, conversion of C6+ non-aromatics can be increased, but also increases the yield of methane and the hydrogenation of aromatic rings to cyclohexane species which can be cracked to LPG species. This results in a reduction in aromatic yield as the pressure is increased and, as some cyclohexane and its isomer methylcyclopentane, are not fully hydrocracked, there is an optimum in the purity of the resultant benzene at a pressure of 1200-1600 kPa.

Preferably, the second hydrocracking step is performed at a Weight Hourly Space Velocity (WHSV) of 0.1-15 h^{-1} , more preferably at a Weight Hourly Space Velocity of 1-6 h^{-1} . When the space velocity is too high, not all BTX co-boiling paraffin components are hydrocracked, so it will not be possible to achieve BTX specification by simple distillation of the reactor product. At too

low space velocity the yield of methane rises at the expense of propane and butane. By selecting the optimal Weight Hourly Space Velocity, it was surprisingly found that sufficiently complete reaction of the benzene co-boilers is achieved to produce on spec BTX without the need for a liquid recycle.

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Accordingly, preferred conditions for the second hydrocracking step thus include a temperature of 425-580 °C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-15 h⁻¹. More preferred hydrocracking conditions include a temperature of 450-550 °C, a pressure of 1200-4000 kPa gauge and a Weight Hourly Space Velocity of 1-6 h⁻¹.

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Preferably, the molar ratio of hydrogen to hydrocarbon species (H₂/HC molar ratio) is 1:1 – 4:1, more preferably 1:1 – 2:1.

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Hydrocracking catalysts that are particularly suitable for the process of the present invention comprise a molecular sieve, preferably a zeolite, having a pore size of 5-8 Å.

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Zeolites are well-known molecular sieves having a well-defined pore size. As used herein, the term "zeolite" or "aluminosilicate zeolite" relates to an aluminosilicate molecular sieve. An overview of their characteristics is for example provided by the chapter on Molecular Sieves in Kirk-Othmer Encyclopedia of Chemical Technology, Volume 16, p 811-853; in Atlas of Zeolite Framework Types, 5th edition, (Elsevier, 2001). Preferably, the hydrocracking catalyst comprises a medium pore size aluminosilicate zeolite or a large pore size aluminosilicate zeolite. Suitable zeolites include, but are not limited to, ZSM-5, MCM-22, ZSM-11, beta zeolite, EU-1 zeolite, zeolite Y, faujastite, ferrierite and mordenite. The term "medium pore zeolite" is commonly used in the field of zeolite catalysts. Accordingly, a medium pore size zeolite is a zeolite having a pore size of about 5-6 Å. Suitable medium pore size zeolites are 10-ring zeolites, i.e. the pore is formed by a ring consisting of 10 SiO₄ tetrahedra. Suitable large pore size zeolites have a pore size of about 6-8 Å and are of the 12-ring structure type. Zeolites of the 8-ring structure type are called small pore size zeolites. In the above cited Atlas of Zeolite Framework Types various zeolites are listed based on ring structure. Most preferably the zeolite is ZSM-5 zeolite, which is a well-known zeolite having MFI structure.

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Preferably, the silica to alumina ratio of the ZSM-5 zeolite is in the range of 20-200, more preferably in the range of 30-100.

The zeolite is in the hydrogen form: i.e. having at least a portion of the original cations associated therewith replaced by hydrogen. Methods to convert an aluminosilicate zeolite to the hydrogen form are well known in the art. A first method involves direct ion exchange employing an acid and/or salt. A second method involves base-exchange using ammonium salts followed by calcination.

Furthermore, the catalyst composition comprises a sufficient amount of hydrogenation metal to ensure that the catalyst has a relatively strong hydrogenation activity. Hydrogenation metals are well known in the art of petrochemical catalysts.

The catalyst composition preferably comprises 0.01-1 wt-% hydrogenation metal, more preferably 0.01-0.7 wt-%, most preferably 0.01-0.5 wt-% hydrogenation metal, more preferably 0.01-0.3 wt-%. The catalyst composition may more preferably comprise 0.01-0.1 wt-% or 0.02-0.09 wt-% hydrogenation metal. In the context of the present invention, the term "wt%" when relating to the metal content as comprised in a catalyst composition relates to the wt% (or "wt-%") of said metal in relation to the weight of the total catalyst, including catalyst binders, fillers, diluents and the like. Preferably, the hydrogenation metal is at least one element selected from Group 10 of the Periodic Table of Elements. The preferred Group 10 element is platinum (Pt). Accordingly, the hydrocracking catalyst used in the process of the present invention comprises a zeolite having a pore size of 5-8 Å, a silica (SiO_2) to alumina (Al_2O_3) molar ratio of 5-200 and 0.01-1 wt-% platinum (in relation to the total catalyst).

The hydrocracking catalyst composition may further comprise a binder. Alumina (Al_2O_3) is a preferred binder. The catalyst composition of the present invention preferably comprises at least 10 wt-%, most preferably at least 20 wt-% binder and preferably comprises up to 40 wt-% binder. In some embodiments, the hydrogenation metal is deposited on the binder, which preferably is Al_2O_3 .

According to some embodiments of the invention, the hydrocracking catalyst is a mixture of the hydrogenation metal on a support of an amorphous alumina and the zeolite.

According to other embodiments of the invention, the hydrocracking catalyst comprises the hydrogenation metal on a support of the zeolite. In this case, the hydrogenation metal and the

zeolite giving cracking functions are in closer proximity to one another which translates into a shorter diffusion length between the two sites. This allows high space velocity, which translates into smaller reactor volumes and thus lower CAPEX. Accordingly, in some preferred embodiments, the hydrocracking catalyst is the hydrogenation metal on a support of the zeolite and the second hydrocracking is performed at a Weight Hourly Space Velocity of 10-15 h⁻¹.

The hydrocracking catalyst may be free of further metals or may comprise further metals. In case the hydrocracking catalyst comprises a further element that reduces the hydrogenation activity of the catalyst, such as tin, lead or bismuth, lower temperatures may be selected for the second hydrocracking step; see e.g. WO 02/44306 A1 and WO 2007/055488.

In case the reaction temperature is too high, the yield of LPG's (especially propane and butanes) declines and the yield of methane rises. As the catalyst activity may decline over the lifetime of the catalyst, it is advantageous to increase the reactor temperature gradually over the life time of the catalyst to maintain the hydrocracking conversion rate. This means that the optimum temperature at the start of an operating cycle preferably is at the lower end of the hydrocracking temperature range. The optimum reactor temperature will rise as the catalyst deactivates so that at the end of a cycle (shortly before the catalyst is replaced or regenerated) the temperature preferably is selected at the higher end of the hydrocracking temperature range.

The second hydrocracking step is performed in the presence of an excess amount of hydrogen in the reaction mixture. This means that a more than stoichiometric amount of hydrogen is present in the reaction mixture that is subjected to hydrocracking. Preferably, the molar ratio of hydrogen to hydrocarbon species (H₂/HC molar ratio) in the reactor feed is between 1:1 and 4:1, preferably between 1:1 and 3:1 and most preferably between 1:1 and 2:1. A higher benzene purity in the product stream can be obtained by selecting a relatively low H₂/HC molar ratio. In this context the term "hydrocarbon species" means all hydrocarbon molecules present in the reactor feed such as benzene, toluene, hexane, cyclohexane etc. It is necessary to know the composition of the feed to then calculate the average molecular weight of this stream to be able to calculate the correct hydrogen feed rate. The excess amount of hydrogen in the reaction mixture suppresses the coke formation which is believed to lead to catalyst deactivation.

First hydrocracking

- The first hydrocracking is a hydrocracking process suitable for converting a complex hydrocarbon feed that is relatively rich in naphthenic and paraffinic hydrocarbon compounds to a product stream rich in LPG and aromatic hydrocarbons. Such hydrocracking is described e.g. in US3718575, GB1148967 and US6379533. Preferably, the amount of the LPG in the first
- 5 hydrocracking product stream is at least 50 wt%, more preferably at least 60 wt%, more preferably at least 70 wt% and more preferably at least 80 wt% of the total first hydrocracking product stream. Preferably, the amount of the C2-C3 in the first hydrocracking product stream is at least 40 wt%, more preferably at least 50 wt%, more preferably at least 60 wt% and more preferably at least 65 wt% of the total first hydrocracking product stream. Preferably, the amount
- 10 of the aromatic hydrocarbons in the first hydrocracking product stream is 3-20 wt%, e.g. 5-15 wt%. As described elsewhere, the first hydrocracking is relatively mild and does not result in a high amount of methane. Preferably, the amount of methane in the first hydrocracking product stream is at most 5 wt%, more preferably at most 3wt.
- 15 The first hydrocracking catalyst may be a conventional catalyst generally used for hydrocracking of a mixture of hydrocarbons. For example, the first hydrocracking catalyst may be a catalyst containing one metal or two or more associated metals of group VIII, VI B or VII B of the periodic classification of elements, deposited on a carrier of sufficient surface and volume, such as, for example, alumina, silica, alumina-silica, zeolite, etc; when using a zeolite, the metal (s)
- 20 may be introduced by appropriate exchange. The metals are, for example, palladium, iridium, tungsten, rhenium, cobalt, nickel, etc. used alone or as mixtures. The metal concentrations may be preferably 0.1 to 10 wt%.
- Preferably, the conditions for the first hydrocracking include a temperature of 250 – 580 °C,
- 25 more preferably 300 – 450 °C, a pressure of 300 – 5000 kPa gauge, more preferably 1200 – 4000 kPa gauge and a WHSV of 0.1 – 15 h⁻¹, more preferably 1 - 6 h⁻¹. Preferably, the molar ratio of hydrogen to hydrocarbon species (H₂/HC molar ratio) is 1:1 – 4:1, more preferably 1:1 – 2:1.
- 30 The first hydrocracking may be optimized to keep the aromatic ring intact of the aromatics comprised in the feedstream, but to remove most of the longer side-chains from said aromatic ring. In such a case, the process conditions to be employed for the first hydrocracking step are similar to the process conditions to be used in the second hydrocracking step as described herein above: a temperature of 300-580 °C, a pressure of 300-5000 kPa gauge and a Weight

Hourly Space Velocity of 0.1-15 h⁻¹. In this case, the suitable catalyst used for the first hydrocracking step is the same as the ones described for the second hydrocracking step. For example, the catalyst for the first hydrocracking step is a hydrocracking catalyst comprising 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and a silica (SiO₂) to alumina (Al₂O₃) molar ratio of 5-200.

The first hydrocracking is however less severe than the second hydrocracking, as described above. Preferably, the first hydrocracking conditions comprise a lower process temperature than the second hydrocracking step. Accordingly, the first hydrocracking step conditions preferably comprise a temperature of 300-450 °C, more preferably 300-425 °C, more preferably 300-400 °C.

definitions

The term "alkane" or "alkanes" is used herein having its established meaning and accordingly describes acyclic branched or unbranched hydrocarbons having the general formula C_nH_{2n+2}, and therefore consisting entirely of hydrogen atoms and saturated carbon atoms; see e.g. IUPAC. Compendium of Chemical Terminology, 2nd ed. (1997). The term "alkanes" accordingly describes unbranched alkanes ("normal-paraffins" or "n-paraffins" or "n-alkanes") and branched alkanes ("iso-paraffins" or "iso-alkanes") but excludes naphthenes (cycloalkanes).

The term "aromatic hydrocarbons" or "aromatics" is very well known in the art. Accordingly, the term "aromatic hydrocarbon" relates to cyclically conjugated hydrocarbon with a stability (due to delocalization) that is significantly greater than that of a hypothetical localized structure (e.g. Kekulé structure). The most common method for determining aromaticity of a given hydrocarbon is the observation of diatropicity in the ¹H NMR spectrum, for example the presence of chemical shifts in the range of from 7.2 to 7.3 ppm for benzene ring protons.

The terms "naphthenic hydrocarbons" or "naphthenes" or "cycloalkanes" is used herein having its established meaning and accordingly describes saturated cyclic hydrocarbons.

The term "olefin" is used herein having its well-established meaning. Accordingly, olefin relates to an unsaturated hydrocarbon compound containing at 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 as used herein generally consists of a blend of C2-C4 hydrocarbons i.e. a mixture of C2, C3, and C4 hydrocarbons.

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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 ethylbenzene. Accordingly, the present invention preferably provides a process for producing a mixture of benzene, toluene xylenes and ethylbenzene ("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 ethylbenzene product stream.

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As used herein, the term "C# hydrocarbons", wherein "#" is a positive integer, is meant to describe all hydrocarbons having # carbon atoms. C# hydrocarbons are sometimes indicated as just "C#". Moreover, the term "C#+ hydrocarbons" is meant to describe all hydrocarbon molecules having # or more carbon atoms. Accordingly, the term "C5+ hydrocarbons" is meant to describe a mixture of hydrocarbons having 5 or more carbon atoms. The term "C5+ alkanes" accordingly relates to alkanes having 5 or more carbon atoms.

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step a)

A mixed hydrocarbon stream as well as a recycled middle hydrocarbon stream is subjected to the first hydrocracking in step a) to produce a first hydrocracking product stream. The mixed hydrocarbon stream and the recycled middle hydrocarbon stream may be combined before being fed to the first hydrocracking unit or the mixed hydrocarbon stream and the recycled middle hydrocarbon stream may be fed to the first hydrocracking unit at different inlets. It will be appreciated that, in the cases where further hydrocarbon stream(s) are recycled to step a), the further recycled stream(s) may be combined with the mixed hydrocarbon stream and/or the recycled middle hydrocarbon stream before being fed to the first hydrocracking reactor, or may be fed to the first hydrocracking reactor at different inlets.

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mixed hydrocarbon stream

The mixed hydrocarbon stream comprises C5+ hydrocarbons. Typically, the mixed hydrocarbon feedstream is a naphtha or a naphtha-like product, preferably having a boiling point range of 20-200°C. Suitable hydrocracking feed streams include, but are not limited to first stage or multi-stage hydro-treated pyrolysis gasoline, straight run naphtha, hydrocracked gasoline, light coker naphtha and coke oven light oil, FCC gasoline, reformate, FT (Fischer-Tropsch) or synthetic naphtha, or mixtures thereof.

first hydrocracking product stream

By step a), the proportion of LPG (C2-C4 hydrocarbons) is increased compared to the feed stream. The first hydrocracking product stream obtained by step a) comprises H₂ and C₁, LPG (C2-C4 hydrocarbons), C₅ and C₆+ hydrocarbons. The C₄ hydrocarbons includes normal C₄ hydrocarbons (herein sometimes referred as nC₄ hydrocarbons) such as n-butane and iso C₄ hydrocarbons (herein sometimes referred as iC₄ hydrocarbons) such as isobutane.

step b)

According to the invention, the first hydrocracking product stream comprising a range of hydrocarbons is separated to provide at least a light hydrocarbon stream, a middle hydrocarbon stream and a heavy hydrocarbon stream. The separation may be performed using any known technology for the separation of a mixed hydrocarbon stream, for example, gas-liquid separation, distillation or solvent extraction. The separation may be performed in one unit or multiple units.

H₂ may be separated from the first hydrocracking product stream before the separation between the light, middle and heavy hydrocarbon streams. It is also possible to separate out C₁ as well as H₂ from the first hydrocracking product stream before the separation between the light, middle and heavy hydrocarbon streams.

more than one middle hydrocarbon stream

In some embodiments, the entire middle hydrocarbon stream is recycled back. In other embodiments, part of the middle hydrocarbon stream is recycled back and part of the middle hydrocarbon stream is used as the final product or subjected to suitable further steps depending on needs. It will be appreciated that a separation of the middle hydrocarbon stream takes place in this case. The separation of the middle hydrocarbon stream may take place in the same separator as the separator for making the light hydrocarbon stream and the heavy hydrocarbon

stream. Alternatively, the separation of the middle hydrocarbon stream is performed in a separate separator.

The middle hydrocarbon stream can be provided by step b) in the form of one stream or a plurality of streams. Accordingly, in some embodiments, the middle hydrocarbon stream is provided by step b) as a first middle hydrocarbon stream and a second middle hydrocarbon stream, wherein the boiling point range of the second middle hydrocarbon stream is higher than the average boiling point of the first middle hydrocarbon stream. For example, the first middle hydrocarbon stream may comprise iC4 and the second middle hydrocarbon stream may comprise nC4. Preferably, at least part of the second middle hydrocarbon stream is recycled back to the first hydrocracking in step a).

various separations

The separation between the light hydrocarbon stream and the middle hydrocarbon stream may be performed at various points, for example between C3 and iC4, between iC4 and nC4 and between nC4 and C5.

The separation between the middle hydrocarbon stream and the heavy hydrocarbon stream may be performed at various points, for example between iC4 hydrocarbon and nC4 hydrocarbon, between nC4 and C5 and between C5 and C6.

The light hydrocarbon stream comprises at least C2 and C3. The light hydrocarbon stream may be used as the final product or subjected to suitable further steps, optionally after further separation(s). For example, in the cases where the light hydrocarbon stream comprises C4, the C4 may be separated out from the light hydrocarbon stream to be subjected to suitable further steps. Due to the separation point between the light hydrocarbon stream and the middle hydrocarbon stream, the light hydrocarbon stream comprises little or no amount of C5+ hydrocarbons. Preferably, the light hydrocarbon stream comprises at most 10 wt% more preferably at most 5 wt%, and most preferably at most 3 wt% of C5+ hydrocarbons.

The middle hydrocarbon stream comprises C4 and/or C5. Part or all of the middle hydrocarbon stream is recycled back to the first hydrocracking, optionally after further separation(s). Part of the middle hydrocarbon stream may be used as the final product or subjected to suitable further steps, optionally after further separation(s). Preferably, the middle hydrocarbon stream or the

part of the middle hydrocarbon stream subjected to C4 hydrocracking substantially consists of C4 and C5 hydrocarbons. Preferably, the amount of the C4 and C5 hydrocarbons in the middle hydrocarbon stream or the part of the middle hydrocarbon stream subjected to C4 hydrocracking is at least 70 wt%, more preferably 80 wt%, even more preferably 90 wt%... Preferably, the amount of the C3- hydrocarbons in the middle hydrocarbon stream or the part of the middle hydrocarbon stream subjected to C4 hydrocracking is at most 10 wt%, more preferably 5 wt%... Preferably, the amount of the C6+ hydrocarbons in the middle hydrocarbon stream or the part of the middle hydrocarbon stream subjected to C4 hydrocracking is at most 10 wt%, more preferably 5 wt%.

The heavy hydrocarbon stream comprises at least C6+. The heavy hydrocarbon stream is subjected to the second hydrocracking. Due to the separation point between the middle hydrocarbon stream and the heavy hydrocarbon stream, the heavy hydrocarbon stream comprises little or no amount of C4- hydrocarbons. Preferably, the heavy hydrocarbon stream comprises at most 5 wt%, more preferably at most 2 wt%, most preferably at most 1 wt% of C4- hydrocarbons.

C3/iC4 and iC4/C5

In some embodiments, the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between C3 and iC4 and the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate iC4 and nC4. In this case, the light hydrocarbon stream consists of C3-, the middle hydrocarbon stream consists of iC4 and the heavy hydrocarbon stream consists of nC4 and C5+. When the middle hydrocarbon stream consists of iC4, part of the iC4 is recycled back to the first hydrocracking in step a). The remainder of the iC4 may be used as the final product or subjected to suitable further steps depending on needs.

C3/iC4 and nC4/C5

In some embodiments, the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between C3 and iC4 and the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate nC4 and C5. In this case, the light hydrocarbon stream consists of C3-, the middle hydrocarbon stream consists of C4 (iC4 and nC4) and the heavy hydrocarbon stream consists of C5+. When the middle hydrocarbon stream consists of C4, part of the C4 is recycled back to the first

hydrocracking in step a). The remainder of the C4 may be used as the final product or subjected to suitable further steps depending on needs. For example, the part of the C4 recycled back to the first hydrocracking in step a) may be nC4 and the remainder of the C4 which may be used as the final product or subjected to suitable further steps may be iC4.

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C3/iC4 and C5/C6

In some embodiments, the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between C3 and iC4 and the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate C5 and C6. In this case, the light hydrocarbon stream consists of C3-, the middle hydrocarbon stream consists of C4 (iC4 and nC4) and C5 and the heavy hydrocarbon stream consists of C6+. When the middle hydrocarbon stream consists of C4 and C5, part or all of the C5 and part of the C4 is recycled back to the first hydrocracking in step a). The remainder of the C4 may be used as the final product or subjected to suitable further steps depending on needs. For example, the part of the C4 recycled back to the first hydrocracking in step a) may be nC4 and the remainder of the C4 which may be used as the final product or subjected to suitable further steps may be iC4.

iC4/nC4 and nC4/C5

In some embodiments, the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between iC4 and nC4 and the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate nC4 and C5. In this case, the light hydrocarbon stream consists of C3- and iC4, the middle hydrocarbon stream consists of nC4 and the heavy hydrocarbon stream consists of C5+. When the middle hydrocarbon stream consists of nC4, part of the nC4 is recycled back to the first hydrocracking in step a). The remainder of the nC4 may be used as the final product or subjected to suitable further steps depending on needs.

iC4/nC4 and C5/C6

In some embodiments, the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between iC4 and nC4 and the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate C5 and C6. In this case, the light hydrocarbon stream consists of C3- and iC4, the middle hydrocarbon stream consists of nC4 and C5 and the heavy hydrocarbon stream consists of

C6+. When the middle hydrocarbon stream consists of nC4 and C5, part or all of the C5 is recycled back to the first hydrocracking in step a) and nC4 is used as the final product or subjected to suitable further steps depending on needs; or part or all of the C5 and part of the nC4 are recycled back to the first hydrocracking in step a) and the remainder of the nC4 is used as the final product or subjected to suitable further steps depending on needs.

nC4/C5 and C5/C6

In some embodiments, the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between nC4 and C5 and the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate C5 and C6. In this case, the light hydrocarbon stream consists of C3-, iC4 and nC4, the middle hydrocarbon stream consists of C5 and the heavy hydrocarbon stream consists of C6+. When the middle hydrocarbon stream consists of C5, part or all of the C5 is recycled back to the feed hydrocracking in step a).

In all cases, all of the C5 is preferably recycled back to the first hydrocracking. However, when only part of the C5 is recycled back, the remainder of the C5 may be used as the final product or subjected to suitable further steps depending on needs.

non-recycled C4

Non-recycled C4 from the middle hydrocarbon stream may be used as the final product or subjected to suitable further steps depending on needs. The further steps may preferably be selected from the group consisting of isomerization, butane dehydrogenation (non-oxidative and oxidative), reaction with methanol and reaction with ethanol and combinations thereof. Specific examples of said combinations thereof include isomerization followed by dehydrogenation.

N-butane in the non-recycled C4 may e.g. be subjected to isomerization to obtain i-butane or to dehydrogenation to obtain n-butene and butadiene.

Iso-butane in the non-recycled C4 and i-butane obtained by isomerization of n-butane may e.g. be subjected to dehydrogenation to obtain iso-butene, reacted with methanol to obtain methyl tert-butyl ether (MTBE) or reacted with ethanol to obtain ethyl tert-butyl ether (ETBE).

Non-recycled C4 from the middle hydrocarbon stream may also be subjected to a cracking process for converting C4 to smaller hydrocarbons such as C2 and C3.

In some embodiments, the product obtained by the further steps may be combined with the light hydrocarbon stream, optionally after separation of the components in said product.

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step c)

The heavy hydrocarbon stream obtained by step b) is subjected to second hydrocracking as described above to produce a second hydrocracking product stream comprising BTX.

- 10 The second hydrocracking product stream substantially consists of H₂, C₁₋₄ and BTX. The conditions of the second hydrocracking can be adjusted such that the second hydrocracking product stream comprises substantially no co-boilers of BTX.

- The C₄₋ may be separated from the second hydrocracking product stream to be recycled back to the separation of step b).
- 15

Alternatively, the C₄₋ may be separated from the second hydrocracking product stream to be combined with the light hydrocarbon stream.

- 20 Alternatively, the C₄₋ may be separated from the second hydrocracking product stream to be recycled back to the first hydrocracking of step a).

preferred embodiments

In some particularly preferred embodiments,

- 25 the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between C₃ and iC₄;
the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate C₅ and C₆;
step b) involves separating between the C₄ of the middle hydrocarbon stream and the C₅ of the
30 middle hydrocarbon stream;
at least part of the C₅ in the middle hydrocarbon stream is recycled back to the first hydrocracking in step a); and

at least part of the C4 in the middle hydrocarbon stream is subjected to a further step selected from the group consisting of isomerization, butane dehydrogenation (non-oxidative and oxidative), reaction with methanol and reaction with ethanol and combinations thereof.

- 5 In some particularly preferred embodiments,
the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between iC4 and nC4;
the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate C5 and C6;
10 step b) involves separating between the nC4 of the middle hydrocarbon stream and the C5 of the middle hydrocarbon stream;
at least part of the C5 in the middle hydrocarbon stream is recycled back to the first hydrocracking in step a); and
at least part of the nC4 in the middle hydrocarbon stream is subjected to a further step selected
15 from the group consisting of isomerization, butane dehydrogenation (non-oxidative and oxidative), reaction with methanol and reaction with ethanol and combinations thereof.

System

- In a further aspect, the present invention also relates to a process installation suitable for
20 performing the process of the invention, an example of which is illustrated in Figure 1. The present invention therefore relates to a system for producing LPG and BTX, comprising
- a first hydrocracking unit (101) arranged for performing first hydrocracking of a mixed hydrocarbon feed stream (105) in the presence of a first hydrocracking catalyst to produce a first hydrocracking product stream (106);
25 - a separation unit (102) for separating the first hydrocracking product stream (106) arranged to provide at least a light hydrocarbon stream (107) comprising at least C2 and C3, a middle hydrocarbon stream (108) comprising C4 and/or C5 and a heavy hydrocarbon stream (112) comprising at least C6+ and
- a second hydrocracking unit (103) arranged for performing second hydrocracking of the heavy
30 hydrocarbon stream (112) in the presence of a second hydrocracking catalyst to produce a second hydrocracking product stream (114) comprising BTX, wherein
the system (100) is arranged for recycling back at least part (108A) of the middle hydrocarbon stream (108) to the first hydrocracking unit (101).

The separation unit (102) may use any known technology for the separation of a mixed hydrocarbon stream, for example, gas-liquid separation, distillation or solvent extraction.

The separation unit (102) may be one fractionating column having outlets for different hydrocarbon streams or a combination of multiple fractionating columns. For example, the

5 separation unit (102) may comprise a fractionating column having respective outlets for the light hydrocarbon stream (107), the middle hydrocarbon stream (108) and the heavy hydrocarbon stream (112). In some embodiments, the separation unit (102) comprises a further column connected to the outlet for the middle hydrocarbon stream (108), the further column having
10 respective outlets for a first middle hydrocarbon stream and a second middle hydrocarbon stream having a higher boiling point range than the boiling point range of the first middle hydrocarbon stream.

In other embodiments, the separation unit (102) comprises a column having respective outlets for the light hydrocarbon stream (107), a first middle hydrocarbon stream (108), a second
15 middle hydrocarbon stream (108) having a higher boiling point range than the boiling point range of the first middle hydrocarbon stream and a heavy hydrocarbon stream (112).

In other embodiments, the separation unit (102) comprises a first column having an outlet for the light hydrocarbon stream (107) and an outlet for the remainder; and a second column having
20 an inlet connected to the outlet for the remainder of the first column, an outlet for the middle hydrocarbon stream (108) and an outlet for the heavy hydrocarbon stream (112).

The system according to the invention may further comprise a C4 processing unit (104) arranged for processing the part of the middle hydrocarbon stream (108) which is not recycled
25 back to the first hydrocracking unit (101). The C4 processing unit (104) may be formed of one or more processing units. For example, the C4 processing unit (104) may be a unit for processing C4 hydrocarbon by isomerization, butane dehydrogenation (non-oxidative and oxidative) or reaction with methanol and reaction with ethanol. The C4 processing unit may also be a combination of units, e.g. a unit for isomerization followed by a unit for reaction with methanol or
30 a unit for reaction with ethanol.

Figure 1 is hereinafter described in detail. Figure 1 schematically illustrates a system 100 comprising a first hydrocracking unit 101, a separation unit 102, a second hydrocracking unit 103 and a C4 processing unit 104.

As shown in figure 1, a mixed hydrocarbon feed stream 105 is fed to the first hydrocracking unit 101 which produces a first hydrocracking product stream 106. The first hydrocracking product stream 106 is fed to the separation unit 102, which produces a light hydrocarbon stream 107, a middle hydrocarbon stream 108 and a heavy hydrocarbon stream 112.

In this embodiment, the separation between the light hydrocarbon stream 107 and the middle hydrocarbon stream 108 is performed to separate between C3 and iC4 and the separation between the middle hydrocarbon stream 108 and the heavy hydrocarbon stream 112 is performed to separate nC4 and C5. In this case, the light hydrocarbon stream 107 consists of C3-, the middle hydrocarbon stream 108 consists of C4 (iC4 and nC4) and the heavy hydrocarbon stream 112 consists of C5+.

The light hydrocarbon stream 107 of C3- is obtained as a final product or subjected to suitable further steps (not shown).

The heavy hydrocarbon stream 112 of C5+ is subjected to the second hydrocracking unit 103, which produces a second hydrocracking product stream 114 comprising BTX.

A part of the middle hydrocarbon stream 108 (iC4 and nC4) is fed to the C4 processing unit 104, which produces desired hydrocarbons. A C3- stream 113 obtained from the C4 processing unit 104 is mixed with the light hydrocarbon stream 107 from the separation unit 102. A C4 stream 110 from the C4 processing unit 104 is obtained as a final product or subjected to suitable further steps (not shown).

A part 108A of the middle hydrocarbon stream 108 (iC4 and nC4) is recycled back to the first hydrocracking unit 101. Due to the recycling of part 108A of the middle hydrocarbon stream 108 from the separation unit 102 to the first hydrocracking unit 101, the final amount of C2-C3 in the light hydrocarbon stream 107 is increased.

In figure 1, the separation of the middle hydrocarbon stream is drawn at a location outside of the separation unit 102. It will be appreciated that this separation can be done in the separation unit 102, i.e. the middle hydrocarbon stream 108 may be provided in the form of two already separated streams.

Examples

Example 1

A feed consisting of n-pentane was subjected to hydrocracking in order to determine the influence of hydrocracking conditions to the product compositions. The experiments were carried out in a 12 mm reactor, wherein the catalyst bed was located in the isothermal zone of the reactor heater. The catalyst used was a mixture of 2 grams of Pt on alumina (Pt-loading of 0.75 wt%) and H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=80$).

The feed stream was fed to the reactor. The feed stream enters a vaporizer section prior to the reactor where it is vaporized at 280 °C and mixed with hydrogen gas. The conditions used throughout these experiments were: WHSV=1/hr, pressure was 1379 kPa (200 psig) and the molar ratio H_2 /hydrocarbons was 3. The temperature of the isothermal zone of the reactor was varied between 375 and 450 °C. The effluent of the reactor was sampled in the gas phase to an online gas chromatograph. Product analyses were carried out once per hour.

Table 1: Compositions of hydrocracking product effluent

Component	375 °C	400 °C	425 °C	450 °C
Methane (wt%)	0.5	1.1	2.2	3.9
Ethane (wt%)	3.3	7.2	12.7	19.4
Propane (wt%)	16.3	24.4	32.8	39.7
Butanes (wt%)	16.9	19.8	20.8	19.0
i-Pentane (wt%)	11.9	13.8	13.4	9.6
n-Pentane (wt%)	49.0	32.3	17.3	7.2
C6+ (wt%)	2.1	1.4	0.8	1.2
Selectivity (-)	98.7	98	96.8	95.3

The compositions of the product effluent at different reactor temperatures are provided in Table 1. The selectivity was defined as (100% - (amount of methane formed / amount of C5 converted)). The amount of C5 converted is defined as (total amount - (i-pentane and n-pentane)). By comparing the results in Table 1, it was observed that when the reactor temperature is decreased, the overall selectivity is increased during hydrocracking. It is anticipated that a similar trend will be observed when a feed consisting of butanes is subjected

to hydrocracking (based on experiments using different carbon number paraffin feeds and conversions and production rates obtained using naphtha type feeds).

5 It can therefore be concluded that a higher selectivity can be achieved by operating at a lower temperature. A higher selectivity can be achieved by recycling the unconverted paraffins as in the process of the invention, instead of operating the hydrocracking unit at increased temperatures.

10

CLAIMS

1. A process for producing LPG and BTX, comprising
- 5 a) subjecting a mixed hydrocarbon feedstream to first hydrocracking in the presence of a first hydrocracking catalyst to produce a first hydrocracking product stream;
- b) separating the first hydrocracking product stream to provide at least a light hydrocarbon stream comprising at least C2 and C3 hydrocarbons, a middle hydrocarbon stream comprising C4 and/or C5 hydrocarbons and
- 10 a heavy hydrocarbon stream comprising at least C6+ hydrocarbons and
- c) subjecting the heavy hydrocarbon stream to second hydrocracking in the presence of a second hydrocracking catalyst to produce a second hydrocracking product stream comprising BTX, wherein the second hydrocracking is more severe than the first hydrocracking, wherein at least part of the middle hydrocarbon stream is recycled back to the first
- 15 hydrocracking in step a).
2. The process according to any one of the preceding claims, wherein the first hydrocracking is a hydrocracking process suitable for converting a hydrocarbon feed that is relatively rich in naphthenic and paraffinic hydrocarbon compounds to a stream rich in LPG and
- 20 aromatic hydrocarbons.
3. The process according to any one of the preceding claims, wherein the first hydrocracking catalyst is a catalyst containing one metal or two or more metals of group VIII, VI B or VII B of the periodic classification of elements deposited on a carrier.
- 25
4. The process according to any one of the preceding claims, wherein the second hydrocracking product stream is substantially free from non-aromatic C6+ hydrocarbons.
5. The process according to any one of the preceding claims, wherein the second
- 30 hydrocracking is performed using a hydrocracking catalyst comprising 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and a silica (SiO₂) to alumina (Al₂O₃) molar ratio of 5-200 under conditions comprising a temperature of 300-580 °C, preferably 425-580 °C, a pressure of 0.3-5 MPa gauge and a Weight Hourly Space Velocity (WHSV) of 0.1-15 h⁻¹.

6. The process according to any one of the preceding claims, wherein the first hydrocracking conditions comprise a lower process temperature than the second hydrocracking conditions.

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7. The process according to any one of the preceding claims, wherein the mixed hydrocarbon feedstream comprises a naphtha or a naphtha-like product, preferably having a boiling point range of 20-200°C.

10 8. The process according to any one of the preceding claims, wherein H₂ or H₂ and C₁ hydrocarbon is separated from the first hydrocracking product stream before the separation between the light, middle and heavy hydrocarbon streams.

15 9. The process according to any one of the preceding claims, wherein the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between C₃ hydrocarbon and iC₄ hydrocarbon, between iC₄ hydrocarbon and nC₄ hydrocarbon or between nC₄ hydrocarbon and C₅ hydrocarbon.

20 10. The process according to any one of the preceding claims, wherein the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate between iC₄ hydrocarbon and nC₄ hydrocarbon, between nC₄ hydrocarbon and C₅ hydrocarbon or between C₅ hydrocarbon and C₆ hydrocarbon.

25 11. The process according to any one of the preceding claims, wherein at least part of non-recycled C₄ hydrocarbon from the middle hydrocarbon stream is subjected to a further step selected from the group consisting of isomerization, butane dehydrogenation (non-oxidative and oxidative), reaction with methanol and reaction with ethanol and combinations thereof.

30 12. The process according to any one of the preceding claims, wherein the separation between the light hydrocarbon stream and the middle hydrocarbon stream is performed to separate between C₃ hydrocarbon and iC₄ hydrocarbon; the separation between the middle hydrocarbon stream and the heavy hydrocarbon stream is performed to separate C₅ hydrocarbon and C₆ hydrocarbon;

step b) involves separating between the C4 hydrocarbon of the middle hydrocarbon stream and the C5 hydrocarbon of the middle hydrocarbon stream;

at least part of the C5 hydrocarbon in the middle hydrocarbon stream is recycled back to the first hydrocracking in step a); and

5 at least part of the C4 hydrocarbon in the middle hydrocarbon stream is subjected to a further step selected from the group consisting of isomerization, butane dehydrogenation (non-oxidative and oxidative), reaction with methanol and reaction with ethanol and combinations thereof.

10 13. The process according to any one of the preceding claims, wherein C4- hydrocarbon in the second hydrocracking product stream is separated from the second hydrocracking product stream to be recycled back to the separation of step b) or combined with the light hydrocarbon stream.

15 14. The process according to any one of the preceding claims, wherein the amount of methane in the first hydrocracking product stream is at most 5 wt%.

15. The process according to any one of the preceding claims, wherein the amount of the C4 and C5 hydrocarbons in the at least part of the middle hydrocarbon stream is at least 70
20 wt%.