

Process for producing BTX and LPG

The invention is directed to a process for producing BTX and LPG.

- 5 Aromatics hydrocarbons have a wide variety of applications in the petrochemical and chemical industries. These are important raw materials for many intermediates of commodity petrochemicals and valuable fine chemicals, such as monomers for polyesters, engineering plastics, intermediates for detergents, pharmaceuticals, agricultural products and explosives. Among them, benzene, toluene and xylene (BTX)
- 10 are the three basic materials for most intermediates of aromatic derivatives. About 70% of the global production of BTX is by extraction from either reformat or pyrolysis gasoline (pygas). Reformate is formed in the catalytic reforming of naphtha, a technology primarily directed at the production of high octane gasoline components. Pygas is a liquid byproduct formed in the production of olefins by hydrocracking liquid
- 15 feeds such as naphtha or gas oil. Extraction from reformat and pygas are the most economical sources of BTX. The composition of BTX depends on the source. Pygas is typically rich in benzene, whereas xylenes and toluene are the main components of reformat. Apart from BTX, LPG is produced during extraction from reformat or pygas.
- 20 WO2013/182534 discloses a process for producing BTX from a C5-C12 hydrocarbon mixture using a hydrocracking/hydrodesulphurisation catalyst. According to WO2013/182534, the process results in a mixture comprising substantially no co-boilers of BTX, thus chemical grade BTX can easily be obtained.
- 25 The product stream obtained by the process of WO2013/182534 comprises BTX and LPG as well as methane and unreacted hydrogen. The product stream is separated into methane and unreacted hydrogen as a first separate stream, the LPG as a second separate stream and the BTX as a third separate stream.
- 30 The BTX is separated from the hydrocracking product stream by gas-liquid separation or distillation. A series of distillation steps may be applied. The first distillation step at moderate temperature is for separating most of the aromatic species (liquid product) from the hydrogen, H₂S, methane and LPG species. The gaseous stream from this distillation is further cooled (to about -30 °C) and distilled again to separate the
- 35 remaining aromatics species and most of the propane and butane.

The gaseous product (mainly hydrogen, H₂S, methane and ethane) is then further

cooled (to about -100 °C) to separate the ethane and leave the hydrogen, H₂S and methane in the gaseous stream that will be recycled to the reactor. The gaseous product subjected to this cryogenic cooling must be substantially free from BTX in order to avoid freezing of BTX which would block the system. The separation step requires
5 cryogenic cooling using special equipment, which is energy intensive.

It is an object of the present invention to provide a process for producing BTX and LPG by hydrocracking, which is less energy intensive.

- 10 This object is achieved by a process for producing BTX and LPG, comprising:
(a) contacting a feed stream comprising C5-C12 hydrocarbons in the presence of hydrogen with a hydrocracking catalyst in a hydrocracking reactor to produce a hydrocracking product stream comprising hydrogen, methane, LPG and BTX,
(b) separating the hydrocracking product stream into a first gas stream and a first liquid
15 stream,
(c) separating the first gas stream to obtain a second gas stream comprising hydrogen and methane and a second liquid stream comprising LPG and BTX, wherein the separation is performed such that the second liquid stream is substantially free of hydrogen and methane,
20 (d) separating the second liquid stream into a third gas stream comprising LPG and a third liquid stream comprising BTX,
wherein step (c) involves
adding a part of the third liquid stream to the first gas stream to absorb the LPG in the first gas stream to obtain the second liquid stream
25 or
adding a part of the third liquid stream to a gas stream separated from the first gas stream to absorb the LPG in said gas stream separated from the first gas stream to obtain the second liquid stream.
- 30 In the process of the invention, the hydrocracking product stream obtained by step (a) is separated into a first gas stream and a first liquid stream in step (b). The first gas stream comprises hydrogen, methane and LPG. The first liquid stream comprises BTX. In step (c), LPG is removed from the first gas stream. This removal of LPG from the first gas stream is performed utilizing the BTX generated by the hydrocracking step (a).
35 As a result of step (c), a second liquid stream is formed, which comprises the LPG from the first gas stream and the BTX added to the first gas. The hydrogen and methane remaining from the first gas stream forms a second gas stream.

The BTX used for the separation step (c) is obtained by the subsequent separation step (d) in which LPG and BTX in the second liquid stream are separated from each other as a third gas stream and a third liquid stream. A part of the BTX obtained is fed
5 back to the separation unit used in step (c).

The separation of step (c) is performed such that the second liquid stream is substantially free of hydrogen and methane. Preferably, the second liquid stream substantially consists of LPG and BTX. This allows an easy separation of the second
10 liquid stream in the subsequent step (d) between the third gas stream (LPG) and the third liquid stream (BTX). The separation in step (d) can be performed simply by a gas-liquid separation due to the large difference in the boiling points of C4 hydrocarbons and benzene. LPG as the desired product is directly obtained thereby. It is herein understood that 'the second liquid stream is substantially free of hydrogen and
15 methane' means that the total amount of hydrogen and methane in the second liquid stream is less than 1 wt-%, preferably less than 0.7 wt-%, more preferably less than 0.6 wt-% and most preferably less than 0.5 wt-%.

Preferably, the second gas stream mainly comprises hydrogen and methane, i.e. much
20 of heavier hydrocarbons in the first gas stream go to the second liquid stream. Preferably, the total amount of hydrogen and methane in the second gas stream is at least 60 wt-%, preferably at least 65 wt-%, more preferably at least 70 wt-%, more preferably at least 80 wt-%, more preferably at least 90 wt-%, more preferably at least 95 wt-%, more preferably at least 98 wt-%. Most preferably, the second gas stream
25 substantially consists of hydrogen and methane, i.e. all heavier hydrocarbons in the first gas stream go to the second liquid stream. It is herein understood that 'the second gas stream substantially consists of hydrogen and methane' means that the total amount of hydrogen and methane in the second gas stream is at least 99 wt-%, preferably at least 99.3 wt-%, more preferably at least 99.4 wt-%, most preferably at
30 least 99.5 wt-%.

Preferably, the third gas stream mainly comprises LPG. Preferably, the total amount of LPG in the third gas stream is at least 80 wt-%, preferably at least 85 wt-%, more preferably at least 90 wt-%, more preferably at least 95 wt-%, more preferably at least
35 98 wt-%. Most preferably, the third gas stream substantially consists of LPG. It is herein understood that 'the third gas stream substantially consists of LPG' means that the amount of LPG in the third gas stream is at least 99 wt-%, preferably at least 99.3

wt-%, more preferably at least 99.4 wt-%, most preferably at least 99.5 wt-%. It is herein understood that 'the third liquid stream substantially consists of BTX' means that the amount of BTX in the third liquid stream is at least 99 wt-%, preferably at least 99.3 wt-%, more preferably at least 99.4 wt-%, most preferably at least 99.5 wt-%.

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In step (b), a gas-liquid separation is performed for the hydrocracking product stream. In one case, a large portion of BTX ends up in the liquid phase (first liquid stream).

However, there may be a case in which the gas phase still contains a substantial amount of BTX (especially benzene) after one separation. In this case, the gas phase

10 is preferably further subjected to one or more gas-liquid separations until the gas phase contains a small portion of BTX. These two cases relate to the two options in step (c):

I) adding a part of the third liquid stream to the first gas stream to absorb the LPG in the first gas stream to obtain the second liquid stream or

15 II) adding a part of the third liquid stream to a gas stream separated from the first gas stream to absorb the LPG in said gas stream separated from the first gas stream to obtain the second liquid stream

As described above, the gas-liquid separation of the hydrocracking product stream may be performed such that the first gas stream comprises a small portion of BTX. In this
20 case, option I) is preferred for step (c). In option I), the hydrocracking product stream is separated into the first gas stream and the first liquid stream, and subsequently the first gas stream is directly mixed with the recycled third liquid stream without a further separation. This recycled third liquid stream which absorbed the LPG in the first gas stream is called the second liquid stream.

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As described above, the gas-liquid separation of the hydrocracking product stream may be performed such that the first gas stream comprises a large portion of BTX. In this case, option II) is preferred for step (c). In option II), the addition of the third liquid stream is performed after the first gas stream is further separated. In other words, the
30 hydrocracking product stream is separated into the first gas stream and the first liquid stream, and subsequently the first gas stream is separated into a further gas stream and a further liquid stream. This further gas stream obtained from the first gas stream is mixed with the recycled third liquid stream. This recycled third liquid stream which absorbed the LPG in the gas stream obtained from the first gas stream is called the
35 second liquid stream.

It is an advantage of the process of the invention that the separation of LPG and

methane/hydrogen does not require cryogenic cooling. Instead of cryogenic cooling to separate methane and C2 hydrocarbon, C2 hydrocarbon is absorbed by the added BTX to be separated from methane.

- 5 It is a further advantage of the process of the invention that no additional solvent is required for the separation since the BTX generated by the process is used for the separation.

10 According to the invention, BTX in a liquid form is used for the absorption of the LPG present in the first gas stream. Due to the high affinity between BTX and LPG, LPG present in the first gas stream will be absorbed by BTX. Due to the very low affinity between BTX and H₂ or C₁, hydrogen and methane are not absorbed by BTX, and accordingly remains as a gas stream.

- 15 It is noted that US4212726 discloses a method for recovering hydrogen gas of increased purity from a hydrotreatment process effluent stream. The method comprises a gas-liquid separation of the effluent stream and producing a stream of relatively pure hydrogen from the gaseous phase by the use of two absorber liquids.

20 In US4212726, the absorber liquids consist of the liquid phase hydrocarbon stream obtained by the first gas-liquid separation and heavier stabilized converted hydrocarbons. Since the objective of the process of US4212726 is to obtain pure H₂, methane in the gaseous phase is absorbed by the absorber liquid. This is performed in US4212726 by the use of a relatively broad range of hydrocarbons as absorbing liquid,
25 unlike in the process of the invention in which substantially only BTX is used as the absorbing liquid. Further, in US4212726, the stream obtained by the absorption is separated into a stream of C₁-C₄ gaseous hydrocarbon fraction and a stream of C₅+ hydrocarbon fraction. Unlike in the process of the present invention, the gaseous hydrocarbon fraction requires a further separation to obtain the desired product
30 consisting mainly of C₃ and C₄.

It is noted that US7563307 discloses a process for separating a hydrocarbon gas stream, such as natural gas, by contacting the stream with a circulating solvent comprising an internal solvent contained in the feed gas. In the process, the gas
35 stream is contacted with a solvent in an extractor to produce an overhead stream enriched with unabsorbed component(s) and a rich solvent bottoms stream enriched with absorbed component(s). The rich solvent bottoms stream is then flashed at

reduced pressure to regenerate lean solvent and to recover the absorbed component(s) as an overhead stream. The regenerated solvent is recycled to the extractor. A portion of the circulating solvent comprises external solvent added to the system. A second portion of the circulating solvent comprises internal solvent
5 contained in the feed gas. US7563307 does not disclose a process for separating a hydrocracking product stream. US7563307 further does not disclose using only the internal solvent for the recirculation. US7563307 further does not disclose use of a BTX stream for absorbing LPG for separation from methane and hydrogen.

10 As used herein, the term "C# hydrocarbons", wherein "#" is a positive integer, is meant to describe all hydrocarbons having # carbon atoms. 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.

15 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 C2-C4 hydrocarbons i.e. a mixture of C2, C3, and C4 hydrocarbons.

20 The term "BTX" as used herein is well known in the art and relates to a mixture of benzene, toluene and xylenes.

The term "aromatic hydrocarbon" is very well known in the art. Accordingly, the term "aromatic hydrocarbon" relates to cyclically conjugated hydrocarbon with a stability
25 (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.

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Step (a)

The process according to the invention comprises (a) contacting a feed stream comprising C5-C12 hydrocarbons in the presence of hydrogen with a hydrocracking catalyst in a hydrocracking reactor. Step (a) can be performed in one hydrocracking
35 reactor or in more than one hydrocracking reactors. Preferably, step (a) is performed in at least two hydrocracking reactors arranged in series.

Feed stream

The feed stream used in the process of the present invention is a mixture comprising C5-C12 hydrocarbons. Preferably, the source feed stream comprises at least 40 wt%, more preferably at least 45 wt%, most preferably at least 50 wt% of the C5-C12

5 hydrocarbons. Preferably, the feed stream mainly comprises C6-C8 hydrocarbons. Preferably the feed stream has a boiling point in the range of 30-195°C. Suitable feed streams include, but are not limited to pyrolysis gasoline, straight run naphtha, hydrocracked gasoline, light coker naphtha and coke oven light oil, FCC gasoline, reformate or mixtures thereof. The feed stream may have a relatively high sulphur
10 content, such as pyrolysis gasoline (pygas), straight run naphtha, light coker naphtha and coke oven light oil and mixtures thereof. Furthermore, it is preferred that the non-aromatic species comprised in the hydrocarbon feed are saturated (e.g. by prior hydrogenation) in order to reduce the exotherm within the catalyst bed used in the present process.

15 For instance, a typical composition of pyrolysis gasoline may comprise 10-15 wt-% C5 olefins, 2-4 wt-% C5 paraffins and cycloparaffins, 3-6 wt-% C6 olefins, 1-3 wt-% C6 paraffins and naphthenes, 25-30 wt-% benzene, 15-20 wt-% toluene, 2-5 wt-% ethylbenzene, 3-6 wt-% xylenes, 1-3 wt-% trimethylbenzenes, 4-8 wt-%
20 dicyclopentadiene, and 10-15 wt-% C9+ aromatics, alkylstyrenes and indenenes; see e.g. Table E3.1 from Applied Heterogeneous Catalysis: Design, Manufacture, and Use of Solid Catalysts (1987) J. F. Le Page. However, also hydrocarbon mixtures that are depentanised and tailed so the concentrations of all the C6 to C9 hydrocarbon species are relatively high compared with the typical figures above can be advantageously
25 used as a feed stream in the process of the present invention.

In some embodiments, the feed stream used in the process of the present invention is treated so that it is enriched in mono-aromatic compounds. As used herein, the term
30 "mono-aromatic compound" relates to a hydrocarbon compound having only one aromatic ring. Means and methods suitable to enrich the content of mono-aromatic compounds in a mixed hydrocarbon stream are well known in the art such as the Maxene process; see Bhirud (2002) Proceedings of the DGMK-conference 115-122. The feed stream used in the process of the present invention may comprise up to 300 wppm of sulphur (i.e. the weight of sulphur atoms, present in any compound, in relation
35 to the total weight of the feed).

In preferred embodiments the feed stream is depentanized, which means that the feed

stream is substantially free from C5 hydrocarbons. As meant herein, the term "feed stream substantially free from C5 hydrocarbons" means that said feed stream comprises less than 1 wt-% C5 hydrocarbons, preferably less than 0.7 wt-% C5 hydrocarbons, more preferably less than 0.6 wt-% C5 hydrocarbons and most
5 preferably less than 0.5 wt-% C5 hydrocarbons.

The feed stream can be subjected to hydrodesulphurisation before hydrocracking.

Hydrocracking catalyst

10 The feed stream comprising C5-C12 hydrocarbons is contacted in the presence of hydrogen with a hydrocracking catalyst.

In preferred embodiments, the hydrocracking catalyst further has a hydrodesulphurisation activity. This is advantageous in that it is not necessary to
15 subject the hydrocarbon feed stream to a desulphurisation treatment prior to subjecting said hydrocarbon feed stream to the hydrocracking treatment.

Catalysts having hydrocracking/hydrodesulphurisation activity ("hydrocracking/hydrodesulphurisation catalyst") are described on pages 13-14 and
20 174 of Hydrocracking Science and Technology (1996) Ed. Julius Scherzer, A.J. Gruia, Pub. Taylor and Francis. Hydrocracking and hydrodesulphurisation reactions proceed through a bifunctional mechanism which requires a relatively strong acid function, which provides for the cracking and isomerization and which provides breaking of the sulphur-carbon bonds comprised in the organic sulfur compounds comprised in the
25 feed, and a metal function, which provides for the olefin hydrogenation and the formation of hydrogen sulfide. Many catalysts used for the hydrocracking/hydrodesulphurisation process are formed by composting various transition metals with the solid support such as alumina, silica, alumina-silica, magnesia and zeolites.

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In preferred embodiments of the invention, 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 (SiO₂) to alumina (Al₂O₃) molar ratio of 5-200 and the process conditions comprise a temperature of 425-580 °C, a pressure of
35 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-15 h⁻¹.

In these embodiments, the obtained 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 product stream.

- 5 The advantageous effects of these embodiments are obtained by strategically selecting the hydrocracking catalyst in combination with the hydrocracking conditions. Hydrocracking is performed under process conditions including 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. By combining a hydrocracking catalyst having a relatively strong acid function
- 10 (e.g. by selecting a catalyst comprising a zeolite having a pore size of 5-8 Å and a silica (SiO₂) to alumina (Al₂O₃) molar ratio of 5-200) and a relatively strong hydrogenation activity (e.g. by selecting a catalyst comprising 0.01-1 wt-% hydrogenation metal) with process conditions comprising a relatively high process temperature (e.g. by selecting a temperature of 425-580 °C), chemical grade BTX and LPG can be produced from the
- 15 hydrocracking product stream.

- Preferably, the hydrocracking of the feed stream is performed at a pressure of 300-5000 kPa gauge, more preferably at a pressure of 600-3000 kPa gauge, particularly preferably at a pressure of 1000-2000 kPa gauge and most preferably at a pressure of
- 20 1200-1600 kPa gauge. By increasing reactor pressure, conversion of C5+ 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,
- 25 there is an optimum in the purity of the resultant benzene at a pressure of 1200-1600 kPa.

- Preferably, the hydrocracking/hydrodesulphurisation of the feed stream is performed at a Weight Hourly Space Velocity (WHSV) of 0.1-15 h⁻¹, more preferably at a Weight
- 30 Hourly Space Velocity of 1-10 h⁻¹ and most preferably at a Weight Hourly Space Velocity of 2-9 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
- 35 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.

Accordingly, preferred hydrocracking conditions 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 600-3000 kPa gauge and a Weight Hourly Space Velocity of 1-10 h⁻¹. Particularly preferred hydrocracking conditions include a temperature of 450-550 °C, a pressure of 1000-2000 kPa gauge and a Weight Hourly Space Velocity of 2-9 h⁻¹.

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.

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.

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.

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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 step (b) is performed at a Weight Hourly Space Velocity of 10-15 h^{-1} .

The 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 (H_2/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 H_2/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.

In these embodiments where 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 first 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} , the product produced by the hydrocracking step of the process of the present invention (hydrocracking product stream) mainly comprises hydrogen, methane, LPG and BTX.

According to these embodiments of the present invention, chemical grade BTX can easily be separated from the hydrocracking product stream.

As used herein, the term “chemical grade BTX” relates to a hydrocarbon mixture comprising less than 5 wt-% hydrocarbons other than benzene, toluene and xylenes, preferably less than 4 wt-% hydrocarbons other than benzene, toluene and xylenes, more preferably less than 3 wt-% hydrocarbons other than benzene, toluene and xylenes, and most preferably less than 2.5 wt-% hydrocarbons other than benzene, toluene and xylenes.

Furthermore, the “chemical grade BTX” produced by the process of the present invention 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-% non-aromatic C6+ hydrocarbons. The most critical contaminants are the non-aromatic species

which have boiling points close to benzene including, but not limited to, cyclohexane, methylcyclopentane, n-hexane, 2-methylpentane and 3-methylpentane.

It is a particular advantage of these embodiments that the hydrocracking product stream is substantially free from non-aromatic C6+ hydrocarbons as these hydrocarbons usually have boiling points close to the boiling point of C6+ aromatic hydrocarbons. Hence, it can be difficult to separate the non-aromatic C6+ hydrocarbons from the aromatic C6+ hydrocarbons comprised in the hydrocracking product stream by distillation.

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As meant herein, the term "product stream substantially free from non-aromatic C6+ hydrocarbons" means that said product 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-% non-aromatic C6+ hydrocarbons.

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Preferably, the hydrocracking product stream is also substantially free from C5 hydrocarbons. As meant herein, the term "hydrocracking product stream substantially free from C5 hydrocarbons" means that said hydrocracking product stream comprises less than 1 wt-% C5 hydrocarbons, preferably less than 0.7 wt-% C5 hydrocarbons, more preferably less than 0.6 wt-% C5 hydrocarbons and most preferably less than 0.5 wt-% C5 hydrocarbons.

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Preferably, the hydrocarbons of the hydrocracking product stream substantially consist of methane, LPG and BTX. As meant herein, the term "the hydrocarbons of the hydrocracking product stream substantially consist of methane, LPG and BTX" means that the total amount of methane, LPG and BTX in the hydrocarbons of the hydrocracking product stream is at least 99 wt-%, preferably at least 99.3 wt-%, more preferably at least 99.4 wt-%, most preferably at least 99.5 wt-% .

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30 step (b)

During step (b) the hydrocracking product stream is separated into a first gas stream mainly comprising hydrogen, methane and LPG and a first liquid stream mainly comprising BTX. The hydrocracking product stream is subjected to separation by standard means and methods suitable for separating the gases from the liquids comprised in the hydrocracking product stream. The separation may be performed e.g. by flashing, conventional distillation or absorption. The separation of step (b) is preferably performed in a flash vessel. In the flash vessel the temperature is for

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example between 100 and 300 °C, and the pressure is the same as or lower than the pressure in the hydrocracking reactor.

5 The first liquid stream is preferably combined with the second liquid stream obtained by step (c) and the mixture is subjected to step (d).

step (c)

10 During step (c) the first gas stream is separated to obtain a second gas stream mainly comprising hydrogen and methane and a second liquid stream mainly comprising LPG and BTX. The first gas stream is subjected to separation by standard means and methods suitable for separating the gases from the liquids comprised in the first gas stream. The separation may be performed e.g. by flashing, conventional distillation or absorption. The separation of step (c) is preferably performed by distillation.

15 Step (c) involves using a part of a third liquid stream mainly comprising BTX to absorb the LPG in the gas stream. In this way the second gas stream is obtained having little amount of components other than hydrogen and methane.

20 Preferably, the part of the third liquid stream to be added to the first gas stream is cooled before it is added to the first gas stream. The conditions of the cooling, such as the temperature and the pressure, are chosen such that the BTX of the third liquid stream remains liquid. The temperature of the third liquid stream is not very low, unlike the temperature required for the separation of ethane and methane (e.g. -100 °C). The process of the invention can therefore be carried out in a simpler and less energy-
25 intensive manner even when the part of the third liquid stream to be added to the first gas stream is cooled.

The cooling of the part of the third liquid stream to be added to the first gas stream has an advantage that the amount of the LPG absorbed in the BTX is increased. For
30 example, the third liquid stream to be added to the first gas stream is cooled to a temperature of below 0 °C. Preferably, the third liquid stream to be added to the first gas stream is cooled to a temperature of -40 °C to 0 °C, more preferably -40 °C to -10 °C, more preferably -40 °C to -20 °C, more preferably -40 °C to -30 °C, e.g. -35 °C. The pressure of the cooled stream may e.g. be 25-50 bar, for example 30 bar. Most
35 preferably, the part of the third liquid stream to be added to the first gas stream is cooled to a temperature just above the temperature at which the third liquid stream freezes, before being added to the first gas stream. For example, the part of the third

liquid stream to be added to the first gas stream is cooled to a temperature 0.5-5 °C higher than the temperature at which the third liquid stream freezes, before being added to the first gas stream. The temperature at which the third liquid stream freezes can easily be determined by the skilled person depending on the pressure.

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In some embodiments of the invention, step (c) involves adding a part of the third liquid stream directly to the first gas stream. This is also described as option (I) elsewhere in the description.

10 Step (c) may involve compressing the first gas stream and adding the part of the third liquid stream to the compressed first gas stream. Compressing the first gas stream will further improve the separation of components between the second gas stream and the second liquid stream by increasing the absorption of LPG in BTX.

15 In other embodiments of the invention, step (c) is performed in two or more steps. In these embodiments step (c) involves

(c1) separating the first gas stream into a gas stream and a liquid stream and

(c2) adding the part of the third liquid stream to the gas stream.

This is also described as option (II) elsewhere in the description.

20

The liquid stream obtained by step (c1) is preferably combined with the second liquid stream obtained by step (c2) and the mixture is subjected to step (d).

25 Step (c2) may involve compressing the gas stream of step (c1) and adding the part of the third liquid stream to the compressed gas stream. Compressing the gas stream of (c1) will further improve the separation of components between the second gas stream and the second liquid stream by increasing the absorption of LPG in BTX.

30 Preferably, at least part of the second gas stream is fed back to be mixed with the feed stream. In this way the hydrogen that is not consumed during hydrocracking is recycled within the process. This is an economical and environmental advantage.

35 To control the level of methane in the hydrocracking reactor feed, a proportion of recycle gas stream is removed from the system as a purge. The quantity of material that is purged depends on the levels of methane in the recycle stream which in-turn depend on the feed composition. The purge stream will have the same composition as the recycle stream. As the purge will contain mainly hydrogen and methane it is

suitable for use as a fuel gas or may be further treated (e.g. via a pressure swing adsorption unit) to separately recover a high purity hydrogen stream and a methane stream which can be used as a fuel gas.

5 step (d)

During step (d) the second liquid stream is separated into a third gas stream comprising LPG and a third liquid stream comprising BTX. The second liquid stream may be subjected to separation by standard means and methods suitable for separating a third gas stream comprising LPG and a third liquid stream comprising BTX
10 from each other. Preferably, the separation is performed by gas-liquid separation or distillation.

step (e)

In preferred embodiments the process according to the invention further comprises
15 step (e) of separating benzene from the third liquid stream.

More preferably, the third liquid stream is separated into benzene and a liquid stream comprising toluene and xylene and (part of) the liquid stream comprising toluene and xylene is used for absorbing the LPG and BTX in step (c). Since the liquid stream
20 comprising toluene and xylene comprises heavier hydrocarbons than the third liquid stream before separation, a more effective absorption will occur in step (c) resulting in a better separation during step (c).

Although the invention has been described in detail for purposes of illustration, it is
25 understood that such detail is solely for that purpose and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention as defined in the claims.

It is further noted that the invention relates to all possible combinations of features
30 described herein, preferred in particular are those combinations of features that are present in the claims.

It is noted that the term "comprising" does not exclude the presence of other elements. However, it is also to be understood that a description on a product comprising certain
35 components also discloses a product consisting of these components. Similarly, it is also to be understood that a description on a process comprising certain steps also discloses a process consisting of these steps.

The present invention is further elucidated referring to the drawings in which:

Figure 1 illustrates a scheme of an example of a process not according to the invention
5 and

Figure 2 illustrates a scheme of an example of a process according to the invention.

Figure 1 illustrates a scheme of an example of a process not according to the
10 invention. A feed stream comprising C5-C12 hydrocarbons is hydrocracked in the reaction section illustrated in the left part of the figure and the obtained hydrocracking product stream comprising hydrogen, methane, LPG and BTX is fed to the separation section illustrated in the right part of the figure via a heat exchanger H-003.

15 The hydrocracking product stream is fed to a heat exchanger H-003 where it is cooled to e.g. 140 °C, after which it is fed to a flash vessel V0001. The hydrocracking product stream is separated in the flash vessel V001 into a gas stream and a liquid stream. The gas stream from the flash vessel V0001 is compressed in a compressor K0002 and separated again in a flash vessel V002 at e.g. -100 °C into a gas stream and a liquid
20 stream. The flash vessel V002 separates most of C4+ hydrocarbons as a liquid stream from a gas stream. From the flash vessel V002 a gas stream mostly comprising hydrogen and C1-C3 hydrocarbons is led to a heat exchanger H005 which compresses the gas to e.g. 30 bar and -100 °C and then to a flash vessel V003 wherein a cryogenic separation between hydrogen and methane and C2-C3 hydrocarbons is performed.

25 The gas stream containing hydrogen and methane is recycled to the reaction section, wherein it is partly recycled and partly purged. The liquid stream leaving the flash vessel V003 comprising C2-C3 is combined with the LPG stream obtained from the liquid stream from V001.

30 The liquid steam leaving V001 is, together with the liquid stream coming from V002, fed to a distillation column C001 via a heat exchanger H006. In the distillation column C001 the liquid steam is separated into an LPG stream and a BTX stream. The BTX stream is fed to a distillation column C002 for separation of the BTX stream in a stream 17 of lighter products, a benzene stream 18 and a toluene/xylene stream 19.

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Figure 2 illustrates a scheme of an example of a process according to the invention.

The reaction section of Figure 2 is the same as that of Figure 1.

In the separation section illustrated in Figure 2, the hydrocracking product stream is fed to a flash vessel V001, where it is separated into a gas stream and a liquid stream. The gas stream from the flash vessel V001 is heated in a heat exchanger H003 and
5 separated again in a flash vessel V002. The gas stream from the flash vessel V002 is compressed in a compressor K002 and fed to a distillation column C003.

The liquid streams from V001, V002 and C003 go through a heat exchanger H004 and enter a distillation column C001, which separates the liquid streams into an LPG
10 stream and a BTX stream. Part of the BTX stream is led to a distillation column C002 for separation of the BTX stream into a stream of lighter products, a benzene stream and a toluene/xylene stream. A part of the BTX stream is fed via a pump 003 to the top of the distillation column C003. In the distillation column C003 this BTX stream is used
15 to obtain a better separation between hydrogen and methane and the heavier components in the gas mixture fed to C003. As already described, the liquid stream leaving C003 is combined with the liquid streams from V001 and V002 and fed to the distillation column C001.

CLAIMS

1. A process for producing BTX and LPG, comprising:
 - (a) contacting a feed stream comprising C5-C12 hydrocarbons in the presence
5 of hydrogen with a hydrocracking catalyst in a hydrocracking reactor to produce a hydrocracking product stream comprising hydrogen, methane, LPG and BTX,
 - (b) separating the hydrocracking product stream into a first gas stream and a first liquid stream,
 - (c) separating the first gas stream to obtain a second gas stream comprising
10 hydrogen and methane and a second liquid stream comprising LPG and BTX, wherein the separation is performed such that the second liquid stream is substantially free of hydrogen and methane,
 - (d) separating the second liquid stream into a third gas stream comprising LPG and a third liquid stream comprising BTX,
 - 15 wherein step (c) involves adding a part of the third liquid stream to the first gas stream to absorb the LPG in the first gas stream to obtain the second liquid stream or adding a part of the third liquid stream to a gas stream separated from the first gas stream to absorb the LPG in said gas stream separated from the first gas stream to obtain the second liquid stream.
- 20 2. The process according to claim 1, wherein step (c) involves
 - (c1) separating the first gas stream into a gas stream and a liquid stream and
 - (c2) adding the part of the third liquid stream to the gas stream obtained by step (c1).
3. The process according to claim 2, wherein step (c2) involves compressing the
25 gas stream obtained by step (c1) and adding the part of the third liquid stream to the compressed gas stream.
4. The process according to claim 1, wherein step (c) involves adding a part of the third liquid stream to the first gas stream.
5. The process according to any one of the preceding claims, wherein the second
30 liquid stream substantially consists of LPG and BTX.
6. The process according to any one of the preceding claims, wherein at least part of the second gas stream is fed back to be mixed with the feed stream.
7. The process according to any one of the preceding claims, wherein the process further comprises step (e) of separating benzene from the third liquid stream.
- 35 8. The process according to claim 6, wherein the third liquid stream is separated into benzene and a liquid stream comprising toluene and xylene and the liquid stream comprising toluene and xylene is used for absorbing the LPG in step (c).

9. The process according to any one of the preceding claims, wherein the part of the third liquid stream to be added to the first gas stream is cooled to a temperature below 0 °C before being added to the first gas stream.
- 5 10. The process according to any one of the preceding claims, wherein the part of the third liquid stream to be added to the first gas stream is cooled to -40 °C to -30 °C before being added to the first gas stream.
- 10 11. The process according to any one of the preceding claims, wherein the part of the third liquid stream to be added to the first gas stream is cooled to a temperature 0.5-5 °C higher than the temperature at which the third liquid stream freezes, before being added to the first gas stream.
- 15 12. The process according to any one of the preceding claims, wherein the hydrocracking catalyst of step (a) comprises 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 and step (a) is performed under process conditions including 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.
- 20 13. The process according to claim 12, wherein the hydrogenation metal of the hydrocracking catalyst is at least one element selected from Group 10 of the periodic table of Elements, preferably Pt.
14. The process according to claim 12 or 13, wherein the zeolite is selected from the group consisting of ZSM-5, MCM-22, ZSM-11, beta zeolite, EU-1 zeolite, zeolite Y, faujastite, ferrierite and mordenite, preferably ZSM-5.
- 25 15. The process according to any one of the preceding claims, wherein the feed stream comprises pyrolysis gasoline, straight run naphtha, light coker naphtha and coke oven light oil, FCC gasoline, reformate or mixtures thereof, preferably the feed stream is depentanized.