PROCESS FOR PRODUCING C2 AND C3 HYDROCARBONS

The invention is directed to a process for producing C2 and C3 hydrocarbons from a mixed hydrocarbon feedstream and a system for performing such process.

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.

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.

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.

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.

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-butanes) as this will determine the ratio between the different C4 derivatives that will be produced.

There is a need in the industry for a process for producing C2 and C3 hydrocarbons with a relatively high yield.

Accordingly, the invention provides a process for producing LPG and BTX, comprising
a) subjecting a mixed hydrocarbon stream to first hydrocracking in the presence of a first hydrocracking catalyst to produce a first hydrocracking product stream; and
b) subjecting the first hydrocarbon product stream to C4 hydrocracking optimized for converting C4 hydrocarbons into C3 hydrocarbons in the presence of a C4 hydrocracking catalyst to obtain a C4 hydrocracking product stream comprising C2 and C3 hydrocarbons.

In another aspect, the invention provides a process for producing C2 and C3 hydrocarbons, comprising
a) subjecting a mixed hydrocarbon stream to first hydrocracking in the presence of a first hydrocracking catalyst to produce a first hydrocracking product stream; and
b) subjecting the first hydrocarbon product stream to C4 hydrocracking optimized for converting C4 hydrocarbons into C3 hydrocarbons in the presence of a C4 hydrocracking catalyst to obtain a C4 hydrocracking product stream comprising C2 and C3 hydrocarbons.

The present invention is based on the realization that shorter hydrocarbons require higher severity or different catalyst to be converted. The mixed hydrocarbon stream is subjected to a relatively mild first hydrocracking and the obtained product stream is subjected to a more severe C4 hydrocracking. The C4 hydrocracking is optimized for converting C4 to C3. Due to the high selectivity towards C3, conversion of C3 already present in the feed would not be significant. The degree of conversion of C2 and C1 would be even less. As a result, it is possible to feed the entire stream from the first hydrocracking to the C4 hydrocracking and selectively shift the composition of the LPG from C4 to C3.

US3718575 discloses production of LPG from heavy hydrocarbon distillates through the utilization of a two-stage hydrocracking process. In US3718575, hydrocracking is performed in

two stages, as described in reactor 4 and reactor 9 of the figure. The product 5 from the reactor 4 is separated by separator 6 to produce a vaporous phase 7 which is combined with unreacted naphtha and fed to the reactor 9. The composition of the vaporous phase 7 from the separator 6 does not lead to a high conversion of C4 into C3. Further, the addition of the unreacted naphtha comprising heavy components to the feed for the reactor 9 further reduces the conversion of C4 into C3. Accordingly, the process of US3718575 does not result in high amounts of C2/C3 and low amounts of C4.

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.

One of the petrochemical products which may be 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.

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.

step a)

A mixed hydrocarbon stream is subjected to the first hydrocracking in step a). In some embodiments, part of the hydrocarbon stream produced in the downstream of the process of the invention is recycled back to be subjected to the first hydrocracking of step a), as described later. The mixed hydrocarbon stream and the recycled 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.

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℃. 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.

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

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 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 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 3 wt%,

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) 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 ºC, more preferably 300 – 450 ºC, a pressure of 300 – 5000 kPa gauge, more preferabaly 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 (H_2/HC molar ratio) is 1:1 – 4:1, more preferably 1:1 – 2:1.

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)

The first hydrocarbon product stream is subjected to C4 hydrocracking in the presence of a C4 hydrocracking catalyst to obtain a C4 hydrocracking product stream comprising C2 and C3 hydrocarbons.

In some preferred embodiments, at least part of C4 is separated from the C4 hydrocracking product stream to be recycled back to the C4 hydrocracking of step c). In these embodiments, unconverted C4 is subjected again to the C4 hydrocracking to increase the C2 and C3 yield. For example, the portion to be separated and recycled back may be nC4 or iC4.

As used herein, the term “C4 hydrocracking” refers to a hydrocracking process optimized for converting C4 hydrocarbons to C3 hydrocarbons. Such a process is known from, for example

US-4061690. Due to the high selectivity towards C3, conversion of C3 already present in the feed would not be significant. The degree of conversion of C2 and C1 would be even less. Hence, the C4 hydrocracking product stream will contain a high ratio of C3 to C4.

Preferably, the amount of non-aromatic C6+ hydrocarbons in the first hydrocarbon product stream subjected to C4 hydrocracking is at most 10 wt%, more preferably 5 wt%.

Preferably, the amount of methane in the C4 hydrocracking product stream is at most 15 wt%, more preferably 10 wt% and most preferably at most 7 wt%. Preferably, the amount of the C2-C3 hydrocarbons in the C4 hydrocracking product stream is at least 60 wt%, more preferably 70 wt%, even more preferably at least 80 wt%…Preferably, the amount of the C4+ hydrocarbons in the C4 hydrocracking product stream is at most 30 wt%, more preferably at most 20 wt% and even more preferably at most 15 wt%……

C4 hydrocracking is a catalytic hydrocracking process. The catalyst used preferably comprises zeolites of the mordenite (MOR)-type or of the erionite (ERI)-type.

The chemical composition of mordenite related to one cellular unit can be represented by the formula: $M(8/n)[(AlO_2)_8(SiO_2)_{40}].24H_2O$ wherein M is a cation having a valence n. M is preferably sodium, potassium or calcium.

The chemical composition of erionite can be represented by the formula $(Na_2,K_2,Ca)_2Al_4Si_{14}O_{36}\cdot 15H_2O$.

As in the case of all zeolites, erionite and mordenite are crystalline silico-aluminate constituted by SiO_4 and AlO_4^- tetrahedron groups, the negative charge being compensated by an exchangeable cation. Erionite and mordenite occur in the natural state in the form of a salt of sodium, calcium and/or potassium. Preferably, erionite and mordenite are employed in their acid form by replacing the cation which is present by the hydrogen ion (to form hydrogenated erionite, H-erionite, or hydrogenated mordenite, H-mordenite) or a plurivalent cation. By way of example, this replacement can be achieved by ion exchange with the plurivalent cation or the ammonium ion for the hydrogen form, followed by drying and calcination of the zeolite. The plurivalent cations which endow the erionite or the mordenite with acidity and therefore

hydrocracking activity can be the alkaline-earth cations such as beryllium, magnesium, calcium, strontium and barium or else the cations of the rare earths.

Erionite and mordenite can be employed in its hydrogen form by virtue of its higher activity, with a residual proportion of sodium of less than 1% by weight with respect to the dehydrated erionite or mordenite.

The erionite or mordenite can occur in two types, namely the large-pore type and the small pore type. By way of indication, the erionites and mordenites in the form of sodium are capable of sorbing hydrocarbons having a diameter of less than approximately 7 Å in the case of the large-pore type and approximately 5 Å in the case of the small pore type. If the erionite or mordenite is in its hydrogen form, the size of the sorbed molecules can increase to 8-9 Å in the case of the large pore types and 7 Å in the case of the small pore types.

It should be noted that erionite or mordenite are not completely characterized by the formula given above since it can be modified by selective dissolution of alumina by means of suitable solvents such as mineral acids.

Further, a dealuminated or desilicated erionite or mordenite can be employed for C4 hydrocracking. The dealumination or desilication treatment often confers better activity and especially higher stability on the catalyst in the hydrocracking processes. It can be considered that an erionite or mordenite is really dealuminated when the silicon/aluminum molar ratio is equal to or higher than 10. By way of indication, the dealumination treatment can be performed as follows: the erionite or mordenite is treated at the boiling point for a period of a few hours with a twice normal hydrochloric acid solution, whereupon the solid is filtered, washed and finally dried.

It is desirable to provide a catalyst having good mechanical or crush strength or attrition resistance, because in an industrial environment the catalyst is often subjected to rough handling, which ends to break down the catalyst into powder-like material. The latter causes problems in the processing. Preferably, the zeolite is therefore mixed with a matrix and a binder material and then spray-dried or shaped to the desired shape, such as pellets or extrudates. Examples of suitable binder materials include active and inactive materials and synthetic or

naturally occurring zeolites as well as inorganic materials such as clays, silica, alumina, silica-alumina, titania, zirconia and zeolite. Silica and alumina are preferred because these may prevent unwanted side reactions. Preferably, the catalyst comprises, in addition to the zeolite, 2-90 wt%, preferably 10-85 wt% of a binder material.

In some embodiments, the catalyst consists of mordenite or erionite and an optional binder. In other embodiments, the catalyst further comprise one or more metals chosen from group VIB, VIIB and/or VIII of the Periodic Table of Elements. Preferably the catalyst comprises at least one group VIB and/or VIII metals, more preferably at least one group VIII metal.

One preferred catalyst comprises one or more group VIII metals, more preferably one or more VIII noble metals such as Pt, Pd, Rh and Ir, even more preferably Pt and/or Pd. The catalyst preferably comprises in the range of from 0.05 to 10 wt%, more preferably of from 0.1 to 5 wt%, even more preferably of from 0.1 to 3 wt % of such metals, based on the total weight of the catalyst.

Another preferred catalyst comprises at least one group VIB, VIIB and/or VIII metal in combination with one or more other metals, i.e. metals which are not from group VIB, VIIB or VIII. Examples of such combinations of a group VIB, VIIB and VIII in combination with another metal include, but are not limited to PtCu, PtSn or NiCu. The catalyst preferably comprises in the range of from 0.05 to 10 wt%, more preferably of from 0.1 to 5 wt%, even more preferably of from 0.1 to 3 wt% of such metals, based on the total weight of the catalyst.

Yet another preferred catalyst comprises a combination of a group VIB and a group VIII metal. Examples of such combinations of a group VIB and group VIII metal include, but are not limited to, CoMo, NiMo and NiW. The catalyst preferably comprises in the range of from 0.1 to 30 wt%, more preferably of from 0.5 to 26 wt%, based on the total weight of the catalyst.

In the C4 hydrocracking process the hydrocarbon feed stream is contacted with the catalyst at elevated temperatures and elevated pressures. Preferably, the feed stream is contacted with the catalyst at a temperature in the range of 200 – 650 ℃, more preferably 250 – 550 ℃, most preferably 325 – 450 ℃ or 397-510 ℃. The temperat ure that is chosen will depend on the composition of the feed stream and the desired product. Preferably, the feed stream is

contacted with the catalyst at a pressure of 0.3 – 10 MPa, more preferably 0.5 – 6 MPa, most preferably 2-3 MPa.

Preferably, the feed stream is contacted with the catalyst at a weight hourly space velocity (WHSV) of 0.1 to 20 hr^{-1}, more preferably 0.5 to 10 hr^{-1}. For the C4 hydrocracking the rate of injection is represented by the spatial velocity of introduction of the hydrocarbon charge in liquid form: VVH is the hourly volume rate of flow of charge per volume of catalyst. The value of VVH ranges preferably from 0.1 to 10 h^{-1} and more preferably 0.5 to 5 h^{-1}.

The C4 hydrocracking is carried out in the presence of hydrogen. The partial hydrogen pressure in the reaction zone is preferably high; that is within the range of 0.5 to 10 MPa. The partial hydrogen pressure is usually within the range of 2 to 8 MPa and preferably between 2 and 4 MPa.

Hydrogen may be provided in any suitable ratio to the hydrocarbon feed. Preferably, the hydrogen is provided in a molar ratio hydrogen to the hydrocarbon feed of 1:1 to 100:1, more preferably 1:1 to 50:1, more preferably 1:1 to 20:1, most preferably 2:1 to 8:1, wherein the number of moles of the hydrocarbon feed is based on the average molecular weight of the hydrocarbon feed.

A further particularly preferred example of the C4 hydrocracking catalyst comprises sulfided-nickel/H-Erionite1. Heck and Chen (1992), Hydrocracking of n-butane and n-heptane over a sulfide nickel erionite catalyst. Applied Catalysis A: General 86, P83-99, describes such catalyst. The C4 hydrocracking may be performed at conditions comprising a temperature of 397-510 ℃ and a pressure of 2-3 MPa.

In one embodiment the C4 hydrocracking catalyst consists of a hydrogenated mordenite with a residual proportion of sodium of less than 1% by weight with respect to the dehydrated mordenite, and an optional binder or comprises sulfided-nickel/H-Erionite1 and the C4 hydrocracking is performed under conditions comprising a temperature between 325 and 450 ℃, a partial hydrogen pressure between 2 and 4 MPa , a molar ratio hydrogen to hydrocarbon feed of 2:1 to 8:1, wherein the number of moles of the hydrocarbon feed is based on the average molecular weight of the hydrocarbon feed and a VVH of 0.5 to 5 h^{-1}.

Relationship between steps a) and b)

Generally, the pressure of the C4 hydrocracking is higher than the pressure of the first hydrocracking. In some preferred embodiments, the C4 hydrocracking is performed without compressing or expanding the first hydrocracking product stream. This is advantageous for better heat integration and is more energy efficient by not requiring a compressing unit or an expanding unit.

Step a) and step b) may be performed in different reactors. However, more preferably, step a) and step b) are performed in a single reactor, as described below.

According to the present invention, the first hydrocracking product stream is directly subjected to the C4 hydrocracking without a separation step. Therefore, steps a) and b) can be performed in a single reactor. The use of a single reactor is advantageous since the reactor will have a better operability and less flow streams. Further, the single reactor has a lower capital expenditure (CAPEX) than two reactors. The single reactor is beneficial for better heat utility and heat integration. The heat generated by the first hydrocracking may be used to heat the C4 hydrocracking catalyst. By having only one reactor, the utilty cost is reduced.

The first hydrocracking catalyst and the C4 hydrocracking catalyst may be arranged in the single reactor in various configurations as long as more first hydrocracking occurs earlier in the process and more C4 hydrocracking occurs later in the process.

Preferably, steps (a) and (b) are performed in a single reactor having a first catalyst layer comprising the first hydrocracking catalyst and a last catalyst layer comprising the C4 hydrocracking catalyst. The first catalyst layer and the last catalyst layer are herein meant that the first catalyst layer is the catalyst layer closest to the inlet of the reactor and the last catalyst layer is the catalyst layer closest to the outlet of the reactor. The reactor may comprise further catalyst layers between the first catalyst layer and the last catalyst layer, each of which comprising the first hydrocracking catalyst and/or the C4 hydrocracking catalyst.

The first catalyst layer comprising the first hydrocracking catalyst and the last catalyst layer comprising the C4 hydrocracking catalyst may be in the form of a continuous dense packing (or sock loading) of the C4 hydrocracking catalyst and the first hydrocracking catalyst directly on

top of and in contact with the C4 hydrocracking catalyst. Alternatively, the two catalysts may be in two separately spaced beds within the same reactor with a space between them.

In some embodiments, the single reactor comprises a bed comprising both the first hydrocracking catalyst and the C4 hydrocracking catalyst. In this case, the proportion of the C4 hydrocracking catalyst at the end of the bed is higher than the proportion of the C4 hydrocracking catalyst at the beginning of the bed.

Preferably, the temperature for the C4 hydrocracking is higher than the temperature for the first hydrocracking. This is particularly advantageous when the steps a) and b) are performed in a single reactor. The heat generated in the section of the reactor for the first hydrocracking can be used in the section of the reactor for the C4 hydrocracking. Accordingly, interbed cooling is minimized.

step c)

Separations of the C4 hydrocracking product stream are possible. The separations 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. Preferably, C2 and C3 are separated out from the C4 hydrocracking product stream.

Preferably, the process of the invention further comprises the step of c) separating the C4 hydrocracking product stream to provide at least a light hydrocarbon stream comprising at least C2 and C3, a middle hydrocarbon stream comprising C4 and/or C5 and a heavy hydrocarbon stream comprising at least 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. Preferably, part or all of the middle hydrocarbon stream is recycled back to the first hydrocracking and/or the C4 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 recycled 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 recycled 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 recycled 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 recycled is at most 10 wt%, more preferably 5 wt%.

The heavy hydrocarbon stream comprises at least C6+. Preferably, the heavy hydrocarbon stream is subjected to a second hydrocracking as described below. 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.

H2 may be separated from the C4 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 C4 hydrocracking product stream before the separation between the light, middle and heavy hydrocarbon streams.

<u>more than one middle hydrocarbon stream</u>

In some embodiments, the entire middle hydrocarbon stream is recycled back to the first hydrocracking and/or the C4 hydrocracking. 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 c) in the form of one stream or a plurality of streams. Accordingly, in some embodiments, the middle hydrocarbon stream is provided by step c) 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 boiling point range 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 C4 hydrocracking in step b).

In some preferred embodiments, at least part of C5 hydrocarbon in the middle hydrocarbon stream is recycled back to the first hydrocracking of step a). In these embodiments, the unconverted C5 in the C4 hydrocracking product stream is recycled back to the first hydrocracking, which increases the yield of C2 and C3. The recycling of the C5 to the first hydrocracking rather than the C4 hydrocracking is advantageous for lower methane make. The coking of the C4 hydrocracking catalyst may also be reduced.

In some preferred embodiments, at least part of C4 hydrocarbon in the middle hydrocarbon stream is recycled back to the C4 hydrocracking of step b). In these embodiments, the unconverted C4 in the C4 hydrocracking product stream is recycled back to the C4 hydrocracking, which increases the yield of C2 and C3. It is possible to recycle back only normal C4 (nC4) or iso C4 (iC4).

<u>various separations</u>

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.

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 preferably recycled back to the C4 hydrocracking in step b). 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 preferably recycled back to the C4 hydrocracking in step b). 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 C4 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.

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 is preferably recycled back to the first hydrocracking in step a) and part or all of the C4 is preferably recycled back to the C4 hydrocracking in step b). 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 C4 hydrocracking in step b) 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 preferably recycled back to the C4 hydrocracking in step b). 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 preferably recycled back to the first hydrocracking in step a) and part or all of the nC4 is preferably recycled back to the C4 hydrocracking in step b). The remainder of the nC4 may be 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 preferably recycled back to the first hydrocracking in step a).

In all cases, all of the C5 in the middle hydrocarbon stream is preferably recycled back to the first hydrocracking or to the C4 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

Part of C4 hydrocarbon in the C4 hydrocracking product 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 C4 hydrocracking product stream may e.g. be subjected to isomerization to obtain i-butane or to dehydrogenation to obtain n-butene and butadiene.

Iso-butane in the C4 hydrocracking product stream 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).

step d)

In some preferred embodiments, the heavy hydrocarbon stream obtained by step c) is subjected 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.

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.

The second hydrocracking process is a hydrocracking process suitable for converting a complex 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 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-% 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.

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.

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}.

Preferably, the molar ratio of hydrogen to hydrocarbon species (H_2/HC molar ratio) is 1:1 – 4:1, more preferably 1:1 – 2:1.

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 SiO_4 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 alimuna 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 (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.

<u>first hydrocracking</u>

As mentioned above, 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.

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 pressu re 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 (SiO_2) to alumina (Al_2O_3) 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 preferab ly 300-425 °C, more preferably 300-400 °C.

second hydrocracking product stream

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

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

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

Alternatively, the C4- may be separated from the second hydrocracking product stream to be recycled back to the separation of step c).

preferred embodiments

In some particularly preferred embodiments, the process of the invention further comprises the steps of c) separating the first hydrocracking product stream to provide at least a light hydrocarbon stream comprising at least C2 and C3, a middle hydrocarbon stream comprising C4 and/or C5 and a heavy hydrocarbon stream comprising at least C6+; and

d) subjecting the heavy hydrocarbon stream to a second hydrocracking step in the presence of a second hydrocracking catalyst to produce a second hydrocracking product stream, wherein the second hydrocracking is more severe than the first hydrocracking,

wherein

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 c) involves separating between the C4 of the middle hydrocarbon stream and the C5 of the middle hydrocarbon stream,
wherein at least part of the C4 is recycled back to the C4 hydrocracking in step b); and
wherein at least part of the C5 is recycled back to the first hydrocracking in step a).

System

In a further aspect, the present invention also relates to a process installation suitable for 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 C2 and C3 hydrocarbons, 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); and
- a C4 hydrocracking unit (115) arranged for performing C4 hydrocracking of the first hydrocracking product stream (106), optimized for converting C4 hydrocarbons into C3 hydrocarbons in the presence of a C4 hydrocracking catalyst to produce a C4 hydrocracking product stream (116).

The system (100) according to the invention may further comprise

- a separation unit (102) for separating the C4 hydrocracking product stream (116) 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+.

The system (100) according to the invention may further comprise

- a second hydrocracking unit (103) arranged for performing second hydrocracking of the heavy hydrocarbon stream (112) in the presence of a second hydrocracking catalyst to produce a second hydrocracking product stream (114) comprising BTX.

The system (100) according to the invention may further be arranged for recycling back at least part of the middle hydrocarbon stream (108) to the first hydrocracking unit (101).

The system (100) according to the invention may further be arranged for recycling back at least part of the middle hydrocarbon stream (108) to the C4 hydrocracking unit (115).

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 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 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 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 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 arranged for processing the part (108) of the middle hydrocarbon stream which is not recycled back to the first hydrocracking unit (101) or the C4 hydrocracking unit. The C4 processing unit may be formed of one or more processing units. For example, the C4 processing unit 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 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 C4 hydrocracking unit 115, a separation unit 102 and a second hydrocracking unit 103.

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 C4 hydrocracking unit 115, which produces a C4 hydrocracking product stream 116. The C4 hydrocracking product stream 116 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 C4 and C5 and the separation between the middle hydrocarbon stream 108 and the heavy hydrocarbon stream 112 is performed to separate C5 and C6. In this case, the light hydrocarbon stream 107 consists of C4-, the middle hydrocarbon stream 108 consists of C5 and the heavy hydrocarbon stream 112 consists of C6+.

The light hydrocarbon stream 107 of C4- is obtained as a final product or subjected to suitable further steps (not shown).

The heavy hydrocarbon stream 112 of C6+ is subjected to the second hydrocracking unit 103, which produces a second hydrocracking product stream 114 comprising BTX.

The middle hydrocarbon stream 108 (C5) is recycled back to the first hydrocracking unit 101. Due to the recycling of the middle hydrocarbon stream 108 from the separation unit 102 to the first hydrocracking unit 101, the amount of C2-C3 in the light hydrocarbon stream 107 is increased.

Figure 2 illustrates a further embodiment 200 of the system of the invention. Figure 2 is identical to Figure 1 except that the system is arranged for recycling back two streams from the

separation unit 102. In this embodiment, the separation unit 102 produces a light stream comprising C3-; a first middle stream 108A comprising C4; a second middle stream 108B comprising C5 and a heavy stream comprising C6+. The first middle stream 108A (C4) is recycled back to the C4 hydrocracking unit 115. The second middle stream 108B (C5) is recycled back to the first hydrocracking unit 101. A further difference in Figure 2 with respect to Figure 1 is that the second hydrocracking unit 103 produces a second hydrocracking product stream 114 which is separated into a stream 117 comprising BTX and a stream 111 comprising C4- which is recycled back to the C4 hydrocracking unit 115.

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 (SiO_2/Al_2O_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 ºC 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 ºC. 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 ºC	400 ºC	425 ºC	450 ºC
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).

It can therefore be concluded that a higher selectivity can be achieved by operating at a lower temperature.

Example 2

A feed consisting of a normal paraffin was subjected to hydrocracking in order to determine the influence of hydrocarbon chain length to the extent of conversion. 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 (SiO_2/Al_2O_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 ºC 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 300 and 500 ºC. 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 2: Single-pass conversion of normal paraffins

Feed component	300 ºC	350 ºC	375 ºC	400 ºC	425 ºC	450 ºC	500 ºC
n-Pentane			51.03	67.74	82.70	92.82	
n-Hexane		92.76	96.35	98.20	98.96	99.67	
n-Heptane	92.76	99.10	99.51	99.73	99.90	99.98	100

n-Octane		99.89					100

The conversion level at different reactor temperatures is provided in Table 2. The conversion level was defined as ((n-paraffin effluent concentration in wt% - 100) / 100). By comparing the results in Table 2, it was observed that when the chain length of the normal paraffin is reduced, the extent of conversion is reduced at a similar temperature. Alternatively, increased reaction temperatures are required to achieve sufficient conversion levels for normal paraffins with shorter chain length. By interpolation of the data presented in Table 2, the temperature required to achieve 80% conversion could be estimated for n-pentane, n-hexane and n-octane. The estimated reaction temperatures are depicted in Figure 3. Extrapolation of the data confirms that significantly higher reaction temperatures are required to achieve sufficient conversion of n-butane.

As illustrated by Example 1, the feed components that are to be exposed to these higher temperatures should be minimized to achieve high selectivities. This could be achieved by sending the butanes and pentanes to a dedicated hydrocracker optimized for converting C4 to C3 instead of subjecting them to second hydrocracking having severe conditions.

CLAIMS

1. A process for producing C2 and C3 hydrocarbons, comprising
a) subjecting a mixed hydrocarbon stream to first hydrocracking in the presence of a first hydrocracking catalyst to produce a first hydrocracking product stream; and
b) subjecting the first hydrocarbon product stream to C4 hydrocracking optimized for converting C4 hydrocarbons into C3 hydrocarbons in the presence of a C4 hydrocracking catalyst to obtain a C4 hydrocracking product stream comprising C2 and C3 hydrocarbons.

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 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.

4. The process according to any one of the preceding claims, wherein the C4 hydrocracking catalyst comprises a mordenite or an erionite.

5. The process according to any one of the preceding claims, wherein the C4 hydrocracking catalyst consists of a mordenite and an optional binder or comprises sulfided-nickel/H-Erionite1 and the C4 hydrocracking is performed under conditions comprising a temperature between 325 and 450 °C, a partial hydro gen pressure between 2 and 4 MPa, a molar ratio hydrogen to hydrocarbon feed of 2:1 to 8:1, wherein the number of moles of the hydrocarbon feed is based on the average molecular weight of the hydrocarbon feed and a VVH of 0.5 to 5 h^{-1}.

6. The process according to any one of the preceding claims, wherein the C4 hydrocracking is performed without compressing or expanding the first hydrocracking product stream.

7. The process according to any one of the preceding claims, wherein steps (a) and (b) are performed in a single reactor having a first catalyst layer comprising the first hydrocracking catalyst and a last catalyst layer comprising the C4 hydrocracking catalyst.

8. The process according to any one of the preceding claims, wherein steps (a) and (b) are performed in a single reactor comprising a layer comprising both the first hydrocracking catalyst and the C4 hydrocracking catalyst, wherein the proportion of the C4 hydrocracking catalyst at the end of the bed is higher than the proportion of the C4 hydrocracking catalyst at the beginning of the bed.

9. The process according to any one of the preceding claims, wherein the temperature for the C4 hydrocracking is higher than the temperature for the first hydrocracking.

10. 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℃.

11. The process according to any one of the preceding claims, further comprising the step of c) separating the C4 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.

12. The process according to claim 11, further comprises the step of d) 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.

13. The process according to claim 11 or 12, wherein at least part of C5 hydrocarbon in the middle hydrocarbon stream is recycled back to the first hydrocracking of step a).

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 C2-C3 hydrocarbons in the C4 hydrocracking product stream is at least 60 wt%.

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