

Title: Process for converting hydrocarbons into olefins.

The present invention relates to a process for converting hydrocarbons, e.g. naphtha into olefins and preferably also into BTX. More in detail,
5 the present invention relates to an integrated process based on a combination of hydrocracking, thermal and catalytic dehydrogenation to convert hydrocarbons into olefins and preferably also into BTX.

US Patent No. 4,137,147 relates to a process for manufacturing ethylene and propylene from a charge having a distillation point lower than about
10 360 DEG C. and containing at least normal and iso-paraffins having at least 4 carbon atoms per molecule, wherein: the charge is subjected to a hydrogenolysis reaction in a hydrogenolysis zone, in the presence of a catalyst, (b) the effluents from the hydrogenolysis reaction are fed to a separation zone from which are discharged (i) from the top, methane and possibly hydrogen, (ii) a fraction consisting essentially of
15 hydrocarbons with 2 and 3 carbon atoms per molecule, and (iii) from the bottom, a fraction consisting essentially of hydrocarbons with at least 4 carbon atoms per molecule, (c) only the fraction consisting essentially of hydrocarbons with 2 and 3 carbon atoms per molecule is fed to a steam-cracking zone, in the presence of steam, to transform at least a portion of the hydrocarbons with 2 and 3 carbon atoms
20 per molecule to monoolefinic hydrocarbons; the fraction consisting essentially of hydrocarbons with at least 4 carbon atoms per molecule, obtained from the bottom of the separation zone, is supplied to a second hydrogenolysis zone where it is treated in the presence of a catalyst, the effluent from the second hydrogenolysis zone is supplied to a separation zone to discharge, on the one hand, hydrocarbons with at
25 least 4 carbon atoms per molecule which are recycled at least partly to the second hydrogenolysis zone, and, on the other hand, a fraction consisting essentially of a mixture of hydrogen, methane and saturated hydrocarbons with 2 and 3 carbon atoms per molecule; a hydrogen stream and a methane stream are separated from the mixture and there is fed to the steam-cracking zone the hydrocarbons of the
30 mixture with 2 and 3 carbon atoms, together with the fraction consisting essentially of hydrocarbons with 2 and 3 carbon atoms per molecule as recovered from the separation zone following the first hydrogenolysis zone. At the outlet of the steam-cracking zone are thus obtained, in addition to a stream of methane and hydrogen and a stream of paraffinic hydrocarbons with 2 and 3 carbon atoms per molecule,

olefins with 2 and 3 carbon atoms per molecule and products with at least 4 carbon atoms per molecule. According to this US Patent No. 4,137,147 all C4+ compounds are further processed in the second hydrogenolysis zone.

WO2010/111199 relates to a process for producing olefins comprising the steps of: (a) feeding a stream comprising butane to a dehydrogenation unit for converting butane to butenes and butadiene to produce a dehydrogenation unit product stream; (b) feeding the dehydrogenation unit product stream to a butadiene extraction unit to produce a butadiene product stream and a raffinate stream comprising butenes and residual butadiene; (c) feeding the raffinate stream to a selective hydrogenation unit for converting the residual butadiene to butenes to produce a selective hydrogenation unit product stream; (d) feeding the selective hydrogenation unit product stream to a deisobutenizer for separating isobutane and isobutene from the hydrogenation unit product stream to produce an isobutane/isobutene stream and a deisobutenizer product stream; (e) feeding the deisobutenizer unit product stream and a feed stream comprising ethylene to an olefin conversion unit capable of reacting butenes with ethylene to form propylene to form an olefin conversion unit product stream; and (f) recovering propylene from the olefin conversion unit product stream.

WO2013/182534 in the name of the present applicant relates to a process for producing chemical grade BTX from a mixed feedstream comprising C5-C12 hydrocarbons by contacting said feedstream in the presence of hydrogen with a catalyst having hydrocracking/hydrodesulphurisation activity.

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

Light crude oil cuts such as naphtha and some gas oils can be used for producing light olefins and single ring aromatic compounds via processes such as steam cracking in which the hydrocarbon feed stream is evaporated and diluted with steam then exposed to a very high temperature (750°C to 900°C) in short residence time (<1 second) furnace (reactor) tubes. In such a process the hydrocarbon molecules in the feed are transformed into (on average) shorter molecules and molecules with lower hydrogen to carbon ratios (such as olefins) when compared to the feed molecules. This process also generates hydrogen as a useful by-product

and significant quantities of lower value co-products such as methane and C9+ Aromatics and condensed aromatic species (containing two or more aromatic rings which share edges).

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

An aspect of such a combination of crude oil distillation and steam cracking of the lighter distillation cuts is the capital and other costs associated with the fractional distillation of crude oil. Heavier crude oil cuts (i.e. those boiling beyond ~350°C) are relatively rich in substituted aromatic species and especially substituted condensed aromatic species (containing two or more aromatic rings which share edges) and under steam cracking conditions these materials yield substantial quantities of heavy by products such as C9+ aromatics and condensed aromatics. Hence, a consequence of the conventional combination of crude oil distillation and steam cracking is that a substantial fraction of the crude oil, for example 50% by weight, is not processed via the steam cracker as the cracking yield of valuable products from heavier cuts is not considered to be sufficiently high.

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

as with most petrochemicals processes, the capital cost of these units typically scales with throughput raised to the power of 0.6 or 0.7. Consequently, the capital costs of a small scale hydro-cracking unit are normally considered to be too high to justify such an investment to process steam cracker heavy by-products.

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

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

US 2012/0125813, US 2012/0125812 and US 2012/0125811 relate to a process for cracking a heavy hydrocarbon feed comprising a vaporization step, a distillation step, a coking step, a hydroprocessing step, and a steam cracking step.
30 For example, US 2012/0125813 relates to a process for steam cracking a heavy hydrocarbon feed to produce ethylene, propylene, C4 olefins, pyrolysis gasoline, and other products, wherein steam cracking of hydrocarbons, i.e. a mixture of a hydrocarbon feed such as ethane, propane, naphtha, gas oil, or other hydrocarbon fractions, is a non-catalytic petrochemical process that is widely used to produce

olefins such as ethylene, propylene, butenes, butadiene, and aromatics such as benzene, toluene, and xylenes.

US 2009/0050523 relates to the formation of olefins by thermal cracking in a pyrolysis furnace of liquid whole crude oil and/or condensate derived from natural gas in a manner that is integrated with a hydrocracking operation.

US 2008/0093261 relates to the formation of olefins by hydrocarbon thermal cracking in a pyrolysis furnace of liquid whole crude oil and/or condensate derived from natural gas in a manner that is integrated with a crude oil refinery.

Steam cracking of naphtha results in a high yield of methane and a relatively low yield in propylene (propylene/ethylene ratio, P/E ratio, of about 0.5) as well as a relatively low yield of BTX, BTX is also accompanied by co-boilers of the valuable components benzene, toluene and xylenes which do not allow recovering those on-spec by simple distillation but by more elaborate separation techniques such as solvent extraction.

FCC technology applied to naphtha feed does result in a much higher relative propylene yield (propylene/ethylene ratio of 1-1.5) but still has relatively large losses to methane and cycle oils in addition to the desired aromatics (BTX).

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

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 generally consists of a blend of C3-C4 hydrocarbons i.e. a mixture of C3 and C4 hydrocarbons.

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

An object of the present invention is to provide a method for converting naphtha into olefins and preferably also into BTX.

Another object of the present invention is to provide a method having high carbon efficiency by much lower methane production and a minimum of heavy by-products.

The present invention thus relates to a process for converting a hydrocarbon feedstock into olefins and preferably also into BTX, the converting process comprising the following steps of:

feeding a hydrocarbon feedstock to a first hydrocracking unit,
feeding the effluent from said first hydrocracking unit to a first separation section,

separating said effluent in said first separation section into one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising ethane, a stream comprising propane, a stream comprising butanes, a stream comprising C1-minus, a stream comprising C2-minus, a stream comprising C3-minus, a stream comprising C4-minus, a stream comprising C1-C2, a stream comprising C1-C3, a stream comprising C1-C4, a

stream comprising C2-C3, a stream comprising C2-C4, a stream comprising C3-C4 and a stream comprising C5+;

feeding at least one stream chosen from the group of a stream comprising propane, a stream comprising butanes, a stream comprising C3-minus, a stream comprising C4-minus, a stream comprising C2-C3, a stream comprising C1-C3, a stream comprising C1-C4, a stream comprising C2-C3, a stream comprising C2-C4 and a stream comprising C3-C4 to at least one dehydrogenation unit chosen from the group of a butanes dehydrogenation unit, a propane dehydrogenation unit, a combined propane-butanes dehydrogenation unit, or a combination of units thereof,

feeding from said first separation section at least one stream chosen from the group of a stream comprising ethane, a stream comprising C1-C2 and a stream comprising C2-minus to a steam cracking unit and/or a second separation section.

feeding the effluent(s) from said steam cracking unit and at least one dehydrogenation unit to a said second separation section.

According to the present invention the separation of the upstream first separation section is simplified to allow ethane or ethane and methane to be separated as a single stream directly going together with propane and/or butanes to a propane dehydrogenation unit or the combined propane/dehydrogenation unit ("PDH/BDH") rather than being further separated. In other words the present method allows for a less 'perfect' separation with ethane and/or methane being allowed to slip with or being routed into the C3-C4 intermediate product(s) fed to the dehydrogenation units. In these dehydrogenation units methane can be regarded as inert and ethane is hardly dehydrogenated, and both will reduce or eliminate the amount of dilution steam normally applied in these units to improve selectivity and prevent coking of the catalyst. The sentence "at least one dehydrogenation unit chosen from the group of a butanes dehydrogenation unit and a propane dehydrogenation unit, or a combination thereof" includes embodiments of separate propane and butanes dehydrogenation units, as well as the combined propane/dehydrogenation unit. The hydrogen content of the dehydrogenation feed should preferably contain less than 1 to 2 vol. % of hydrogen. This gives opportunities particularly when applying non-cryogenic separation technology to

specifically remove hydrogen whilst the purity of the C2-C4 product stream is much less important when compared to a typical gas plant separation process.

The present process thus comprises feeding at least one stream chosen from the group of a stream comprising ethane, a stream comprising C1-C2 and a stream comprising C2-minus to steam cracking unit and/or the second separation section. Steam cracking of ethane is the most common ethane dehydrogenation process.

According to the present invention the in the at least one dehydrogenation unit carried out dehydrogenating process is a catalytic process and said steam cracking process is a thermal cracking process. This means that the effluent from the first separation section is further processed in the combination of a catalytic process, i.e. a dehydrogenation process, and a thermal process, i.e. a steam cracking process.

It is also preferred to feed a stream comprising C1-minus unit to the second separation section.

The stream comprising C5+ is preferably fed to a second hydrocracking unit, wherein the effluent from the second hydrocracking unit is separated into a stream comprising C4-, a stream comprising unconverted C5+, and a stream comprising BTX. The stream comprising C4-minus is preferably returned to the first separation section.

The present process thus preferably comprises feeding the stream comprising C5+ to a second hydrocracking unit. An extra advantage is the possibility to integrate the re-heating of the C5+ feed to the second hydrocracking unit coming from the first hydrocracking unit with the hot effluent.

The present second hydrocracking unit can be identified here as a "gasoline hydrocracking unit" or "GHC reactor". As used herein, the term "gasoline hydrocracking unit" or "GHC" refers to an unit for performing a hydrocracking process suitable for converting a complex hydrocarbon feed that is relatively rich in aromatic hydrocarbon compounds -such as refinery unit-derived light-distillate including, but not limited to, reformer gasoline, FCC gasoline and pyrolysis gasoline (pygas)- to LPG and BTX, wherein said process is optimized to keep one aromatic ring intact of the aromatics comprised in the GHC feed stream, but to remove most of the side-chains from said aromatic ring. Accordingly, the main product produced by gasoline hydrocracking is BTX and the process can be optimized to provide a BTX

mixture which can simply be separated into chemical-grade benzene, toluene and mixed xylenes. Preferably, the hydrocarbon feed that is subject to gasoline hydrocracking comprises refinery unit-derived light-distillate. More preferably, the hydrocarbon feed that is subjected to gasoline hydrocracking preferably does not
5 comprise more than 1 wt.-% of hydrocarbons having more than one aromatic ring. Preferably, the gasoline hydrocracking conditions include a temperature of 300-580 °C, more preferably of 450-580 °C and even more preferably of 470-550 °C. Lower temperatures must be avoided since hydrogenation of the aromatic ring becomes favourable. However, in case the catalyst comprises a further element that reduces
10 the hydrogenation activity of the catalyst, such as tin, lead or bismuth, lower temperatures may be selected for gasoline hydrocracking; see e.g. WO 02/44306 A1 and WO 2007/055488. In case the reaction temperature is too high, the yield of LPG (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
15 increase the reactor temperature gradually over the life time of the catalyst to maintain the hydrocracking reaction 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
20 regenerated) the temperature preferably is selected at the higher end of the hydrocracking temperature range.

Preferably, the gasoline hydrocracking of a hydrocarbon feed stream is performed at a pressure of 0.3-5 MPa gauge, more preferably at a pressure of 0.6-3 MPa gauge, particularly preferably at a pressure of 1-2 MPa gauge and most
25 preferably at a pressure of 1.2-1.6 MPa gauge. By increasing reactor pressure, conversion of C5+ non-aromatics can be increased, but this 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 methyl
30 cyclopentane, are not fully hydrocracked, there is an optimum in the purity of the resultant benzene at a pressure of 1.2-1.6 MPa.

Preferably, gasoline hydrocracking of a hydrocarbon feed stream is performed at a Weight Hourly Space Velocity (WHSV) of 0.1-20 h⁻¹, more preferably at a Weight Hourly Space Velocity of 0.2-10 h⁻¹ and most preferably at a Weight

Hourly Space Velocity of 0.4-5 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 chemical grade benzene, toluene and mixed xylenes 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 benzene.

Accordingly, preferred gasoline hydrocracking conditions thus include a temperature of 450-580 °C, a pressure of 0.3-5 MPa gauge and a Weight Hourly Space Velocity of 0.1-20 h⁻¹. More preferred gasoline hydrocracking conditions include a temperature of 470-550 °C, a pressure of 0.6-3 MPa gauge and a Weight Hourly Space Velocity of 0.2-10 h⁻¹. Particularly preferred gasoline hydrocracking conditions include a temperature of 470-550 °C, a pressure of 1-2 MPa gauge and a Weight Hourly Space Velocity of 0.4-5 h⁻¹.

The first hydrocracking unit can be identified here as a "feed hydrocracking unit" or "FHC reactor". As used herein, the term "feed hydrocracking unit" or "FHC" refers to a unit for performing a hydrocracking process suitable for converting a complex hydrocarbon feed that is relatively rich in naphthenic and paraffinic hydrocarbon compounds -such as straight run cuts including, but not limited to, naphtha- to LPG and alkanes. Preferably, the hydrocarbon feed that is subject to feed hydrocracking comprises naphtha. Accordingly, the main product produced by feed hydrocracking is LPG that is to be converted into olefins (i.e. to be used as a feed for the conversion of alkanes to olefins). The FHC process may be optimized to keep one aromatic ring intact of the aromatics comprised in the FHC feed stream, but to remove most of the side-chains from said aromatic ring. In such a case, the process conditions to be employed for FHC are comparable to the process conditions to be used in the GHC process as described herein above. Alternatively, the FHC process can be optimized to open the aromatic ring of the aromatic hydrocarbons comprised in the FHC feed stream. This can be achieved by modifying the GHC process as described herein by increasing the hydrogenation activity of the catalyst, optionally in combination with selecting a lower process temperature, optionally in combination with a reduced space velocity. In such a case, preferred feed hydrocracking conditions thus include a temperature of 300-550 °C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-20 h⁻¹. More

preferred feed hydrocracking conditions include a temperature of 300-450 °C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-10 h⁻¹. Even more preferred FHC conditions optimized to the ring-opening of aromatic hydrocarbons include a temperature of 300-400 °C, a pressure of 600-3000 kPa gauge and a Weight Hourly Space Velocity of 0.2-5 h⁻¹.

In case of the presence of a stream comprising unconverted C5+ coming from second hydrocracking unit it is preferred to combine that stream with the naphtha feed and feed the combined stream thus obtained to the first hydrocracking unit.

According to a preferred embodiment of the present invention it is preferred to pre-treat the naphtha feed by separating the naphtha feed into a stream having a high aromatics content and a stream having a low aromatics content, and feeding the stream having a low aromatics content into the first hydrocracking unit, further comprising feeding the stream having a high aromatics content to the second hydrocracking unit.

According to another embodiment of the present process it is preferred to feed the stream comprising butanes to said butanes dehydrogenation unit and to feed a stream chosen from the group of a stream comprising C2-C3, a stream comprising C1-C3, a stream comprising C3 minus and a stream comprising C3 to said propane dehydrogenation unit.

In the process according to the present invention a stream chosen from the group of a stream comprising C3-C4, a stream comprising C2-C4, a stream comprising C1-C4 and a stream comprising C4 minus is preferably fed to said combined butanes and propane dehydrogenation unit.

The effluent from the steam cracking unit is preferably fed to the second separation unit.

According to a preferred embodiment of the present invention it is preferred to separate any effluent from the steam cracker unit, i.e. ethane dehydrogenation unit, the first separation section and the at least one propane, butanes or combined propane-butanes dehydrogenation unit in the second separation section into one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising C3, a stream comprising C2=, a stream comprising C3=, a stream comprising C4mix, a stream comprising C5+, a stream comprising C2 and a stream comprising C1-minus.

The stream comprising C2 is preferably fed to the gas steam cracker unit, i.e. ethane dehydrogenation unit.

The stream comprising C5+ is preferably fed to the first hydrocracking unit and/or the second hydrocracking unit.

5 According to a preferred embodiment of the present invention it is preferred to feed the stream comprising hydrogen to the first hydrocracking unit and/or the second hydrocracking unit.

In addition it is preferred to feed the stream comprising C1-minus to the first separation section.

10 According to a preferred embodiment the present process further comprises feeding the stream comprising C3 to the propane dehydrogenation unit and /or the combined propane-butane dehydrogenation unit.

The stream comprising hydrogen from the first and/or second separation section is preferably sent to the first and/or hydrocracking unit.

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

20

25

30

temperature and furnace residence time. Light hydrocarbon feeds such as ethane, propane, butanes or light naphtha give product streams rich in the lighter polymer grade olefins, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphtha and gas oil fractions) also give products rich in aromatic hydrocarbons.

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

The term "propane dehydrogenation unit" as used herein relates to a petrochemical process unit wherein a propane feedstream is converted into a product comprising propylene and hydrogen. Accordingly, the term "butane dehydrogenation unit" relates to a process unit for converting a butane feedstream into C₄ olefins. Together, processes for the dehydrogenation of lower alkanes such as propane and butanes are described as lower alkane dehydrogenation process. Processes for the dehydrogenation of lower alkanes are well-known in the art and include oxidative hydrogenation processes and non-oxidative dehydrogenation

processes. In an oxidative dehydrogenation process, the process heat is provided by partial oxidation of the lower alkane(s) in the feed. In a non-oxidative dehydrogenation process, which is preferred in the context of the present invention, the process heat for the endothermic dehydrogenation reaction is provided by external heat sources such as hot flue gases obtained by burning of fuel gas or steam. For instance, the UOP Oleflex process allows for the dehydrogenation of propane to form propylene and of (iso)butane to form (iso)butylene (or mixtures thereof) in the presence of a catalyst containing platinum supported on alumina in a moving bed reactor; see e.g. US 4,827,072. The Uhde STAR process allows for the dehydrogenation of propane to form propylene or of butane to form butylene in the presence of a promoted platinum catalyst supported on a zinc-alumina spinel; see e.g. US 4,926,005. The STAR process has been recently improved by applying the principle of oxydehydrogenation. In a secondary adiabatic zone in the reactor part of the hydrogen from the intermediate product is selectively converted with added oxygen to form water. This shifts the thermodynamic equilibrium to higher conversion and achieve higher yield. Also the external heat required for the endothermic dehydrogenation reaction is partly supplied by the exothermic hydrogen conversion. The Lummus Catofin process employs a number of fixed bed reactors operating on a cyclical basis. The catalyst is activated alumina impregnated with 18-20 wt-% chromium; see e.g. EP 0 192 059 A1 and GB 2 162 082 A. The Catofin process is reported to be robust and capable of handling impurities which would poison a platinum catalyst. The products produced by a butane dehydrogenation process depends on the nature of the butane feed and the butane dehydrogenation process used. Also the Catofin process allows for the dehydrogenation of butane to form butylene; see e.g. US 7,622,623.

The invention will be described in further detail below and in conjunction with the attached drawings in which the same or similar elements are referred to by the same number.

Figure 1 is a schematic illustration of an embodiment of the process of the invention.

Figure 2 is a schematic illustration of another embodiment of the process of the invention.

Figure 3 is a schematic illustration of another embodiment of the process of the invention.

Figure 4 is a schematic illustration of another embodiment of the process of the invention.

Figure 5 is a schematic illustration of another embodiment of the process of the invention.

5 Figure 6 is a schematic illustration of another embodiment of the process of the invention.

Figure 1 is an embodiment of an integrated process 101 based on a combination of hydrocracking, steam cracking and dehydrogenation to convert naphtha into olefins and BTX using different separation units and reduced steam
10 dilution.

Feedstock 42 is sent to hydrocracking unit 6, and its effluent 7 is sent to first separation section 8, 9. Stream 20, mainly comprising C5+ is sent to a hydrocracking unit 10 from which its effluent is sent to separation unit 11, producing stream 19, mainly comprising C4-, and stream 41, mainly comprising BTX. A stream
15 from separation unit 11 can be recycled to the inlet of hydrocracking unit 6 (not shown). Stream 7 is separated into a stream 24, mainly comprising hydrogen, a stream 22, mainly comprising C2, a stream 23, mainly comprising C1, a stream 62, mainly comprising C3-C4 and a stream 20, mainly comprising C5+. Stream 22 is sent to steam cracking unit 14 from which its effluent is separated in second separation
20 section 15, 16 into stream 63, mainly comprising C2=, and stream 35, mainly comprising C2. Stream 35 is recycled to the inlet of steam cracking unit 14. Stream 43, mainly comprising C1-, coming from second separation section 15,16 is sent to first separation section 8, 9. Stream 62, mainly comprising C3-C4 is sent to a combined propane dehydrogenation unit/butane dehydrogenation unit 60 from which
25 its effluent 61 is sent to second separation section 15, 16 producing stream 30, mainly comprising C3=, stream 29, mainly comprising C4 mix, stream 31, mainly comprising C5+ and a stream 33, mainly comprising C3, which stream 33 is recycled to the inlet of unit 60. Stream 31 can be recycled (not shown) to the inlet of hydrocracking unit 6. The hydrogen containing stream 24 coming from first
30 separation section 8, 9 is sent to hydrocracking unit 6, via line 25, and to hydrocracking unit 10, via line 17, respectively. In another preferred embodiment stream 62 mainly comprises C2-C4. Stream 20, coming from first separation section 8, 9, is sent to hydrocracking unit 10 from which its effluent 18 is separated in separation unit 11 into stream 19, mainly comprising C4-, and stream 41, mainly

comprising BTX. The surplus of hydrogen is sent, via line 38, to other chemical processes.

Referring now to the process and apparatus schematically depicted in figure 2, where an integrated process 102 is shown based on a combination of hydrocracking, steam cracking and dehydrogenation to convert naphtha into olefins and BTX using different separation units and reduced steam dilution. In the integrated process 102 ethane is allowed to go to a chosen extent with the C3 in the first separation section. The ethane serves as a diluent in the propane dehydrogenation unit (PDH) and replaces part or all of the traditional steam dilution. The ethane is then separated in the effluent from the propane dehydrogenation unit and further separated in the separation part of the steam cracking unit. From here the ethane is then routed to the steam cracking furnaces. Any ethane that is not going with the C3 stream (depending on separation characteristics/demand or simplification) will go via the C1- effluent from the first separation section to the second separation section.

A hydrocarbon feedstock 42 is sent to a separation unit 2 for separating feed 42 into a stream 3 having a low aromatics content and a stream 4 having a high aromatics content, wherein stream 4 is fed to a hydrocracking unit 10. Stream 3 is also sent to a hydrocracking unit 6. The effluent 7 from hydrocracking unit 6 is sent to a separation unit 50 for separating stream 7 into a stream 52 mainly comprising C1-, a stream 27, mainly comprising C2-C3 and a stream 26, mainly comprising C4. Separation unit 50 also provides a stream 20 mainly comprising C5+, which stream 20 is sent to hydrocracking unit 10. The effluent 18 from hydrocracking unit 10 is sent to separation unit 11 producing stream 19, mainly comprising C4-, a stream 41, mainly comprising BTX and a stream 5, mainly comprising unconverted C5+. Stream 5 is recycled to the inlet of hydrocracking unit 6, preferably before the separation unit 2. Stream 27 is sent to a propane dehydrogenation unit 13 producing an effluent 39, which effluent is separated in second separation section 15, 16. Stream 26 is sent to a butane dehydrogenation unit 12 producing effluent 28, wherein effluent 28 is also separated in second separation section 15, 16. Second separation section 15, 16 provides stream 30, mainly comprising C3=, stream 29, mainly comprising C4 mix, stream 31, mainly comprising C5+, and a stream 33, mainly comprising C3. Stream 33 is recycled to the inlet of propane dehydrogenation unit 13. Stream 31 can be combined with stream 5 in order to return (not shown) the

stream thus combined to the inlet of hydrocracking unit 6. Stream 52 is sent to second separation section 15,16, producing stream 51, mainly comprising C1, stream 34, mainly comprising C2=, stream 37, mainly comprising hydrogen and stream 35, mainly comprising C2. Stream 35 is sent to the inlet of a steam cracking unit 14 and its effluent thereof is also sent to second separation section 15, 16. Stream 37, mainly comprising hydrogen is sent to hydrocracking unit 6, via line 25, and to hydrocracking unit 10, via line 17, respectively. The surplus of hydrogen is sent, via line 38, to other chemical processes.

Referring now to the process and apparatus 103 schematically depicted in figure 3, there is shown another embodiment of an integrated process based on a combination of hydrocracking, steam cracking and dehydrogenation to convert naphtha into olefins and BTX using different separation units and reduced steam dilution. In the integrated process 103 a combined C2, C3 and C4 cut is obtained in the first separation section that will be processed as one feed in a combined PDH/BDH process. C3 and C4 will be co-reacted/converted to propylene and butenes whilst the ethane again acts mainly as a diluent.

Hydrocarbon feedstock 42, e.g. naphtha, is sent to hydrocracking unit 6 producing effluent stream 7. Effluent stream 7 is separated in separation unit 50 into a stream 20, mainly comprising C5+, a stream 62, mainly comprising C2-C4, and a stream 52, mainly comprising C1-. Stream 62 is sent to a combined propane dehydrogenation/butane dehydrogenation unit 60. Effluent stream 61 from unit 60 is sent to second separation section 15,16 producing a stream 30, mainly comprising C3=, stream 29, mainly comprising C4 mix, stream 31, mainly comprising C5+, stream 33, mainly comprising C3. Stream 33 is recycled to the inlet of unit 60. Stream 52, coming from separation unit 50 is sent to second separation section 15,16 and separated into stream 51, mainly comprising C1, stream 34, mainly comprising C2=, stream 37, mainly comprising hydrogen and stream 35, mainly comprising C2. Stream 35 is sent to the inlet of steam cracking unit 14 and its effluent is separated in second separation section 15, 16. Stream 37 provides hydrogen, via line 25, to the first hydrocracking unit 6 and, via line 17, to the second hydrocracking unit 10, respectively. Stream 20, coming from separation unit 50, is sent to hydrocracking unit 10 from which its effluent 18 is separated in separation unit 11 into stream 19, mainly comprising C4-, and stream 41, mainly comprising BTX. Although not shown, a stream of unconverted C5+ coming from separation unit

11 can be recycled to the inlet of hydrocracking unit 6, analogous to figure 1. The same applies for the recycle of stream 31. The surplus of hydrogen is sent, via line 38, to other chemical processes.

According to another embodiment (not shown) the separation in separation unit 50 is carried out such that stream 52 now mainly comprises hydrogen-C1 and stream 62 now mainly comprises C1-C4. Stream 52 is directed to second separation section 15, 16 and stream 62 to unit 60, i.e. a combined propane dehydrogenation/butane dehydrogenation unit. The cut point in the first separation section is now around methane, i.e. ethane and some of the methane is allowed to slip into the C3 or combined C3 and C4 stream. Again the ethane and methane act as a diluent and allow reducing or even replacing the normal steam dilution. In this case the demethanizing and hydrogen separation can also be placed only in the first separation section with a C1- stream coming from the steam cracker separation end going into this first separation section.

Figure 4 is another embodiment of the present process 104 based on a combination of hydrocracking, steam cracking and dehydrogenation to convert naphtha into olefins and BTX using different separation units and reduced steam dilution. In the integrated process 104 the methane and hydrogen separation is now only located in the first separation section.

Feedstock 42 is sent to hydrocracking unit 6 and the hydrocracked effluent 7 is sent to first separation section 8, 9 producing stream 20, mainly comprising C5+, stream 26, mainly comprising C4 and stream 27, mainly comprising C2-C3. Stream 20 is sent to hydrocracking unit 10 and its effluent is separated in separation unit 11 into stream 41, mainly comprising BTX, and stream 19, mainly comprising C4-. Unconverted C5+ can be recycled from separation unit 11 to hydrocracking unit 6. Stream 27 is sent to a propane dehydrogenation unit 13 and stream 26 is sent to a butane dehydrogenation unit 12. Effluent 39 is sent to second separation section 15, 16, effluent 28 from unit 12 is also sent to second separation section 15, 16. Second separation section 15, 16 provides stream 30, mainly comprising C3=, stream 29, mainly comprising C4 mix, stream 31, mainly comprising C5+, and stream 33, mainly comprising C3. Stream 33 is recycled to the inlet of unit 13. First separation section 8, 9 provides stream 24, mainly comprising hydrogen, a stream 22, mainly comprising C2, and a stream 23, mainly comprising C1. Stream 22 is sent to steam cracking unit 14 from which its effluent is sent to second separation

section 15, 16. In second separation section 15, 16 a stream 35, mainly comprising C2, is recycled to the inlet of steam cracking unit 14. Stream 63, mainly comprising C2=, is sent to other chemical processes (not shown). Second separation section 15, 16 also provides a stream 43, mainly comprising C1-. Stream 43 is sent to first separation section 8, 9. Hydrogen containing stream 24 is sent to, via line 25, to hydrocracking unit 6, and, via line 17, to hydrocracking unit 10, respectively. Stream 20, coming from first separation section 8, 9, is sent to hydrocracking unit 10 from which its effluent is separated in separation unit 11 into stream 19, mainly comprising C4-, and stream 41, mainly comprising BTX. The surplus of hydrogen is sent, via line 38, to other chemical processes.

Figure 5 shows another embodiment of an integrated process 105 based on a combination of hydrocracking, steam cracking and dehydrogenation to convert naphtha into olefins and BTX using different separation units and reduced steam dilution. In the integrated process 105 the cut point is moved even further to separate the hydrogen in the first separation section and have a combined/un-separated C1-C3 stream going to the propane dehydrogenation unit (PDH). In this embodiment membrane based hydrogen separation techniques might be most applicable to avoid the need for cryogenic separation in the first separation section.

Feedstock 42 is sent to a hydrocracking unit 6 from which its effluent 7 is separated in separation unit 50 into a stream 64, mainly comprising hydrogen, a stream 27, mainly comprising C1-C3, a stream 26, mainly comprising C4 and a stream 20, mainly comprising C5+. Stream 20 is sent to hydrocracking unit 10 and its effluent is further separated in separation unit 11 into stream 19, mainly comprising C4-, and stream 41, mainly comprising BTX. Unconverted C5+ from separation unit 11 can be recycled (not shown) to the inlet of hydrocracking unit 6, analogous to the discussion of Fig 2 above. Stream 27 is sent to a propane dehydrogenation unit 13 from which its effluent 39 is sent to second separation section 15, 16. Stream 26 is sent to a butane dehydrogenation unit 12, from which its effluent 28 is sent to second separation section 15, 16. In second separation section 15, 16 a separation takes place into stream 30, mainly comprising C3=, stream 29, mainly comprising C4 mix, and stream 31 mainly comprising C5+. Second separation section 15, 16 also provides a recycle stream 33, mainly comprising C3, to the inlet of unit 13. In separation unit 15, 16 a separation into stream 37, mainly comprising hydrogen, stream 51, mainly comprising C1, stream 34, mainly comprising C2= takes place,

and a recycle stream 35, mainly comprising C2, to the inlet of steam cracking unit 14 from which its effluent is sent to second separation section 15,16. Hydrogen containing streams 64 and 37 are sent to hydrocracking unit 6, via line 25, and to hydrocracking unit 10, via line 17, respectively. The surplus of hydrogen is sent, via line 38, to other chemical processes.

Figure 6 shows another embodiment of an integrated process 106 based on a combination of hydrocracking, steam cracking and dehydrogenation to convert naphtha into olefins and BTX using different separation units and reduced steam dilution. The integrated process 106 now combines the C3 and C4 components in one single dehydrogenation unit, i.e. a C1-C4 feed stream to a single dehydrogenation reactor. Multi stage membrane separation could be very advantageous here.

Feedstock 42 is sent to hydrocracking unit 6 and its effluent 7 is sent to separation unit 50 and separated into a stream 20, mainly comprising C5+, a stream 64, mainly comprising hydrogen and a stream 63, mainly comprising C1-C4. Stream 20 is sent to hydrocracking unit 10 from which its effluent is sent to separation unit 11 producing stream 19, mainly comprising C4-minus and stream 41, mainly comprising BTX. Stream 19 is recycled to separation unit 50. Stream 63 is sent to a combined propane dehydrogenation/butane dehydrogenation unit 60 from which its effluent 61 is sent to second separation section 15,16 producing stream 30, mainly comprising C3=, stream 29, mainly comprising C4 mix, stream 31, mainly comprising C5+. Recycle stream 33, mainly comprising C3, coming from second separation section 15, 16 is sent to the inlet of unit 60. In second separation section 15,16 there is a separation into stream 37, mainly comprising hydrogen, stream 51, mainly comprising C1, stream 34, mainly comprising C2= and a recycle stream 35, mainly comprising C2. Stream 35 is routed to the inlet of steam cracking unit 14 from which its effluent is separated in second separation section 15, 16. Hydrogen containing streams 64, 37 are sent to hydrocracking unit 6, via line 25, and to hydrocracking unit 10, via line 17, respectively. The surplus of hydrogen is sent, via line 38, to other chemical processes.

Claims

1. A process for converting a hydrocarbon feedstock into olefins and also into BTX, said converting process comprising the following steps of:

feeding a hydrocarbon feedstock to a first hydrocracking unit,
 feeding the effluent from said first hydrocracking unit to a first separation section,
 separating said effluent in said first separation section into one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising ethane, a stream comprising propane, a stream comprising butanes, a stream comprising C1-minus, a stream comprising C2-minus, a stream comprising C3-minus, a stream comprising C4-minus, a stream comprising C1-C2, a stream comprising C1-C3, a stream comprising C1-C4, a stream comprising C2-C3, a stream comprising C2-C4, a stream comprising C3-C4 and a stream comprising C5+;

feeding at least one stream chosen from the group of said stream comprising propane, said stream comprising butanes, said stream comprising C3-minus, said stream comprising C4-minus, said stream comprising C2-C3, said stream comprising C1-C3, said stream comprising C1-C4, said stream comprising C2-C3, said stream comprising C2-C4 and said stream comprising C3-C4 to at least one dehydrogenation unit carrying out a dehydrogenation process being a catalytic process chosen from the group of a butanes dehydrogenation unit, a propane dehydrogenation unit, a combined propane-butenes dehydrogenation unit, or a combination of units thereof,

feeding from said first separation section at least one stream chosen from the group of said stream comprising ethane, said stream comprising C1-C2 and said stream comprising C2-minus to a second separation section,

further comprising separating any effluent from said first separation section and said at least one propane or butanes or combined propane-butenes dehydrogenation unit in said second separation section into one or more streams chosen from the group of a stream comprising hydrogen, a stream comprising methane, a stream comprising C3, a stream comprising C2=, a stream comprising C3=, a stream comprising C4mix, a stream comprising C5+, a stream comprising C2 and a stream comprising C1-minus,

further comprising feeding said stream comprising C2 to a steam cracker unit,
 feeding the effluent(s) from said steam cracking unit and at least one dehydrogenation unit to said second separation section,

further comprising feeding said stream comprising C5+ to a second hydrocracking unit,

further comprising separating the effluent from said second hydrocracking unit into a stream comprising C4-minus, a stream comprising unconverted C5+, and a stream comprising BTX, especially

further comprising feeding said stream comprising C4-minus to said first separation section, especially

further comprising combining said stream comprising unconverted C5+ with said hydrocarbon feedstock and feeding the combined stream thus obtained to said first hydrocracking unit.

2. A process according to claim 1, further comprising feeding a stream comprising C1-minus to said second separation section.
3. A process according to anyone or more of claims 1-2, further comprising pretreating said hydrocarbon feedstock by separating said hydrocarbon feedstock into a stream having a high aromatics content and a stream having a low aromatics content, and feeding said stream having a low aromatics content into said first hydrocracking unit, especially further comprising feeding said stream having high aromatics content to said second hydrocracking unit.
4. A process according to anyone or more of the preceding claims, further comprising feeding said stream comprising butanes to said butanes dehydrogenation unit and feeding a stream chosen from the group of said stream comprising C2-C3, said stream comprising C1-C3, said stream comprising C3 minus and said stream comprising C3 to said propane dehydrogenation unit.
5. A process according to anyone or more of the preceding claims, further comprising feeding a stream chosen from the group of said stream comprising C3-C4, said stream comprising C2-C4, said stream comprising C1-C4 and said stream comprising C4 minus to said combined butanes and propane dehydrogenation unit.
6. A process according to anyone or more of the preceding claims, further comprising feeding said stream comprising C5+ originating from said second separation section to said first hydrocracking unit and/or said second hydrocracking unit.

7. A process according to anyone or more of the preceding claims, further comprising feeding said stream comprising hydrogen originating from said second separation section to said first hydrocracking unit and/or said second hydrocracking unit .
8. A process according to anyone or more of the preceding claims, further comprising feeding said stream comprising C1-minus originating from said second separation section to said first separation section.
9. A process according to anyone or more of the preceding claims, further comprising feeding said stream comprising C3 originating from said second separation section to said propane dehydrogenation unit and/or said combined propane-butenes dehydrogenation unit.
10. A process according to anyone or more of the preceding claims, wherein the process conditions in said first hydrocracking unit include a temperature of 300-550 °C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 0.1-20 h⁻¹.
11. A process according to according to anyone or more of claims 1-10, wherein the process conditions in said second hydrocracking unit include a temperature of 450-580°C, a pressure of 0.3-5 MPa gauge and a Weight Hourly Space Velocity of 0.1-20 h⁻¹.