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(54) Title: PROCESS FOR PRODUCING LPG AND BTX FROM A HEAVY AROMATIC FEED

(57) Abstract: The present invention relates to a process for producing LPG and BTX from a hydrocarbon feed comprising polyaromatics, the process comprising subjecting the hydrocarbon feed to a first hydrocracking process step to produce a first hydrocracked product stream; subjecting the first hydrocracked product stream to a first separation step to produce a light-distillate stream; subjecting the light-distillate stream to a second hydrocracking process step to produce a second hydrocracked product stream; and subjecting the second hydrocracked product stream to a second separation step to provide a LPG stream and a BTX stream.

PROCESS FOR PRODUCING LPG AND BTX FROM A HEAVY AROMATIC FEED

The present invention relates to a process for producing LPG and BTX from a hydrocarbon feed comprising polyaromatics, the process comprising subjecting the hydrocarbon feed to a first hydrocracking process step to produce a first hydrocracked product stream; subjecting the first hydrocracked product stream to a first separation step to produce a light-distillate stream; subjecting the light-distillate stream to a second hydrocracking process step to produce a second hydrocracked product stream; and subjecting the second hydrocracked product stream to a second separation step to provide a LPG stream and a BTX stream.

Processes for producing LPG and BTX from heavy hydrocarbon feedstreams have been previously described. For instance, WO2015/000841A1 describes a process for upgrading refinery heavy residues to petrochemicals comprising the following steps of: (a) separating a hydrocarbon feedstock in a distillation unit into an overhead stream and a bottom stream; (b) feeding said bottom stream to a hydrocracking reaction area; (c) separating reaction products, which are generated from said reaction area of step (b) into a stream rich in mono-aromatics and in a stream rich in poly-aromatics; (d) feeding said stream rich in mono-aromatics to a gasoline hydrocracker (GHC) unit; and (e) feeding said stream rich in poly-aromatics to a ring opening reaction area. WO2015/000841A1 further describes that the effluent of the ring-opening process is highly mono-aromatic and may be fed to the GHC unit for further upgrading into LPG and BTX.

WO2015/000848A1 describes a process to convert crude oil into petrochemical products comprising crude oil distillation, hydrocracking and olefins synthesis, which process comprises subjecting a hydrocracker feed to hydrocracking to produce LPG and BTX and subjecting LPG produced in the process to olefins synthesis. The process of WO2015/000841A1 preferably comprises subjecting a middle-distillate produced by resid upgrading and one or more selected from the group consisting of kerosene and gasoil to aromatic ring opening to produce LPG and light-distillate and subjecting light-distillate produced by resid upgrading, light-distillate produced by aromatic ring opening and naphtha to hydrocracking to produce LPG and BTX.

It was an object of the present invention to provide an improved process for upgrading heavy hydrocarbon streams having a relatively high polyaromatic content into useful petrochemical products such as LPG and BTX comprising at least two subsequent hydrocracking steps wherein yield of LPG and BTX is improved, while reducing feeding the second hydrocracker with polyaromatic hydrocarbons.

Furthermore, it was an object of the present invention to provide an improved process for upgrading heavy hydrocarbon streams, wherein the produced LPG contains a decreased percentage of C5 hydrocarbons.

The solution to the above problem is achieved by providing the embodiments as described herein below and as characterized in the claims. Accordingly, the present invention provides a process for producing LPG and BTX from a hydrocarbon feed comprising polyaromatics, the process comprising:

(a) subjecting the hydrocarbon feed to a first hydrocracking process step to produce a first hydrocracked product stream;

(b) subjecting the first hydrocracked product stream to a first separation step to provide
  - (i) a LPG stream,
  - (ii) a light-distillate stream comprising C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons, and
  - (iii) a middle-distillate stream comprising bicyclic C10 hydrocarbons and C11+ hydrocarbons and;

(c) subjecting the light-distillate stream to a second hydrocracking process step to produce a second hydrocracked product stream; and

(d) subjecting the second hydrocracked product stream to a second separation step to provide a LPG stream and a BTX stream.

In the context of the present invention, it was surprisingly found that in a two-step hydrocracking process for producing BTX and LPG from a heavy hydrocarbon feed, coke formation in the second hydrocracker can be dramatically reduced by subjecting a light-distillate stream comprising C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons to the second hydrocracking process step.

The prior art fails to provide the process of the present invention as in such processes the bicyclic C10 hydrocarbons are not specifically prevented to be subjected to the second hydrocracking process step. In the present invention, accordingly, the light-distillate stream comprising C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons that is subjected to the second hydrocracking process step is substantially free of bicyclic C10 hydrocarbons. As used herein, the light-distillate stream comprising C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons that is substantially free of bicyclic C10 hydrocarbons preferably comprises no more than 5 wt-% bicyclic C10 hydrocarbons, more preferably comprises no more than 3 wt-% bicyclic C10 hydrocarbons, even more preferably comprises no more than 1 wt-% bicyclic C10 hydrocarbons, particularly preferably comprises no more than 0.5 wt-% bicyclic C10 hydrocarbons, and most preferably comprises no more than 0.1 wt-% bicyclic C10 hydrocarbons.

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. As used herein, the term "polyaromatics" or "polyaromatic hydrocarbons" relates to a mixture of aromatic hydrocarbons having more than one aromatic ring. As used herein, the term "monoaromatic hydrocarbons" or "monoaromatics" relates to a mixture of aromatic hydrocarbons having only one aromatic ring.

The term "BTX" as used herein relates to a mixture of benzene, toluene and xylenes. As used herein, the term "chemical grade BTX" relates to a hydrocarbon mixture comprising less than 5 wt% hydrocarbons other than benzene, toluene and xylenes, preferably less than 4 wt% hydrocarbons other than benzene, toluene and xylenes, more preferably less than 3 wt% hydrocarbons other than benzene, toluene and xylenes, and most preferably less than 2.5 wt% hydrocarbons other than benzene, toluene and xylenes. Furthermore, the "chemical grade BTX" produced by the process of the present invention comprises less than 1 wt% non-aromatic C6+ hydrocarbons, preferably less than 0.7 wt% non-aromatic C6+ hydrocarbons, more preferably less than 0.5 wt% non-aromatic C6+ hydrocarbons and most preferably less than 0.2 wt% non-aromatic C6+ hydrocarbons. The most critical contaminants are the non-aromatic species which have boiling points close to benzene including, but not limited to, cyclohexane, methylcyclopentane, n-hexane, 2-methylpentane and 3-methylpentane.Preferably, the product produced in the process of the present invention comprises further useful aromatic hydrocarbons such as ethylbenzene. The BTX 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 and/or a xylene product stream.

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" is meant to describe all hydrocarbon molecules having # or more carbon atoms. Accordingly, the term "C9+ hydrocarbons" is meant to describe a mixture of hydrocarbons having 9 or more carbon atoms. The term "C9+ alkanes" accordingly relates to alkanes having 9 or more carbon atoms.

The term "LPG" as used herein refers to the well-established acronym for the term "liquefied petroleum gas". LPG generally consists of a blend of C2-C4 hydrocarbons i.e. a mixture of C2, C3, and C4 hydrocarbons.

The term "light-distillate" as used herein refers to a mixture comprising C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons. The term "middle-distillate" as used herein refers to comprising bicyclic C10 hydrocarbons and C11+ hydrocarbons. Preferably, the "middle distillate" comprises hydrocarbons having a boiling point of up to 360 °C, preferably of up to 350 °C.

As used herein, the term "hydrocracker unit" or "hydrocracker" relates to a petrochemical process 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) Oil Refining, Ullmann's Encyclopedia of Industrial Chemistry. The products of this process are saturated hydrocarbons, naphthenic (cycloalkane) hydrocarbons and, depending on the reaction conditions such as temperature, pressure and space velocity and catalyst activity, aromatic hydrocarbons including BTX. The process conditions used for hydrocracking generally includes a process temperature of 200-600 °C, elevated pressures of 0.2-40 MPa, space velocities between 0.1-20 h^{-1}. 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, preferably selected from Groups 6-11 of the Periodic Table of Elements, or metal sulphides, unsupported or with a solid catalyst support such as alumina, silica, alumina-silica, magnesia and zeolites.

Preferably, the process conditions of the second hydrocracking process step comprise a higher process temperature and/or a lower process pressure when compared to the process conditions of the first hydrocracking process step.

The present invention provides a process for producing LPG and BTX from a hydrocarbon feed comprising polyaromatics. The term "hydrocarbon feed" as used herein relates to the hydrocarbon mixture that is subjected to the process of the present invention. Preferably, the hydrocarbon feed used in the process of the present invention comprises at least 10 wt-% polyaromatics, more preferably at least 20 wt-% polyaromatics and most preferably at least 30 wt-% polyaromatics. Preferably, the hydrocarbon feed is selected from the group consisting of heavy cycle oil, light cycle oil, carbon black oil, cracked distillate and pyoil.

First hydrocracking step

The process of the present invention comprises as a first step (a) subjecting the hydrocarbon feed to a first hydrocracking process step to produce a first hydrocracked product stream. Said first hydrocracking step involves contacting the hydrocarbon feed in the presence of hydrogen to a hydocracking catalyst at hydrocracking conditions.

The process conditions used for the first hydrocracking step (a) generally includes a process temperature of 200-600 °C, elevated pressures of 0.2-40 MPa, and space velocities between 0.1-20 h^{-1}, together with 5-20 wt-% of hydrogen (in relation to the hydrocarbon feedstock), wherein said hydrogen may flow co-current with the hydrocarbon feedstock or counter current to the direction of flow of the hydrocarbon feedstock, in the presence of a dual functional catalyst active for both hydrogenation-dehydrogenation and cracking. The hydrocracking catalyst used in the first hydrocracking step (a) may be any catalyst composition that combines a hydrogenation function and an acid (cracking) function, either in the form of a mixture of different catalyst components having different catalyst function or in the form of a bifunctional catalyst that combines both the acid and the hydrogenation function in one catalyst component comprised in the catalyst composition. Such hydrocracking catalysts preferably comprise one or more transition metals, preferably selected from Groups 6-11 of the Periodic Table of Elements. Catalysts used in hydrocracking step (a) generally comprise one or more elements selected from the group consisting of Pd, Rh, Ru, Ir, Os, Cu, Co, Ni, Pt, Fe, Zn, Ga, In, Mo, W and V in metallic or metal sulphide form supported on an acidic solid such as alumina, silica, alumina-silica, magnesia and zeolites. In this respect, it is to be noted that the term "supported on" as used herein includes any conventional way to provide a catalyst which combines one or more elements with a catalytic support.

Preferably, the first hydrocracking process step (a) comprises contacting the hydrocarbon feed in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions,
wherein said hydrocracking catalyst comprises one or more elements selected from the group consisting of Pd, Rh, Ru, Ir, Os, Cu, Co, Ni, Pt, Fe, Zn, Ga, In, Mo, W and V in metallic or metal sulphide form supported on an acidic solid, and
wherein said hydrocracking conditions comprise a temperature of 300-500 °C and a pressure of 1-25 MPa. The Weight Hourly Space Velocity used first hydrocracking process step (a) preferably is 0.1-10 h^{-1}.

Preferably, the catalyst used in the first hydrocracking step (a) is a M/A/support catalyst comprising:
0.05-2.5 wt-% of element M, wherein said element M is one or more elements selected from the group consisting of Co, Mo, Ni, Pt and Pd;
0-1 wt-% of element A, wherein said element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements; and
a porous catalyst support selected from the group consisting of alumina, silica and aluminosilicate zeolite, and
wherein the process conditions in the first hydrocracking step (a) comprises a pressure of 1-25 MPa, a temperature of 300-500 °C, a Weight Hourly Space Velocity of 0.1-10 h^{-1} and a H_2/HC ratio of 1-20.

In the event the porous catalyst support is an aluminosilicate zeolite, the zeolite preferably has a pore size of 6-8 Å and a SiO_2/Al_2O_3 ratio of 1-150.

Accordingly, preferred process conditions that may be used in the in the first hydrocracking step (a) of the process of the present invention comprise a pressure of 1-25 MPa, a temperature of 300-500 °C, a Weight Hourly Space Velocity of 0.1-10 h^{-1} and a H_2/HC ratio of 1-20.

In some preferred embodiments, the first hydrocracking step is performed at a pressure of 1-25 MPa, for example at least 2 MPa, at least 3 Mpa or at least 4 Mpa and/or at most 22 Mpa, at most 20 MPa, at most 17 MPa or at most 15 Mpa.

In some preferred embodiments, the first hydrocracking step is performed at a temperature of a temperature of 300-500 °C, for example at least 305 °C, at least 310 °C, at least 315 °C or at least 320 °C and/or at most 490 °C, at most 480 °C, at most 470 °C or at most 460 °C.

In some preferred embodiments, the first hydrocracking step is performed at a Weight Hourly Space Velocity of 0.1-10 h^{-1}, for example at least 0.2 h^{-1}, at least 0.3 h^{-1}, at least 0.4 h^{-1} or at least 0.5 h^{-1} and/or at most 7 h^{-1}, at most 6 h^{-1}, at most 5 h^{-1} or at most 4 h^{-1}.

In some preferred embodiments, the first hydrocracking step is performed at a H_2/HC ratio of 1-20, for example at least 1, at least 2, at least 3 or at least 4 and/or at most 17, at most 15, at most 12 or at most 10. As used herein, the H_2/HC ratio is indicated as a molar ratio.

A preferred catalyst that may be used in the in the first hydrocracking step (a) is described herein as a M/A/zeolite catalyst, wherein said element M is one or more elements selected from Group 10 of the Periodic Table of Elements; 0-1 wt-% of element A, wherein said element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements; and an aluminosilicate zeolite having a pore size of 6-8 Å and a SiO_2/Al_2O_3 ratio of 1-150.

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 used in the first hydrocracking step comprises a large pore size aluminosilicate zeolite. Suitable zeolites include, but are not limited to, zeolite Y, faujasite (FAU), beta zeolite (BEA), and chabazite (CHA). The term "large pore zeolite" is commonly used in the field of zeolite catalysts. Accordingly, a large pore size zeolite is a zeolite having a pore size of 6-8 Å.

The aluminosilicate zeolite used in the in the first hydrocracking step (a) may have a SiO_2/Al_2O_3 ratio of 1-150. Means and methods for quantifying the SiO_2 to Al_2O_3 molar ratio of a zeolite are well known in the art and include, but are not limited to AAS (Atomic Absorption Spectrometer), ICP (Inductively Coupled Plasma Spectrometry) analysis or XRF (X-ray fluorescence). It is noted that the SiO_2 to Al_2O_3 molar ratio referred herein is meant as the ratio in the zeolite prior to being mixed with the binder for forming the shaped body. Preferably, the SiO_2 to Al_2O_3 molar ratio is measured by XRF.

Accordingly, element "M" as used herein is one or more elements selected from Group 10 of the Periodic Table of Elements. Preferably, the M/A/zeolite catalyst comprises 0.5-2 wt-% of element M. All weight percentages of element M as provided herein relate to the amount of element M in relation to the total catalyst composition. Preferably, element M is one or more elements selected from the group consisting of Pd and Pt. Most preferably, element M is Pt.

Accordingly, element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements Preferably, the M/A/zeolite catalyst comprises 0.1-1 wt-% of element A, more preferably 0.25-0.75 wt-% of element A. All weight percentages of element A as provided herein relate to the amount of element A in relation to the total catalyst composition. Selecting a catalyst comprising 0.1-1 wt-% of element A was found to reduce the methane make. Preferably, element A is one or more elements selected from the group consisting of Na, K, Rb, Cs, Mg, Ca, Sr and Ba. More preferably, element A is one or more elements selected from the group consisting of Na, K, Rb and Cs. Most preferably, element A is K.

The catalyst composition as used in the first hydrocracking step (a) may comprise further components such as a binder. Known binders include, but are not limited to silica, alumina and clay, such as kaolin. 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. The catalyst composition is preferably formed into shaped catalyst particles by any known technique, for instance by extrusion.

Preferably, the catalyst used in the first hydrocracking step (a) comprises an aluminosilicate zeolite having a 12-ring structure. These specific aluminosilicate zeolites are well known to the skilled man. An overview of their characteristics is for example provided by the Atlas of Zeolite Framework Types, 5th edition, (Elsevier, 2001). Accordingly, an aluminosilicate zeolite having a 12-ring structure is an aluminosilicate zeolite wherein the pore is formed by a ring consisting of 12 $[SiO_4]$ or $[AlO_4]^+$ tetrahedra.

Preferably, the catalyst used in the first hydrocracking step (a) comprises an aluminosilicate zeolite having super cages having a size of 12-14 Å. Means and methods for preparing zeolites comprising super cages are well-known in the art and comprise zeolite post-treatments such as acid leaching and steaming, among others. (Angew. Chem., Int. Ed. 2010, 49, 10074, ACS nano, 4 (2013) 3698).

Preferably, the aluminosilicate zeolite comprised in the catalyst used in the first hydrocracking step (a) is zeolite Y. Depending on the silica-to-alumina molar ratio

("SiO_2/Al_2O_3 molar ratio" or "SiO_2/Al_2O_3 ratio") of their framework, synthetic faujasite zeolites are divided into zeolite X and zeolite Y. In X zeolites the SiO_2/Al_2O_3 ratio is between 2 and 3, while in Y zeolites it is 3 or higher. Accordingly, zeolite Y is a synthetic faujasite zeolite having a SiO_2/Al_2O_3 ratio in their framework of 3 or more. Preferably, the zeolite in the selective alkylation catalyst is in the so-called hydrogen form, meaning that its sodium or potassium content is very low, preferably below 0.1, 0.05, 0.02 or 0.01 wt-%; more preferably presence of sodium is below detection limits. Preferably, the zeolite Y used in the process of the present invention has a SiO_2/Al_2O_3 ratio of 60-100 in the event the catalyst does not comprise the optional element A and preferably has a SiO_2/Al_2O_3 ratio of 5-25 in the event the catalyst comprises at least 0.1 wt-% of element A. Preferably, the partially dealuminated zeolite is prepared by controlling SiO_2/Al_2O_3 ratio during zeolite synthesis. Alternatively, the zeolite may be partially dealuminated by a post-synthesis modification. Means and methods to obtain dealuminated zeolite by post-synthesis modification are well-known in the art and include, but are not limited to the acid leaching technique; see e.g. Post-synthesis Modification I; Molecular Sieves, Volume 3; Eds. H. G. Karge, J. Weitkamp; Year (2002); Pages 204-255.

<u>First separation step</u>

The process of the present invention comprises as a second step (b) subjecting the first hydrocracked product stream to a first separation step to provide (i) a LPG stream, (ii) a light-distillate stream comprising C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons, and (iii) a middle-distillate stream comprising bicyclic C10 hydrocarbons and C11+ hydrocarbons.

The person skilled in the art is readily capable of selecting suitable process conditions that allow the separation of the first hydrocracked product stream into the LPG stream, the light-distillate stream and the middle-distillate stream as defined herein. Preferably, the initial boiling point of the light-distillate is 20-70 °C, more preferably 30-60°C, and most preferably 35-50 °C to ensure that the C5 hydrocarbons are comprised in the light-distillate that is subsequently subjected to the second hydrocracking step (c). As used herein, the term "initial boiling point" is the *initial boiling point (IBP)* as defined in the ASTM D 86 – 04b standard. Moreover, the light-distillate stream preferably has a final boiling point of 170-195 °C, more preferably 175-190 °C and most preferably 185-190 °C to avoid contamination with substantial amounts of bicyclic C10 hydrocarbons such as decalin into the light-distillate. As used herein, the term "final boiling point" is the *final boiling point (FBP)* as defined in the ASTM D 86 – 04b standard. Similarly, to avoid losing alkylated monoaromatics, such as propylbenzene, into the middle-distillate, the initial boiling point of the middle-distillate preferably is 140-210 °C, more preferably 160-205 °C and most preferably 170-200 °C.

Preferably, the LPG stream obtained in separation step (b) comprises no more than 10 wt-% hydrocarbons other than LPG, more preferably no more than 7 wt-% hydrocarbons other than LPG, even more preferably no more than 5 wt-% hydrocarbons other than LPG and most preferably no more than 3 wt-% hydrocarbons other than LPG.

Preferably, the light-distillate stream obtained in separation step (b) comprises no more than 10 wt-% hydrocarbons other than C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons, more preferably no more than 7 wt-% hydrocarbons other than C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons, even more preferably no more than 5 wt-% hydrocarbons other than C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons and most preferably no more than 3 wt-% hydrocarbons other than C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons.

Preferably, the middle-distillate stream obtained in separation step (b) comprises no more than 10 wt-% hydrocarbons other than bicyclic C10 hydrocarbons and C11+ hydrocarbons, more preferably no more than 7 wt-% hydrocarbons other than bicyclic C10 hydrocarbons and C11+ hydrocarbons, even more preferably no more than 5 wt-% hydrocarbons other than bicyclic C10 hydrocarbons and C11+ hydrocarbons and most preferably no more than 3 wt-% hydrocarbons other than bicyclic C10 hydrocarbons and C11+ hydrocarbons.

Accordingly, the first separation step (b) preferably comprises distillation. Said separation by distillation may be achieved by using a single-column distillation set-up, a dual-column distillation set-up or dividing wall distillation column set-up.

<u>Second hydrocracking step</u>

The process of the present invention comprises as a third step (c) subjecting the light-distillate stream to a second hydrocracking process step to produce a second hydrocracked product stream. Said second hydrocracking step involves contacting the light-distillate stream in the presence of hydrogen to a hydrocracking catalyst at hydrocracking conditions.

Process suitable for hydrocracking of a light-distillate stream are known in the art; see e.g. WO 2013/182534 A1 and US 2008/0287561 A1. Accordingly, the process conditions used for the second hydrocracking step (c) generally includes a temperature of 300-600 °C, a pressure of 0.3-5 MPa gauge and a Weight Hourly Space Velocity of 0.1-30 h^{-1}. The hydrocracking catalyst used in the second hydrocracking step (c) typically comprises 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and a silica (SiO_2) to alumina (Al_2O_3) molar ratio of 5-200.

Preferably, the second hydrocracking process step (c) comprises contacting the light-distillate stream in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions,
wherein said hydrocracking catalyst comprises one or more elements selected from the group consisting of Pt and Pd and an aluminosilicate zeolite, and
wherein said hydrocracking conditions comprise a temperature of 300-600 °C, a pressure of 0.3-5 MPa gauge and a WHSV of 0.1-15 h^{-1}.

Preferably, the catalyst used in the second hydrocracking step (c) comprises 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and SiO_2/Al_2O_3 ratio of 5-200, and
wherein the process conditions in the second hydrocracking step (c) comprises a temperature of 425-580°C, a pressure of 0.3-5 MPa gauge and a Weight Hourly Space Velocity of 0.1-15 h^{-1}.

Accordingly, the process conditions that may be used in the in the second hydrocracking step (c) of the process of the present invention comprise a temperature of 300-600 °C, a pressure of 0.3-5 MPa gauge and a WHSV of 0.1-15 h^{-1}.

Preferably, the process conditions used for the second hydrocracking step comprise 425-580°C, a pressure of 0.3-5 MPa gauge and a Weight Hourly Space Velocity of 0.1-15 h^{-1}.

In some preferred embodiments, the second hydrocracking step is performed at a pressure of 0.3-5 MPa, for example at least 0.6 MPa, 1.0 Mpa or at least 1.2 Mpa and/or at most 3 MPa, at most 2 MPa or at most 1.6 Mpa. By increasing reactor pressure, conversion of C5+ non-aromatics can be increased, but higher pressure 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 1-2.5 MPa.

In some preferred embodiments, the second hydrocracking step is performed at a temperature of a temperature of 300-600 °C, for example at least 350 °C, at least 400 °C, at least 410 °C or at least 425 °C and/or at most 575 °C, at most 550 °C or at most 525 °C. The higher temperature range results in a high hydrocracking conversion rate.

In some preferred embodiments, the second hydrocracking step is performed at a Weight Hourly Space Velocity of 0.1-15 h^{-1}, for example at least 0.3 h^{-1}, at least 0.5 h^{-1}, at least 0.8 h^{-1} or at least 1 h^{-1} and/or at most 13 h^{-1}, at most 10 h^{-1}, at most 8 h^{-1} or at most 5 h^{-1}. A higher WHSV allows particularly small reactor volumes and lower CAPEX.

The catalyst that may be used in the in the second hydrocracking step (c) comprises one or more elements selected from the group consisting of Pt and Pd and an aluminosilicate zeolite.

Preferably, the catalyst used in the second hydrocracking step comprises 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and SiO_2/Al_2O_3 ratio of 5-200.

Preferably, the hydrocracking catalyst used in the second hydrocracking step is a medium pore size zeolite. 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 5-6 Å. Preferably, the catalyst used in the second hydrocracking step comprises an aluminosilicate zeolite having a 10-ring structure. Accordingly, an aluminosilicate zeolite having a 10-ring structure is an aluminosilicate zeolite wherein the pore is formed by a ring consisting of 10 $[SiO_4]$ or $[AlO_4]^+$ tetrahedra.

Preferably, the aluminosilicate zeolite comprised in the catalyst used in the second hydrocracking step (b) is ZSM-5.

Preferably, the silica (SiO_2) to alumina (Al_2O_3) molar ratio of the ZSM-5 zeolite is in the range of 30-100. It was found that using a zeolite having a SiO_2 to Al_2O_3 molar ratio of 30-100 shows the optimum catalyst performances as measured by activity (as measured by WHSV), contents of benzene and total aromatics (BTX, ethylbenzene (EB) and heavies) and methane in the product stream. It is noted that the SiO_2 to Al_2O_3 molar ratio referred herein is meant as the ratio in the zeolite prior to being mixed with the binder for forming the shaped body. Preferably, the SiO_2 to Al_2O_3 molar ratio is measured by XRF.

The aluminosilicate zeolite comprised in the catalyst used in the second hydrocracking step comprises a hydrogenation metal. Preferably, the hydrogenation metal is at least one element selected from Group 10 of the periodic table of Elements. Preferred Group 10 elements are palladium and platinum. Preferably, the hydrogenation metal comprised in the catalyst used in the second hydrocracking step (b) is Pt.

Preferably, the hydrocracking catalyst used in the second hydrocracking step comprises a shaped body comprising a zeolite and a binder and a hydrogenation metal deposited on the shaped body, wherein the amount of the hydrogenation metal is 0.010-0.30 wt% with respect to the total catalyst and wherein the zeolite is ZSM-5 having a the SiO_2 to Al_2O_3 molar ratio molar ratio of 30-100. When using this particularly preferred hydrocracking catalyst used in the second hydrocracking step, the hydrocracking conditions preferably comprise a temperature of 425-580°C, a pressure of 300-5000 kPa gauge and a Weight Hourly Space Velocity of 3-30 h-1 to produce a hydrocracking product stream comprising BTX. The specific selection of this hydrocracking catalyst in combination with these hydrocracking conditions results in a hydrocracking product stream comprising a low proportion of methane and substantially no co-boilers of BTX at a sufficiently high WHSV. A low proportion of methane means that more valuable components such as C2-C4 hydrocarbons and BTX are present in the hydrocracking product stream. The absence of co-boilers of BTX in the product stream allows obtaining a chemical grade BTX by simple distillation of the product stream. This can be achieved at a relatively high level of WHSV, which means that the desired product can be obtained at a higher rate requiring smaller volume reactor resulting in a smaller CAPEX.

<u>Second separation step</u>

The process of the present invention comprises as a fourth step (d) subjecting the second hydrocracked product stream to a second separation step to provide a LPG stream and a BTX stream.

Preferably, the second separation step (d) comprises gas-liquid separation.

The process of the present invention produces LPG as a process product. Preferably, the process of the present invention produces at least 50 wt-% LPG + BTX of the total hydrocarbon process product, more preferably at least 80 wt-% LPG + BTX of the total hydrocarbon process product, even more preferably at least 95 wt-% LPG + BTX of the total hydrocarbon process product and most preferably at least 99 wt-% LPG + BTX of the total hydrocarbon process product. Preferably, the process of the present invention produces less than 15 wt-% methane of the total hydrocarbon process product, more preferably less than 10 wt-% methane of the total hydrocarbon process product, even more preferably less than 5 wt-% methane of the total hydrocarbon process product and most preferably less than 1 wt-% methane of the total hydrocarbon process product.

Preferably, the middle-distillate stream comprising bicyclic C10 hydrocarbons and C11+ hydrocarbons is recycled to the first hydrocracking step (a). In the context of the present invention, it was surprisingly found that in a two-step hydrocracking process for producing BTX and LPG from a heavy hydrocarbon feed, the LPG and BTX yield can be improved by recycling bicyclic C10 hydrocarbons and C11+ hydrocarbons is recycled to the first hydrocracking step.

It is noted that the invention relates to all possible combinations of features described herein, particularly features recited in the claims.

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

Example 1

The experimental data as provided herein were obtained by modelling the fractions obtained by distillation in an Aspen model (AspenPlus V8.2). The modelled configuration comprises a first hydrocracked product stream ("1HPS")produced by a hydrocracking process that aims to convert polyaromatics into monoaromatics and LPG, wherein said first hydrocracked product stream is fed to a separation section to provide a LPG stream ("LPGS"), a light-distillate stream ("LDS") and a middle-distillate stream ("MDS"). The thus obtained light-distillate stream is subjected to a second hydrocracker that aims to produce the second hydrocracked product stream ("2HPS") which preferably is on-spec BTX (by cracking the co-boilers of BTX whilst preserving the monoaromatics present in the light-distillate stream). The middle-distillate stream obtained from the separation section is again subjected to hydrocracking that aims to convert polyaromatics into monoaromatics and LPG to provide the hydrocracked middle-distillate stream ("HMDS").

The following conversions are assumed to occur in the light-distillate hydrocracker. Decane is converted into LPG (2x C2 and 2x C3); pentane is converted into LPG (1x C2 and 1x C3); propylbenzene is converted into LPG and BTX (1x C3 and 1x benzene). It is assumed that the extent of reaction is 100% (with or without recycle).

The following conversions are assumed to occur when the middle-distillate is subjected to a hydrocracking process that aims to convert polyaromatics into monoaromatics and LPG. Components here are converted to extinction, with exception of the eventually present mono-aromatics (benzene, toluene, propylbenzene) that are converted at 10%. Hence, it is assumed that a certain amount of monoaromatics is lost when operating the hydrocracking process at process conditions which maximize conversion of polyaromatics into monoaromatics and LPG. Napthalene is converted into LPG and BTX (1x C3 and 1x toluene); decane is converted into LPG (2x C2 and 2x C3); decalin is converted into LPG (2x C2 and 2x C3); toluene is converted into LPG (2x C2 and 1x C3); benzene (assumed 10% lost) is converted into LPG (2x C3); propylbenzene is converted into LPG (3x C2 and 1x C3).

In Example 1, the above-described configuration is modelled using a separation section wherein a final boiling point of 200 °C (based on Aspen D86 result) was selected for the light-distillate; see also Table 5, below. The configuration of the separation section consists of two consecutive distillation columns wherein in the first distillation column the LPG stream is separated over the top and wherein in the second distillation column the light-distillate stream is separated over the top and the middle-distillate stream is separated over the bottom of the second column.

Table 1: Modelling results Example 1

Compositions & flows of effluent streams of separation section						Flows of products of downstream conversion units	
1HPS (wt-%)		LPGS (wt-%)	LDS (wt-%)	MDS (wt-%)		2HPS	HMDS
10	T/H	1.57	4.10	4.32		(t/h)	(t/h)
0%	benzene	0.0%	0.0%	0.0%		1.94	0.00
0%	toluene	0.0%	0.0%	0.0%		0.000	0.32
5%	butane	30.2%	0.6%	0.0%		0.025	0.00
5%	naphthalene	0.0%	0.0%	11.6%		0.001	0.00
5%	decane	0.0%	12.1%	0.1%		0.000	0.00

40%	decalin	0.0%	4.9%	87.9%		0.200	0.00
5%	pentane	6.4%	9.8%	0.0%		0.000	0.00
30%	propyl benzene	0.0%	72.7%	0.4%		0.000	0.02
5%	ethane	31.8%	0.0%	0.0%		0.38	1.68
5%	propane	31.7%	0.0%	0.0%		1.64	2.62

Table 2: Total yields example 1

IN	feed	hydrogen		
t/h	10	0.40		
Overall product slate	LPG	C5	Monoaromatics	Bicyclic hydrocarbons
t/h	7.82	0.10	2.28	0.20
%-wt	75.2%	1.0%	21.9%	1.9%

As shown herein above, the selection of a separation section having a final boiling point of 200 °C for the light-distillate has the effect that the light-distillate that is subjected to the second hydrocracker comprises 4.9 wt-% decalin.

Example 2

In Example 2, the same configuration as in Example 1 is modelled with the exception that a separation section is used comprising two consecutive distillation columns, wherein a final boiling point of 187 °C (based on Aspen D86 result) for the light-distillate was selected; see also Table 5, below.

Table 3: Modelling results Example 2

Compositions & flows of effluent streams of separation section						Flows of products of downstream conversion units	
1HPS (wt-%)		LPGS (wt-%)	LDS (wt-%)	MDS (wt-%)		2HPS	HMDS
10	T/H	1.57	3.93	4.50		t/h	t/h
0%	benzene	0.0%	0.0%	0.0%		1.95	0.00
0%	toluene	0.0%	0.0%	0.0%		0.000	0.32
5%	butane	30.2%	0.6%	0.0%		0.025	0.00
5%	naphthalene	0.0%	0.0%	11.1%		0.000	0.00
5%	decane	0.0%	12.7%	0.0%		0.000	0.00
40%	decalin	0.0%	0.1%	88.8%		0.004	0.00
5%	pentane	6.4%	10.2%	0.0%		0.000	0.00
30%	propyl benzene	0.0%	76.4%	0.0%		0.000	0.00
5%	ethane	31.8%	0.0%	0.0%		0.38	1.76
5%	propane	31.7%	0.0%	0.0%		1.65	2.74

Table 4: Total yields example 2

IN	feed	hydrogen		
t/h	10	0.41		
Overall product slate	LPG	C5	Monoaromatics	Bicyclic hydrocarbons
t/h	8.03	0.10	2.27	0.00
%-wt	77.2%	1.0%	21.8%	0.04%

As shown herein above, the selection of a separation section having a final boiling point of 187 °C for the light-distillate has the effect that the light-distillate that is subjected to the second hydrocracker comprises only 0.1 wt-% decalin. Moreover, when compared to Example 1, the total LPG + monoaromatics yield is increased from 97.1 wt-% to 99.0 wt-%, while reducing the bicyclic hydrocarbons in effluent to less than 0.1 wt-%. These results show that a final boiling point of lower than 200 °C in the separation section leads to a higher LPG + monoaromatics yield. This separation using a lower final boiling point temperature limits the amount of bicyclic hydrocarbons in the final product slate; see also Table 5 as provided herein below.

Table 5: Aspen D86 distillation curves for Examples 1 and 2

% D86	Example 1 LDS	Example 2 LDS
	°C	°C
0%	40.2	40.0
5%	62.5	61.4
10%	72.1	70.5
30%	133.8	130.6
50%	161.7	160.9
70%	165.7	164.8
90%	171.3	169.2
95%	185.6	178.1
100%	200.0	187.0

Example 3

In Example 3, the same configuration as in Example 1 is modelled with the exception that a separation section is used comprising a single distillation column with a side-draw, wherein the LPG stream is separated over the top of the distillation column, the light-distillate is separated over the side-draw of the distillation column and the middle-distillate is separated over the bottom of the column and wherein a final boiling point of 179 °C (based on Aspen D86 result) for the light-distillate was selected; see also Table 10, below.

Table 6: Modelling results Example 3

Compositions & flows of effluent streams of separation section						Flows of products of downstream conversion units	
1HPS (wt-%)		LPGS (wt-%)	LDS (wt-%)	MDS (wt-%)		2HPS	HMDS
10	T/H	1.60	5.00	3.40		t/h	t/h
10%	benzene	0.0%	20.0%	0.0%		2.53	0.00
10%	toluene	0.0%	20.0%	0.0%		1.00	0.32
5%	butane	29.8%	0.5%	0.0%		0.023	0.00
5%	naphthalene	0.0%	0.0%	14.7%		0.000	0.00
5%	decane	0.0%	4.2%	8.5%		0.000	0.00
20%	decalin	0.0%	0.5%	58.0%		0.027	0.00
5%	pentane	8.3%	7.3%	0.0%		0.000	0.00
30%	propyl benzene	0.0%	47.2%	18.8%		0.000	0.58
5%	ethane	31.1%	0.1%	0.0%		0.25	1.05
5%	propane	30.8%	0.1%	0.0%		1.23	1.65

Table 7: Total yields example 3

IN	feed	hydrogen		
t/h	10	0.26		
Overall product slate	LPG	C5	Monoaromatics	Bicyclic hydrocarbons
t/h	5.66	0.13	4.43	0.03
%-wt	55.2%	1.3%	43.2%	0.27%

Example 4

In Example 4, the same configuration as in Example 1 is modelled with the exception that a final boiling point of 181 °C (based on Aspen D86 result) was selected for the light-distillate; see also Table 10, below.

Table 8: Modelling results Example 4

Compositions & flows of effluent streams of separation section						Flows of products of downstream conversion units	
1HPS (wt-%)		LPGS (wt-%)	LDS (wt-%)	MDS (wt-%)		2HPS	HMDS
10	T/H	1.58	5.92	2.50		t/h	t/h
10%	benzene	0.1%	16.9%	0.0%		2.95	0.00
10%	toluene	0.0%	16.9%	0.0%		1.000	0.32
5%	butane	30.1%	0.4%	0.0%		0.025	0.00
5%	naphthalene	0.0%	0.0%	20.0%		0.000	0.00
5%	decane	0.0%	8.4%	0.0%		0.000	0.00
20%	decalin	0.0%	0.0%	79.9%		0.002	0.00
5%	pentane	6.3%	6.8%	0.0%		0.000	0.00
30%	propyl benzene	0.0%	50.6%	0.1%		0.000	0.00
5%	ethane	31.7%	0.0%	0.0%		0.38	0.89
5%	propane	31.7%	0.0%	0.0%		1.65	1.46

Table 9: Total yields example 4

IN	feed	hydrogen		
t/h	10	0.26		
Overall product slate	LPG	C5	Monoaromatics	Bicyclic hydrocarbons
t/h	5.89	0.10	4.27	0.00
%-wt	57.4%	1.0%	41.6%	0.02%

This shows that for a defined final boiling point for light-distillate stream (here 180 °C; see also Table 10, below), a single column with a side draw only avoids significant amounts of bicyclic hydrocarbons sent to the second hydrocracking step. However, two successive columns, also increases the LPG+BTX yields and limits significantly the amount of bicyclic hydrocarbons in the product slate.

Moreover, a reduction on the concentration of the di-ring species in the "LDS" can be achieved with various types of the separation. Results of Examples 3 and 4 show that different configurations can achieve significant reduction of di-ring species present in the "LDS" stream with a similar Final Boiling Point.

Table 10: Aspen D86 distillation curves for Examples 3 and 4

	Example 3		Example 4	
% D86	LDS °C	MDS °C	LDS °C	MDS °C
0%	34.8	148	46.6	188
5%	67.0	168	73.8	189
10%	81.4	176	85.7	190
30%	110.5	185	117.5	193
50%	130.8	191	140.9	198
70%	152.2	197	156.4	203
90%	160.8	204	163.2	209
95%	169.9	211	172.1	210
100%	179.0	217	181.0	212

CLAIMS

1. Process for producing LPG and BTX from a hydrocarbon feed comprising polyaromatics, the process comprising:
   (a) subjecting the hydrocarbon feed to a first hydrocracking process step to produce a first hydrocracked product stream;
   (b) subjecting the first hydrocracked product stream to a first separation step to provide
      (i) a LPG stream,
      (ii) a light-distillate stream comprising C5-C9 hydrocarbons and linear, branched and monocyclic C10 hydrocarbons, and
      (iii) a middle-distillate stream comprising bicyclic C10 hydrocarbons and C11+ hydrocarbons and;
   (c) subjecting the light-distillate stream to a second hydrocracking process step to produce a second hydrocracked product stream; and
   (d) subjecting the second hydrocracked product stream to a second separation step to provide a LPG stream and a BTX stream.

2. The process according to claim 1, wherein the process conditions of the second hydrocracking process step comprise a higher process temperature and/or a lower process pressure when compared to the process conditions of the first hydrocracking process step.

3. The process according to claim 1 or 2, wherein the first hydrocracking process step (a) comprises contacting the hydrocarbon feed in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions, wherein said hydrocracking catalyst comprises one or more elements selected from the group consisting of Pd, Rh, Ru, Ir, Os, Cu, Co, Ni, Pt, Fe, Zn, Ga, In, Mo, W and V in metallic or metal sulphide form supported on an acidic solid, and
   wherein said hydrocracking conditions comprise a temperature of 300-500 °C and a pressure of 1-25 MPa.

4. The process according to any one of claims 1-3, wherein the first separation step (b) comprises distillation.

5. The process of any one of claims 1-4, wherein the second hydrocracking process step (c) comprises contacting the light-distillate stream in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions,
wherein said hydrocracking catalyst comprises one or more elements selected from the group consisting of Pt and Pd and an aluminosilicate zeolite, and
wherein said hydrocracking conditions comprise a temperature of 300-600 °C, a pressure of 0.3-5 MPa gauge and a WHSV of 0.1-15 h^{-1}.

6. The process according to any one of claims 1-5, wherein the second separation step (d) comprises gas-liquid separation.

7. The process according to any one of claims 1-6, wherein the catalyst used in the first hydrocracking step (a) is a M/A/support catalyst comprising:
0.05-2.5 wt-% of element M, wherein said element M is one or more elements selected from the group consisting of Co, Mo, Ni, Pt and Pd;
0-1 wt-% of element A, wherein said element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements; and
a porous catalyst support selected from the group consisting of alumina, silica and aluminosilicate zeolite, and
wherein the process conditions in the first hydrocracking step (a) comprises a pressure of ambient-20 MPa, a temperature of 350-500 °C, a Weight Hourly Space Velocity of 0.1-10 h^{-1} and a H_2/HC ratio of 1-20.

8. The process according to claim 7, wherein element A is one or more elements selected from the group consisting of Na, K, Rb and Cs.

9. The process according to claim 7 or 8, wherein the catalyst used in the first hydrocracking step (a) comprises an aluminosilicate zeolite having a 12-ring structure.

10. The process according to any one of claims 7-9, wherein the aluminosilicate zeolite comprised in the catalyst used in the first hydrocracking step (a) is zeolite Y.

11. The process according to any one of claims 1-10, wherein the catalyst used in the second hydrocracking step (c) comprises 0.01-1 wt-% hydrogenation metal in relation to the total catalyst weight and a zeolite having a pore size of 5-8 Å and SiO_2/Al_2O_3 ratio of 5-200, and
wherein the process conditions in the second hydrocracking step (c) comprises a temperature of 425-580°C, a pressure of 0.3-5 MPa gauge and a Weight Hourly Space Velocity of 0.1-15 h^{-1}.

12. The process according to claim 11, wherein the aluminosilicate zeolite comprised in the catalyst used in the second hydrocracking step (b) is ZSM-5.

13. The process according to claim 11 or 12, wherein the hydrogenation metal comprised in the catalyst used in the second hydrocracking step (b) is Pt.

14. The process according to any one of claims 1-13, wherein the middle-distillate stream comprising bicyclic C10 hydrocarbons and C11+ hydrocarbons is recycled to the first hydrocracking step (a).

15. The process according to any one of claims 1-14, wherein the hydrocarbon feed is selected from the group consisting of heavy cycle oil, light cycle oil, carbon black oil, cracked distillate and pyoil.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/078225

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G65/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/000848 A1 (SAUDI BASIC IND CORP [SA]; SABIC GLOBAL TECHNOLOGIES BV [NL]; WARD AND) 8 January 2015 (2015-01-08) cited in the application	1-4,6, 14,15
A	figure 4 claims 1-15 page 13, lines 15-19 page 23, lines 12-15 -----	5,7-13
X	WO 2015/128038 A1 (SAUDI BASIC IND CORP [SA]; SABIC GLOBAL TECHNOLOGIES BV [NL]; OPRINS A) 3 September 2015 (2015-09-03)	1,2,4,6, 15
A	figure 1 claims 1-15 page 11, lines 12-13 -----	3,5,7-14
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 January 2017	18/01/2017

Name and mailing address of the ISA/	Authorized officer
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1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 2015/128018 A1 (SAUDI BASIC IND CORP [SA]; SABIC GLOBAL TECHNOLOGIES BV [NL]; OPRINS A) 3 September 2015 (2015-09-03) figure 4 claims 1-14 page 18, line 4 - page 19, line 23 page 27, lines 1-2 -----	1-3,5, 11-15 4,6-10

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/078225

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015000848 A1	08-01-2015	CN 105473690 A	06-04-2016
		EA 201690126 A1	29-07-2016
		EP 3017019 A1	11-05-2016
		JP 2016526596 A	05-09-2016
		KR 20160029806 A	15-03-2016
		SG 11201509168U A	28-01-2016
		US 2016369187 A1	22-12-2016
		WO 2015000848 A1	08-01-2015
WO 2015128038 A1	03-09-2015	CN 106133119 A	16-11-2016
		EA 201691714 A1	30-12-2016
		EP 3110917 A1	04-01-2017
		KR 20160126023 A	01-11-2016
		SG 11201606016Q A	30-08-2016
		WO 2015128038 A1	03-09-2015
WO 2015128018 A1	03-09-2015	CN 106029610 A	12-10-2016
		EP 3110777 A1	04-01-2017
		KR 20160124819 A	28-10-2016
		SG 11201606519W A	29-09-2016
		WO 2015128018 A1	03-09-2015