US 20130118059A1

(19) **United States**

(12) **Patent Application Publication**

LANGE et al.

(10) **Pub. No.: US 2013/0118059 A1**

(43) **Pub. Date: May 16, 2013**

(54) **PROCESS FOR CONVERSION OF A CELLULOSIC MATERIAL**

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(21) Appl. No.: **13/677,124**

(22) Filed: **Nov. 14, 2012**

(30) **Foreign Application Priority Data**

Nov. 14, 2011 (EP) EP11189049.7
Oct. 25, 2012 (EP) EP12190054.2

Publication Classification

(51) **Int. Cl.**
C10G 1/00 (2006.01)
C10L 1/02 (2006.01)

(52) **U.S. Cl.**
CPC .. ***C10G 1/006*** (2013.01); ***C10L 1/02*** (2013.01)
USPC **44/307**

(57) **ABSTRACT**

A process for conversion of a cellulosic material comprising

a) a liquefaction step, comprising

contacting a cellulosic material with a liquid solvent at a temperature of equal to or more than 200° C.; or

contacting a cellulosic material with a liquid solvent at a temperature of equal to or more than 100° C. in the presence of a catalyst,

to produce a final liquefied product;

b) a catalytic cracking step, comprising contacting at least part of the final liquefied product with a fluidized catalytic cracking catalyst at a temperature of equal to or more than 400° C., to produce one or more cracked products.

PROCESS FOR CONVERSION OF A CELLULOSIC MATERIAL

[0001] This application claims the benefit of priority of European Patent Application No. 11189049.7, filed on Nov. 14, 2011, and of European Patent Application No. 12190054.2, filed on Oct. 25, 2012, the disclosures of which are incorporated by reference herein in their entirety.

FIELD OF THE INVENTION

[0002] Embodiments of the invention relate to a process for conversion of a cellulosic material and use of the products produced in such a process.

BACKGROUND OF THE INVENTION

[0003] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present invention. This discussion is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the present invention. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of any prior art.

[0004] With the diminishing supply of crude mineral oil, use of renewable energy sources is becoming increasingly important for the production of liquid fuels. These fuels from renewable energy sources are often referred to as biofuels.

[0005] Biofuels derived from non-edible renewable energy sources, such as cellulosic materials, are preferred as these do not compete with food production. These biofuels are also referred to as second generation, or advanced, biofuels. Most of these non-edible cellulosic materials, however, are solid materials that are cumbersome to convert into biofuels.

[0006] WO2010/135734 describes a method for co-processing a biomass feedstock and a refinery feedstock in a refinery unit comprising catalytically cracking the biomass feedstock and the refinery feedstock in a refinery unit comprising a fluidized reactor, wherein hydrogen is transferred from the refinery feedstock to carbon and oxygen of the biomass feedstock. In one of the embodiments WO2010/135734 the biomass feedstock comprises a plurality of solid biomass particles having an average size between 50 and 1000 microns. In passing, it is further mentioned that solid biomass particles can be pre-processed to increase brittleness, susceptibility to catalytic conversion (e.g. by roasting, toasting, and/or torrefication) and/or susceptibility to mixing with a petrochemical feedstock.

[0007] A disadvantage of the process as described in WO2010/135734, however, is that proper handling of the biomass feedstock comprising the solid biomass particles is critical to avoid instability of the feedstock, clogging of feed lines to a fluidized catalytic cracking unit and/or coking in a fluidized catalytic cracking unit.

[0008] The article of F. de Miguel Mercader et al, published in the Journal of Applied Catalysis B: Environmental, 2010, volume 96, pages 57-66, describes a process for catalytic cracking of an hydrodeoxygenated pyrolysis oil, derived from forest residue, together with long residue in a catalytic cracking reactor. Although the described process gives good results it is indicated that the hydrodeoxygenation reactions lead to a better product (with respect to fluidized catalytic cracking (FCC) co-processing) at the expense of hydrogen. In addition, it is indicated that during hydrodeoxygenation, reaction conditions are critical to obtain thermally stable molecules suitable for further processing in a FCC unit. FIG. 9 of the article further illustrates the competition between hydro (deoxy)genation and (re)polymerization of the pyrolysis oil. As explained in the article, fast polymerization reactions may cause plugging of a reactor.

[0009] It would therefore be an advancement in the art to provide a less critical process for conversion of a cellulosic material.

SUMMARY

[0010] Such an advancement has been achieved with the process according to the invention. According to one aspect of the invention, there is provided a method for conversion of a cellulosic material. The method comprises a liquefaction step to produce a final liquefied product, the liquefaction step comprising: contacting a cellulosic material with a liquid solvent at a temperature of equal to or more than about 200° C.; or contacting a cellulosic material with a liquid solvent at a temperature of equal to or more than about 100° C. in the presence of a catalyst. The method further comprises a catalytic cracking step to produce at least one cracked product, the catalytic cracking step comprising contacting at least part of the final liquefied product with a fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C.

[0011] In one embodiment, the liquid solvent comprises water and/or an organic solvent. In another embodiment, the liquefaction step comprises simultaneously contacting the cellulosic material with an organic solvent, a source of hydrogen, an acid catalyst and a hydrogenation catalyst at a temperature of equal to or more than about 150° C. In another embodiment, the liquefaction step comprises contacting the cellulosic material with an organic solvent in the presence of an acid catalyst at a temperature of equal to or more than about 150° C. to produce an intermediate liquefied product; and subsequently hydrotreating the intermediate liquefied product with a source of hydrogen in the presence of a hydrotreatment catalyst to produce a final liquefied product.

[0012] In one embodiment, the liquid solvent is an organic solvent and wherein the process further comprises a separation step, wherein at least a portion of the final liquefied product produced in the liquefaction step is separated from at least part of the organic solvent. In another embodiment, the separated portion of the organic solvent is used in the liquefaction step. In another embodiment, the catalytic cracking step comprises contacting at least part of the final liquefied product and a fluid hydrocarbon co-feed with the fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C.

[0013] In one embodiment, the fluid hydrocarbon co-feed comprises at least one of a straight run (atmospheric) gas oil, a flashed distillate, a vacuum gas oil (VGO), a light cycle oil, a heavy cycle oil, a hydrowax, a coker gas oil, a gasoline, a naphtha, a diesel, a kerosene, an atmospheric residue ("long residue"), a vacuum residue ("short residue"), and any combination thereof. In another embodiment, the liquefaction step comprises contacting a cellulosic material with an organic solvent at a temperature of equal to or more than about 100° C. in the presence of a catalyst, wherein the organic solvent comprises a fraction of a petroleum oil; and wherein the catalytic cracking step comprises contacting a mixture of at least part of the final liquefied product and the fraction of a petroleum oil with a fluidized catalytic cracking catalyst in a fluidized catalytic cracking reactor at a temperature of equal to or more than about 400° C.

[0014] In one embodiment, the liquefaction step comprises simultaneously contacting the cellulosic material with the fraction of a petroleum oil, with a source of hydrogen, and with a hydrogenation catalyst at a temperature of equal to or more than about 150° C. In another embodiment, a further organic solvent is generated in-situ during the liquefaction step.

[0015] In one embodiment, the liquefaction step comprises simultaneously contacting the cellulosic material with a liquid solvent, with a source of hydrogen, with an acid catalyst and with a hydrogenation catalyst at a temperature of equal to or more than about 150° C.; and wherein the catalytic cracking step comprises contacting at least part of the final liquefied product with a fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C. In one embodiment, the liquid solvent is water or a solvent mixture comprising an organic solvent and water.

[0016] In one embodiment, the final liquefied product or part thereof comprises one, two or more compounds chosen from the group consisting of gamma-valerolactone and/or levulinic acid; tetrahydrofufuryl and/or tetrahydropyranyl; furfural and/or hydroxymethylfurfural; mono- and/or di-alcohols and/or mono- and/or di-ketones; and/or guaiacol and/or syringol components.

[0017] In one embodiment, the process further comprises a fractionation step comprising fractionating the at least one cracked product to produce at least one product fraction. In another embodiment, the process further comprises a hydrotreatment step comprising hydrotreating the at least one product fraction with a source of hydrogen to produce at least one hydrotreated product fraction.

[0018] According to another aspect of the invention, there is provided a biofuel component comprising material produced from certain embodiments of the present invention. In one embodiment, the biofuel component comprises the at least one product fraction or any product derived from the at least one product fraction product fraction. In another embodiment, the biofuel component comprises the at least one hydrotreated product fraction or any product derived from the at least one hydrotreated product fraction.

[0019] According to another aspect of the invention, there is provided a process for the production of a biofuel comprising blending the biofuel component according to certain aspects of the invention with one or more other components to produce a biofuel.

[0020] Without wishing to be bound by any kind of theory it is believed that due to its composition, the final liquefied product of certain embodiments of the present invention allows for a more stable feedstock to a fluidized catalytic cracking process than any pyrolysis oil and/or any solid biomass particles.

[0021] In addition, it has been found that in certain embodiments according to the invention coking may be minimized.

[0022] Certain embodiments of the process according to the invention therefore provide a less critical process for conversion of a cellulosic material.

[0023] The one or more cracked products of certain embodiments of the present invention may advantageously be fractionated to produce one or more product fractions and optionally hydrotreated to produce one or more hydrotreated product fractions. These one or more product fractions and/or one or more hydrotreated product fractions and/or one or more products derived therefrom can advantageously be used as a biofuel component. Embodiments of the present invention therefore further provides a process for the production of a biofuel comprising blending such biofuel components with one or more other components to produce a biofuel. The produced biofuel may advantageously be used in a transportation vehicle.

[0024] Other advantages and features of embodiments of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0025] Embodiments of the present invention include a liquefaction step where a cellulosic material is contacted with a liquid solvent to produce a final liquefied product. This step may also be referred to herein as a liquefaction or liquefying of the cellulosic material. The liquefaction or liquefying may be carried out by means of a liquefaction or liquefying reaction.

[0026] By liquefaction (also herein referred to as liquefying) is herein understood to refer at least to the conversion of a solid material, such as cellulosic material, into one or more liquefied products.

[0027] By a liquefied product is herein understood to refer at least to a product that is liquid at a temperature of about 20° C. and a pressure of about 1 bar absolute (0.1 MegaPascal) and/or a product that can be converted into a liquid by melting (for example by applying heat) or dissolving in a solvent. Preferably the liquefied product is a liquefied product that is liquid at a temperature of about 80° C. and a pressure of about 1 bar absolute (0.1 MegaPascal). The liquefied product may vary widely in its viscosity and may be more or less viscous.

[0028] Liquefaction of a cellulosic material can comprise cleavage of covalent linkages in that cellulosic material. For example liquefaction of lignocellulosic material can comprise cleavage of covalent linkages in cellulose, hemicellulose and/or lignin present and/or cleavage of covalent linkages between lignin, hemicelluloses and/or cellulose.

[0029] As used herein, cellulosic material refers to material containing cellulose. Preferably the cellulosic material is a lignocellulosic material. A lignocellulosic material comprises lignin, cellulose and optionally hemicellulose.

[0030] Advantageously the liquefaction step makes it possible to liquefy not only the cellulose but also the lignin and hemicelluloses.

[0031] Any suitable cellulose-containing material may be used as cellulosic material in the process according to the present invention. The cellulosic material for use according to the invention may be obtained from a variety of plants and plant materials including agricultural wastes, forestry wastes, sugar processing residues and/or mixtures thereof. Examples of suitable cellulose-containing materials include agricultural wastes such as corn stover, soybean stover, corn cobs, rice straw, rice hulls, oat hulls, corn fibre, cereal straws such as wheat, barley, rye and oat straw; grasses; forestry products such as wood and wood-related materials such as sawdust;

waste paper; sugar processing residues such as bagasse and beet pulp; or mixtures thereof.

[0032] The liquefaction step may further comprise drying, torrefaction, steam explosion, particle size reduction, densification and/or pelletization of the cellulosic material before the cellulosic material is contacted with the liquid solvent. Such drying, torrefaction, steam explosion, particle size reduction, densification and/or pelletization of the cellulosic material may advantageously allow for improved process operability and economics.

[0033] Before being used in the process of the invention, the cellulosic material is preferably processed into small particles in order to facilitate liquefaction. Preferably, the cellulosic material is processed into particles having a particle size distribution with an average particle size of equal to or more than about 0.05 millimeter, more preferably equal to or more than about 0.1 millimeter, most preferably equal to or more than about 0.5 millimeter and preferably equal to or less than about 20 centimeters, more preferably equal to or less than about 10 centimeters and most preferably equal to or less than about 3 centimeters. For practical purposes the particle size in the centimeter and millimeter range can be determined by sieving.

[0034] If the cellulosic material is a lignocellulosic material it may also have been subjected to a pre-treatment to remove and/or degrade lignin and/or hemicelluloses. Examples of such pre-treatments include fractionation, pulping and torrefaction processes.

[0035] By a liquid solvent is herein preferably understood to refer at least to a solvent that is liquid at a pressure of about 1 bar atmosphere (0.1 MegaPascal) and a temperature of about 80° C. or higher, more preferably about 100° C. or higher. Most preferably a liquid solvent is herein understood to be a solvent that is liquid at the temperature and pressure at which the liquefaction step is carried out.

[0036] In one preferred embodiment the liquid solvent comprises or is water.

[0037] In another preferred embodiment the liquid solvent comprises or is an organic solvent. By an organic solvent is herein understood at least as a solvent comprising one or more hydrocarbon compounds. By a hydrocarbon compound is herein understood a compound that contains at least one hydrogen atom and at least one carbon atom, more preferably a hydrocarbon compound is herein understood to contain at least one hydrogen atom and at least one carbon atom bonded to each other via at least one covalent bond.

[0038] In addition to hydrogen and carbon the hydrocarbon compound may contain for example heteroatoms such as sulphur, oxygen and/or nitrogen. Examples of hydrocarbon compounds that may preferably be present in the organic solvent include acetic acid, formic acid, levulinic acid and gamma-valerolactone and/or mixtures thereof.

[0039] The organic solvent may comprise polar and/or non-polar hydrocarbon compounds. In a preferred embodiment the organic solvent comprises at least one or more polar hydrocarbon compounds. Preferably the organic solvent comprises more than one, more preferably more than two, more preferably more than three different polar hydrocarbon compounds. A measure of the polarity of a polar hydrocarbon compound is its log P value, where P is defined as the partition coefficient of a compound in a two phase octanol-water system. The log P value can be determined experimentally or calculated according to standard procedures as discussed in Handbook of Chemistry and Physics, 83^{rd} Edition, pages 16-43 to 16-47, CRC Press (2002).

[0040] In one embodiment the organic solvent may preferably comprise one or more polar hydrocarbon compound(s), which one or more polar hydrocarbon compound(s) preferably is/are a hydrocarbon compound having a polarity of log P less than +3, more preferably less than +1. In another embodiment, the polar hydrocarbon compound is a hydrocarbon compound having a polarity of log P less than +0.5. In a further embodiment, the polar hydrocarbon compound is a hydrocarbon compound having a polarity of log P less than 0.

[0041] In another embodiment the organic solvent may preferably comprise one or more non-polar hydrocarbon compounds(s), which one or more non-polar hydrocarbon compound(s) preferably is/are a hydrocarbon compound having a polarity of log P in the range from +5 to +10, more preferably in the range from +7 to +8.

[0042] In a preferred embodiment the organic solvent comprises one or more carboxylic acids. By a carboxylic acid is herein understood a hydrocarbon compound comprising at least one carboxyl (—CO—OH) group. Such carboxylic acids can be polar hydrocarbon compounds as herein described above. More preferably the organic solvent comprises equal to or more than about 5 wt % carboxylic acids, more preferably equal to or more than about 10 wt % carboxylic acids, most preferably equal to or more than about 20 wt % of carboxylic acids, based on the total weight of organic solvent. There is no upper limit for the carboxylic acid concentration, but for practical purposes the organic solvent may comprise equal to or less than about 90 wt %, more preferably equal to or less than about 80 wt % of carboxylic acids, based on the total weight of organic solvent. Preferably the organic solvent comprises at least acetic acid, levulinic acid and/or pentanoic acid. Especially acetic acid may be useful as it can be simultaneous used as (part of) the organic solvent as well as used as an acid catalyst.

[0043] In another embodiment the organic solvent comprises paraffinic compounds, naphthenic compounds, olefinic compounds and/or aromatic compounds. Such compounds may be present in refinery streams such as gas oil, fuel oil and/or residue oil. These refinery streams may therefore also be suitable as organic solvent in the liquefaction step. This is explained in more detail below.

[0044] In another preferred embodiment the organic solvent comprises at least a part of a liquefied product. Preferably part of the liquefied product (for example part of a final liquefied product and/or part of an intermediate liquefied product as described herein below) is therefore recycled to the liquefaction step to be used as organic solvent. In a preferred embodiment equal to or more than about 10 wt %, more preferably equal to or more than about 20 wt % of the organic solvent is obtained from an intermediate and/or final liquefied product.

[0045] In a preferred embodiment, any recycle of liquefied product(s) comprises a weight amount of liquefied product(s) of 2 to 100 times the weight of the cellulosic material, more preferably of 5 to 20 times the weight of the cellulosic material.

[0046] In a preferred embodiment at least part of the organic solvent is derived from cellulosic, and preferably lignocellulosic, material. For example in a preferred embodiment at least part of the organic solvent may be generated in-situ during liquefaction of the cellulosic material. More preferably, at least part of the organic solvent is obtained by acid hydrolysis of cellulosic, and preferably lignocellulosic, material. Examples of possible hydrocarbon compounds in the organic solvent that may be obtained by acid hydrolysis of cellulosic, and preferably lignocellulosic, material include acetic acid, formic acid and levulinic acid. Hydrocarbon compounds which are obtainable from such acid hydrolysis products by hydrogenation thereof may also suitably be used. Examples of such hydrogenated hydrocarbon compounds include gamma-valerolactone which is obtainable from levulinic acid by hydrogenation, tetrahydrofufuryl and tetrahydropyranyl components which are derived from furfural or hydroxymethylfurfural, mono- and di-alcohols and ketones which are derived from sugars, and guaiacol and syringol components which are derived from lignin. Preferably the organic solvent may comprise one, two or more of such hydrocarbon compounds.

[0047] Further, the above compounds may also become part of the final liquefied product. Hence, in a preferred embodiment the final liquefied product or part thereof may comprise one, two or more of the above listed, optionally hydrogenated, compounds such as gamma-valerolactone, which can be obtained from levulinic acid by hydrogenation; tetrahydrofufuryl and tetrahydropyranyl components, which can be derived from furfural or hydroxymethylfurfural; mono- and/or di-alcohols and/or mono- and/or di-ketones, which can be derived from sugars; and/or guaiacol and/or syringol components, which can be derived from lignin.

[0048] One or more hydrocarbon compounds in the organic solvent may advantageously be obtainable from the cellulosic material liquefied in the liquefaction step. The hydrocarbon compound(s) may for example be generated in-situ and/or recycled and/or used as a make-up organic solvent, affording significant economic and processing advantages.

[0049] In one embodiment at least part of the organic solvent in the liquefaction step is not generated in situ by conversion of the cellulosic material. Such an ex-situ provided organic solvent may co-exist with an in-situ formed organic solvent. Such a solvent that is not generated in-situ but is ex-situ provided may therefore herein also be referred to as “co-solvent”.

[0050] In a preferred embodiment the organic solvent comprises at least one or more hydrocarbon compound(s) that are at least partly obtained and/or derived from a source other than the cellulosic material used as a feedstock in the liquefaction step, for example a petroleum source (herein also referred to as fossil source). These one or more hydrocarbon compounds(s) may for example be mixed with the cellulosic material before starting the liquefaction or may be added to the reaction mixture during the liquefaction.

[0051] As explained in more detail herein below, in one embodiment the organic solvent in the liquefaction step comprises one or more hydrocarbon compounds that also may be suitable to act as a fluid hydrocarbon co-feed in the catalytic cracking step. In a further embodiment the organic solvent used in the liquefaction step contains one or more hydrocarbon compounds obtained from a conventional crude oil (also sometimes referred to as a petroleum oil or mineral oil); an unconventional crude oil (that is, oil produced or extracted using techniques other than the traditional oil well method); a renewable source (such as for example a vegetable oil); or a Fisher Tropsch oil and/or a mixture thereof. More preferably the organic solvent used in the liquefaction step comprises or consists of a fraction of a petroleum oil or renewable oil. Preferably the organic solvent comprises or consists of a straight run (atmospheric) gas oils, flashed distillate, vacuum gas oils (VGO), light cycle oil, heavy cycle oil, hydrowax, coker gas oils, diesel, gasoline, kerosene, naphtha, liquefied petroleum gases, atmospheric residue (“long residue”) and vacuum residue (“short residue”) and/or mixtures thereof. Most preferably the organic solvent comprises or consists of a long residue.

[0052] Hence, preferably the co-solvent as mentioned above, is an organic solvent that comprises or consists of a petroleum oil or a fraction thereof. The advantage of using a petroleum oil or a fraction thereof as an organic solvent or organic co-solvent is that this organic solvent or co-solvent may also be a suitable feed to the catalytic cracking step. When the organic solvent or organic co-solvent comprises or is a petroleum oil or a fraction thereof, this may lead to a more efficient and cheaper operation and hardware as no separation of such a organic solvent or organic co-solvent may be needed.

[0053] In a preferred embodiment, the present invention therefore also provides a process for conversion of a cellulosic material comprising

a) a liquefaction step, comprising contacting a cellulosic material with an organic solvent at a temperature of equal to or more than about 100° C. in the presence of a catalyst, wherein the organic solvent comprises a fraction of a petroleum oil, to produce a final liquefied product;

b) a catalytic cracking step, comprising contacting a mixture of at least part of the final liquefied product and the fraction of a petroleum oil with a fluidized catalytic cracking catalyst in a fluidized catalytic cracking reactor at a temperature of equal to or more than about 400° C., to produce one or more cracked products. One skilled in the art will understand that the liquefied product in step b) may suitably be the final liquefied product or any part thereof.

[0054] The fraction of a petroleum oil is preferably chosen from the group consisting of straight run (atmospheric) gas oils, flashed distillate, vacuum gas oils (VGO), light cycle oil, heavy cycle oil, hydrowax, coker gas oils, diesel, gasoline, kerosene, naphtha, liquefied petroleum gases, atmospheric residue (“long residue”) and vacuum residue (“short residue”) and/or mixtures thereof as indicated above. At least part of this fraction of a petroleum oil or the whole of this fraction of a petroleum oil may be contacted with the fluidized catalytic cracking catalyst in step b).

[0055] In a preferred embodiment the liquefaction step comprises contacting the cellulosic material simultaneously with the fraction of a petroleum oil, with a source of hydrogen, with a hydrogenation catalyst, and optionally with an acid catalyst, at a temperature of equal to or more than about 150° C. to produce a final liquefied product.

[0056] Other preferences are as described elsewhere herein.

[0057] In one embodiment, the organic solvent is partly derived from cellulosic, preferably lignocellulosic, material and partly derived from a petroleum source. In a preferred embodiment the organic solvent comprises a mixture of i) a fraction of a petroleum oil and ii) one or more hydrocarbon compounds that may be obtained by acid hydrolysis of cellulosic, preferably lignocellulosic, material.

[0058] In a preferred embodiment the organic solvent comprises at least one or more carboxylic acids, such as for example acidic acid, levulinic acid and/or pentanoic acid, which carboxylic acid(s) are preferably present before beginning the liquefaction reaction, that is, which carboxylic acid

(s) are preferably not in-situ obtained and/or derived from the cellulosic material during the reaction.

[0059] Advantageously, the organic solvent may be water-miscible at the reaction temperature of the liquefaction step. In a preferred embodiment, the liquefaction step comprises contacting the cellulosic material with a solvent mixture comprising the organic solvent and water. Hence, in a preferred embodiment the liquid solvent may comprise a solvent mixture containing water and an organic solvent.

[0060] The water in the solvent mixture may for example be generated in-situ during the liquefaction step. The organic solvent is preferably present in an amount of less than or equal to about 95% by weight, more preferably less than or equal to about 90% by weight and most preferably less than or equal to about 80% by weight, based on the total weight of water and organic solvent. Further the organic solvent is preferably present in an amount of more than or equal to about 5% by weight, more preferably more than or equal to about 10% by weight, and most preferably more than or equal to about 20% by weight, based on the total weight of water and organic solvent. The organic solvent is preferably present in an amount of from about 20% to about 60% by weight, based on the total weight of the water and organic solvent.

[0061] Preferably water is present in an amount of less than or equal to about 95% by weight, more preferably an amount of less than or equal to about 90% by weight, and most preferably less than or equal to about 80% by weight, based on the total weight of water and organic solvent. Further water is preferably present in an amount of more than or equal to about 5% by weight, more preferably in an amount of more than or equal to about 10% by weight, most preferably about 20% by weight, based on the total weight of water and organic solvent. Preferably, water is present in an amount of from about 40% to about 80% by weight based on the total weight of the water and organic solvent. Preferably a solvent mixture contains the organic solvent and water in a weight ratio of organic solvent to water of less than or equal to 9:1, more preferably less than or equal to 8:2. Further a solvent mixture preferably contains the organic solvent and water in a weight ratio of organic solvent to water of more than or equal to 1:9 more preferably more than or equal to 2:8.

[0062] The cellulosic material and the organic solvent or—if a solvent mixture containing water and organic solvent is present—the solvent mixture are preferably mixed in a solvent mixture or organic solvent-to-cellulosic material ratio of 2:1 to 20:1 by weight, more preferably in a solvent mixture or organic solvent-to-cellulosic material ratio of 3:1 to 15:1 by weight and most preferably in a solvent mixture or organic solvent-to-cellulosic material ratio of 4:1 to 10:1 by weight.

[0063] The liquefaction step may be carried out in the presence or absence of a catalyst. The use of a catalyst advantageously allows one to lower the reaction temperature.

[0064] Hence, in one embodiment the liquefaction step may comprise contacting a cellulosic material with an organic solvent, optionally in the essential absence of an externally provided acid catalyst, at a temperature of equal to or more than about 200° C., more preferably equal to or more than about 250° C., still more preferably a temperature of equal to or more than about 300° C. and preferably a temperature equal to or less than about 450° C.

[0065] In another embodiment the liquefaction step may comprise contacting a cellulosic material with an organic solvent in the presence of a, preferably acid, catalyst at a temperature of equal to or more than about 100° C., more preferably a temperature of equal to or more than about 150° C., still more preferably a temperature of equal to or more than about 200° C. and preferably a temperature of equal to or less than about 450° C., more preferably a temperature of equal to or less than about 350° C.

[0066] Preferably the catalyst is an acid catalyst. The acid catalyst for use in liquefaction step to the invention may be any acid catalyst known in the art to be suitable for liquefying of cellulosic material. For example, the acid catalyst may be a Brönsted acid or a Lewis acid. Further the acid catalyst may be a homogeneous catalyst or a heterogeneous catalyst. Preferably the acid catalyst is a homogeneous or finely dispersed heterogeneous catalyst, most preferably the acid catalyst is a homogeneous catalyst. Preferably the acid catalyst remains liquid and stable under the liquefaction conditions and preferably it is sufficiently strong to effect cleavage of the covalent linkages and dehydration of the cellulosic material.

[0067] Preferably the acid catalyst is a Brönsted acid and more preferably the acid catalyst is a mineral or organic acid, preferably a mineral or organic acid having a pKa value below 5.0, more preferably below 4.25, still more preferably below 3.75, even more preferably below 3.0, and most preferably below 2.5.

[0068] Examples of suitable mineral acids include sulphuric acid, para toluene sulphonic acid, nitric acid, hydrochloric acid and phosphoric acid, and mixtures thereof. In a preferred embodiment, the acid catalyst used in the liquefaction step is sulphuric acid or phosphoric acid.

[0069] Examples of suitable organic acids which may be used in the liquefaction step include levulinic acid, acetic acid, oxalic acid, formic acid, lactic acid, citric acid, trichloracetic acid and mixtures thereof. If the acid catalyst is an organic acid, it may suitably be an organic acid that is generated in-situ or ex-situ (i.e. provided externally). By an in-situ generated organic acid is herein understood at least to include an organic catalyst that is generated in-situ during liquefaction of the cellulosic material. An example of such an in-situ generated organic acid may be acetic acid or formic acid.

[0070] The acid catalyst is preferably present in an amount of less than or equal to about 35% by weight, more preferably less than or equal to about 20% by weight, even more preferably less than or equal to about 10% by weight and still more preferably less than or equal to about 5% by weight, and most preferably less than or equal to about 1% by weight, based on the total weight of organic solvent or—if applicable—solvent mixture and acid catalyst. Further the acid catalyst is preferably present in an amount of more than or equal to about 0.01% by weight, more preferably more than or equal to about 0.1% by weight and most preferably more than or equal to about 0.2% by weight, based on the total weight of organic solvent or—if applicable—solvent mixture and acid catalyst. It will be appreciated that for any given acid catalyst the amount of acid required will depend on the strength of the acid. In one preferred embodiment, the acid catalyst is present in an amount of from about 1% to about 10% by weight, preferably from about 2% to about 5% by weight, based on the weight of organic solvent or—if applicable—solvent mixture and acid catalyst.

[0071] In a preferred embodiment at least part of the liquefied product obtained after liquefaction of the cellulosic material is hydrogenated. Liquefaction and hydrogenation may be carried out simultaneously or hydrogenation may be carried out subsequent to the liquefaction.

[0072] In one embodiment the liquefaction step comprises contacting the cellulosic material with the organic solvent in the presence of an acid catalyst at a temperature of equal to or more than about 150° C. to produce an intermediate liquefied product; and subsequently hydrotreating the intermediate liquefied product with a source of hydrogen in the presence of a hydrotreatment catalyst to produce a final liquefied product. Preferably hydrotreating of the intermediate liquefied product comprises hydrogenating of the intermediate liquefied product and preferably the hydrotreatment catalyst is a hydrogenation catalyst.

[0073] In another embodiment the liquefaction step comprises contacting the cellulosic material simultaneously with the organic solvent, a source of hydrogen, the acid catalyst and a hydrogenation catalyst at a temperature of equal to or more than about 150° C. to produce a final liquefied product. In this case the liquefaction step can advantageously comprise the simultaneous hydrolysis and hydrogenation of the cellulosic material, resulting in an improved degree of liquefaction. By simultaneous contact is understood contact of the cellulosic material with one of the specified features in the presence of the remaining features. In this way simultaneous hydrolysis and hydrogenation of the cellulosic material can be effected as any hydrolysis product can be in-situ hydrogenated.

[0074] The hydrogenation catalyst is preferably a hydrogenation catalyst that is resistant to the combination of the organic solvent (or if applicable the solvent mixture) and, if present, the acid catalyst.

[0075] For example the hydrogenation catalyst can comprise a heterogeneous and/or homogeneous catalyst. In a preferred embodiment the hydrogenation catalyst is a homogeneous catalyst. In another preferred embodiment the hydrogenation catalyst is a heterogeneous catalyst. The hydrogenation catalyst preferably comprises a hydrogenation metal known to be suitable for hydrogenation reactions, such as for example iron, molybdenum, cobalt, nickel, copper, ruthenium, rhodium, palladium, iridium, platinum and gold, or mixtures thereof. The hydrogenation catalyst comprising such a hydrogenation metal may be sulfided.

[0076] In a further embodiment sulfided hydrogenation catalysts may be used such as for example a catalyst based on Molybdenum sulfide, potentially including Cobalt and/or Nickel as a promotor.

[0077] If the hydrogenation catalyst is a heterogeneous catalyst, the catalyst preferably comprises a hydrogenation metal supported on a carrier. Suitable carriers include for example carbon, alumina, titanium dioxide, zirconium dioxide, silicon dioxide and mixtures thereof. Examples of preferred heterogeneous hydrogenation catalysts include ruthenium, platinum or palladium supported on a carbon carrier. Other preferred examples of heterogeneous hydrogenation catalysts include ruthenium supported on titanium dioxide (TiO2), platina supported on titanium dioxide and ruthenium supported on zirconium dioxide(ZrO2). The heterogeneous catalyst and/or carrier may have any suitable form including the form of a mesoporous powder, granules or extrudates or a megaporous structure such as a foam, honeycomb, mesh or cloth. The heterogeneous catalyst may be present in a liquefaction reactor comprised in a fixed bed or ebullated slurry. Preferably the heterogeneous catalyst is present in a liquefaction reactor as a fixed bed.

[0078] If the hydrogenation catalyst is a homogeneous hydrogenation catalyst, the catalyst preferably comprises an organic or inorganic salt of the hydrogenation metal, such as for example the acetate-, acetylacetonate-, nitrate-, sulphate- or chloride-salt of ruthenium, platinum or palladium. Preferably the homogeneous catalyst is an organic or inorganic acid salt of the hydrogenation metal, wherein the acid is an acid which is already present in the process as acid catalyst or product.

[0079] The source of hydrogen may be any source of hydrogen known to be suitable for hydrogenation purposes. It may for example include hydrogen gas, but also an hydrogen-donor such as for example formic acid. Preferably the source of hydrogen is a hydrogen gas. Such a hydrogen gas can be applied in the process of the invention at a partial hydrogen pressure that preferably lies in the range from about 2 to 200 bar absolute (0.1 to 20 MegaPascal), more preferably in the range from about 10 to 170 bar absolute (1 to 17 MegaPascal), and most preferably in the range from 30 to about 150 bar absolute (3 to 15 MegaPascal). A hydrogen gas can be supplied to a liquefaction reactor co-currently, cross-currently or counter-currently to the cellulosic material. Preferably a hydrogen gas is supplied counter-currently to the cellulosic material.

[0080] The liquefaction step can be carried out at any total pressure known to be suitable for liquefaction processes. The process can be carried out under a total pressure that preferably lies in the range from about 2 to 200 bar absolute (0.1 to 20 MegaPascal), more preferably in the range from about 10 to 170 bar absolute (1 to 17 MegaPascal), and most preferably in the range from about 30 to 150 bar absolute (3 to 15 MegaPascal).

[0081] The liquefaction process according to the invention can be carried out batch-wise, semi-batch wise and continuously.

[0082] During the liquefaction step, the cellulosic material is liquefied, i.e. the cellulosic material is converted into one or more liquefied products, to produce a final liquefied product.

[0083] By a final liquefied product is herein preferably understood to refer at least to a liquefied product which is ready to be forwarded to the catalytic cracking step. The final liquefied product may have been hydrogenated (as explained herein above) or not. Further the final liquefied product may have been separated from the reaction effluent or not. Preferably the final liquefied product has been hydrogenated and/or is obtained after one or more separations as described herein below.

[0084] The reaction effluent produced in the liquefaction step may include so-called humins, the liquefied product(s) and for example water, co-solvent, acid catalyst, and/or hydrogenation catalyst and/or gaseous products such as for example hydrogen. In a preferred embodiment the liquefaction step may further comprise separating a final liquefied product from a reaction effluent produced in the liquefaction step.

[0085] By humins is understood the solid insoluble material remaining after liquefaction. It is sometimes also referred to as char.

[0086] The liquefied product(s) may comprise monomeric and/or oligomeric compounds and optionally excess water produced during the liquefaction process. From the liquefied product a product containing monomeric and oligomeric compounds may be separated. Also part of the liquefied product may be separated for recycling to the liquefaction step as organic solvent.

[0087] The reaction effluent is preferably forwarded to a separation section. In the separation section insoluble humins, monomeric and/or oligomeric compounds and/or water, co-solvent and/or acid catalyst can be separated off from the reaction effluent.

[0088] In one embodiment the humins may be separated from the reaction effluent in a manner known to be suitable for this purpose. Preferably such humins are separated off via filtration or settling. Any humins formed in the liquefaction step can be converted to diesel, kerosene and gasoline fraction in the catalytic cracking step of the process according to the invention or in another conventional refinery step.

[0089] In another embodiment the liquefied products and/or any co-solvent are separated from the reaction effluent in a manner known to be suitable for this purpose. Preferably liquefied products and/or any co-solvent are separated off by liquid/liquid separation techniques, such as phase separation, (solvent) extraction and/or membrane filtration or (vacuum) distillation.

[0090] If desired the monomeric products and oligomeric products may be conveniently separated from each other using one or more membranes. For example, monomeric compounds and/or optionally water can be separated from any C9-C20 oligomeric compounds and C20+ oligomeric compounds by a ceramic membrane (for example a TiO_2 membrane) or a polymeric membrane (for example a Koch MPF 34 (flatsheet) or a Koch MPS-34 (spiral wound) membrane). The C9-C20 oligomers and the C20+ oligomers can conveniently be separated from each other with for example a polymer grafted ZrO_2 membrane. The use of membranes for these separations can advantageously improve the energy efficiency of the process.

[0091] In another embodiment excess water produced during the liquefaction step is removed by distillation, pervaporation and/or reversed osmosis.

[0092] In a preferred embodiment, at least part of any water, co-solvent, acid catalyst and/or hydrogenation catalyst is advantageously recovered to be recycled for re-use in the liquefaction step. In a further preferred embodiment, this recycle stream also contains at least part of any monomeric compounds and/or oligomeric products. Any excess of water, co-solvent, acid catalyst, hydrogenation catalysts and/or monomeric compounds is preferably purged via a purge stream. In the liquefaction step, preferably more than or equal to about 50% by weight, more preferably more than or equal to about 60% by weight and most preferably more than or equal to about 70% by weight of the cellulosic material may advantageously be liquefied into liquefied product, preferably in less than about 3 hours.

[0093] When the co-solvent is an organic co-solvent such as a petroleum oil or a fraction of a petroleum oil, it may be advantageous not to recycle the co-solvent but to co-feed the co-solvent with the final liquefied product into the catalytic cracking step. If the liquefaction step comprises hydrogenating of the one or more liquefied products, the petroleum oil or a fraction of the petroleum oil may suitably also be hydrogenated. This may be advantageous during the catalytic cracking step.

[0094] The catalytic cracking step comprises contacting at least part of the final liquefied product with a fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C., to produce one or more cracked products.

[0095] In one embodiment the final liquefied product or part thereof may comprises one, two or more compounds chosen from the group consisting of gamma-valerolactone and/or levulinic acid; tetrahydrofufuryl and/or tetrahydropyranyl; furfural and/or hydroxymethylfurfural; mono- and/or di-alcohols and/or mono- and/or di-ketones; and/or guaiacol and/or syringol components.

[0096] In a further embodiment the final liquefied product or part thereof is a fraction of the reaction effluent obtained from the liquefaction step which comprises or essentially consists of one or more, preferably monomeric, compounds containing equal to or less than 9 carbon atoms, preferably equal to or less than 6 carbon atoms and most preferably equal to or less than 5 carbon atoms. More preferably the final liquefied product in this embodiment comprises one or more compounds containing equal to or less than 9 carbon atoms, preferably equal to or less than 6 carbon atoms and most preferably equal to or less than 5 carbon atoms and/or having a molecular weight of equal to or less than about 200 Dalton and/or having an atmospheric boiling point of equal to or less than about 200° C. as determined at about 0.1 MegaPascal.

[0097] Preferably such a final liquefied product includes hydrocarbon compounds and/or oxygenates, such as for example alcohols. For example such a final liquefied product may comprise or may consist of mono- and/or di-alcohols and/or mono- and/or di-ketones which are derived from sugars. More preferably such final liquefied product is a final liquefied product containing butanone, butanol and/or furfural.

[0098] In another embodiment the final liquefied product or part thereof is a fraction of the reaction effluent obtained from the liquefaction step which comprises or essentially consists of one or more, preferably monomeric, compounds containing equal to or more than 9 carbon atoms, preferably equal to or more than 10 carbon atoms, and most preferably equal to or more than 11 carbon atoms. More preferably the final liquefied product in this embodiment comprises one or more compounds containing equal to or more than 9 carbon atoms, preferably equal to or more than 10 carbon atoms and most preferably equal to or more than 11 carbon atoms, and/or having a molecular weight of equal to or more than about 200 Dalton and/or an atmospheric boiling point of equal to or more than about 200° C. as determined at about 0.1 MegaPascal.

[0099] The final liquefied product or part thereof can be produced as described above. The final liquefied product or any part thereof to be contacted with the fluidized catalytic cracking catalyst can optionally be obtained after a separation step as described above. The final liquefied product or any part thereof can be fed to a fluidized catalytic cracking reactor in an essentially liquid state, in an essentially gaseous state or in a partially liquid-partially gaseous state. When entering the fluidized catalytic cracking reactor in an essentially or partially liquid state, the final liquefied product or any part thereof preferably vaporizes upon entry and preferably is contacted in the gaseous state with the fluidized catalytic cracking catalyst.

[0100] In a preferred embodiment the catalytic cracking step comprises contacting at least part of the final liquefied product and a fluid hydrocarbon co-feed with the fluidized catalytic cracking catalyst, preferably in a fluidized catalytic cracking reactor, at a temperature of equal to or more than about 400° C., to produce the one or more cracked products. That is, in a preferred embodiment also a fluid hydrocarbon co-feed other than the at least part of the final liquefied product may be added into a fluidized catalytic cracking reactor.

[0101] By a hydrocarbon co-feed is herein understood to refer at least to a co-feed that contains one or more hydrocarbon compounds. By a fluid hydrocarbon co-feed is herein understood a hydrocarbon feed that is not in a solid state. The fluid hydrocarbon co-feed is preferably a liquid hydrocarbon co-feed, a gaseous hydrocarbon co-feed, or a mixture thereof. The fluid hydrocarbon co-feed can be fed to a catalytic cracking reactor in an essentially liquid state, in an essentially gaseous state or in a partially liquid-partially gaseous state. When entering the catalytic cracking reactor in an essentially or partially liquid state, the fluid hydrocarbon co-feed preferably vaporizes upon entry and preferably is contacted in the gaseous state with the fluidized catalytic cracking catalyst.

[0102] The fluid hydrocarbon co-feed can be any non-solid hydrocarbon co-feed known to the skilled person to be suitable as a co-feed for a catalytic cracking unit. The fluid hydrocarbon co-feed can for example be obtained from a conventional crude oil (also sometimes referred to as a petroleum oil or mineral oil), an unconventional crude oil (that is, oil produced or extracted using techniques other than the traditional oil well method) or a Fisher Tropsch oil and/or a mixture thereof.

[0103] The fluid hydrocarbon co-feed may even be a fluid hydrocarbon co-feed from a renewable source, such as for example a vegetable oil.

[0104] In one embodiment the fluid hydrocarbon co-feed is derived from a, preferably conventional, crude oil. Examples of conventional crude oils include West Texas Intermediate crude oil, Brent crude oil, Dubai-Oman crude oil, Arabian Light crude oil, Midway Sunset crude oil or Tapis crude oil.

[0105] More preferably the fluid hydrocarbon co-feed comprises a fraction of a, preferably conventional, crude oil or renewable oil. Preferred fluid hydrocarbon co-feeds include straight run (atmospheric) gas oils, flashed distillate, vacuum gas oils (VGO), light cycle oil, heavy cycle oil, hydrowax, coker gas oils, diesel, gasoline, kerosene, naphtha, liquefied petroleum gases, atmospheric residue (“long residue”) and vacuum residue (“short residue”) and/or mixtures thereof. Most preferably the fluid hydrocarbon co-feed comprises a long residue.

[0106] The composition of the fluid hydrocarbon co-feed may vary widely. The fluid hydrocarbon co-feed may for example contain paraffins, olefins and aromatics.

[0107] Preferably the fluid hydrocarbon co-feed comprises equal to or more than 1 wt % paraffins, more preferably equal to or more than about 5 wt % paraffins, and most preferably equal to or more than about 10 wt % paraffins, and preferably equal to or less than about 100 wt % paraffins, more preferably equal to or less than about 90 wt % paraffins, and most preferably equal to or less than about 30 wt % paraffins, based on the total fluid hydrocarbon co-feed. By paraffins both normal-, cyclo- and branched-paraffins are understood.

[0108] In a preferred embodiment the fluid hydrocarbon co-feed comprises or consists of a paraffinic fluid hydrocarbon co-feed. By a paraffinic fluid hydrocarbon co-feed is herein understood to refer at least to a fluid hydrocarbon co-feed comprising at least about 50 wt % of paraffins, preferably at least about 70 wt % of paraffins, based on the total weight of the fluid hydrocarbon co-feed. For practical purposes the paraffin content of all fluid hydrocarbon co-feeds having an initial boiling point of at least about 260° C. can be measured by means of ASTM method D2007-03 titled “Standard test method for characteristic groups in rubber extender and processing oils and other petroleum-derived oils by clay-gel absorption chromatographic method”, wherein the amount of saturates will be representative for the paraffin content. For all other fluid hydrocarbon co-feeds the paraffin content of the fluid hydrocarbon co-feed can be measured by means of comprehensive multi-dimensional gas chromatography (GCxGC), as described in P. J. Schoenmakers, J. L. M. M. Oomen, J. Blomberg, W. Genuit, G. van Velzen, J. Chromatogr. A, 892 (2000) p. 29 and further.

[0109] Examples of paraffinic fluid hydrocarbon co-feeds include so-called Fischer-Tropsch derived hydrocarbon streams such as described in WO2007/090884 and herein incorporated by reference, or a hydrogen rich feed like hydrotreater product or hydrowax. By Hydrowax is understood the bottoms fraction of a hydrocracker. Examples of hydrocracking processes which may yield a bottoms fraction that can be used as fluid hydrocarbon co-feed, are described in EP-A-699225, EP-A-649896, WO-A-97/18278, EP-A-705321, EP-A-994173 and U.S. Pat. No. 4,851,109 and herein incorporated by reference.

[0110] In a preferred embodiment the fluid hydrocarbon co-feed comprises equal to or more than about 8 wt % elemental hydrogen, more preferably more than about 12 wt % elemental hydrogen (i.e. hydrogen atoms), based on the total fluid hydrocarbon co-feed on a dry basis (i.e. water-free basis). A high content of elemental hydrogen, such as a content of equal to or more than about 8 wt %, allows the hydrocarbon feed to act as a cheap hydrogen donor in the catalytic cracking process. A particularly preferred fluid hydrocarbon co-feed having an elemental hydrogen content of equal to or more than about 8 wt % is Fischer-Tropsch derived waxy raffinate. Such Fischer-Tropsch derived waxy raffinate may for example comprise about 85 wt % of elemental carbon and about 15 wt % of elemental hydrogen.

[0111] When a fluid hydrocarbon co-feed is present, the weight ratio of fluid hydrocarbon co-feed to liquefied product (s) (or part thereof) is preferably equal to or more than 50 to 50 (5:5), more preferably equal to or more than 70 to 30 (7:3), still more preferably equal to or more than 80 to 20 (8:2), even still more preferably equal to or more than 90 to 10 (9:1). For practical purposes the weight ratio of fluid hydrocarbon co-feed to liquefied product(s) (or part thereof) is preferably equal to or less than 99.9 to 0.1 (99.9:0.1), more preferably equal to or less than 95 to 5 (95:5). The fluid hydrocarbon co-feed and the final liquefied product (or part thereof) are preferably being fed to a fluidized catalytic cracking reactor in a weight ratio within the above ranges.

[0112] The amount of liquefied product(s), based on the total weight of liquefied product(s) and fluid hydrocarbon co-feed supplied to a fluidized catalytic cracking reactor, is preferably equal to or less than about 50 wt %, more preferably equal to or less than about 30 wt %, most preferably equal to or less than about 20 wt % and even more preferably equal to or less than about 10 wt %. For practical purposes the amount of liquefied product(s) present, based on the total weight of liquefied product(s) and fluid hydrocarbon co-feed supplied to a fluidized catalytic cracking reactor, is preferably equal to or more than about 0.1 wt %, more preferably equal to or more than about 1 wt %.

[0113] The catalytic cracking step is preferably carried out in a fluidized catalytic cracking reactor. The fluidized catalytic cracking reactor can be any fluidized catalytic cracking reactor known in the art to be suitable for the purpose, including for example a fluidized dense bed reactor or a riser reactor. Most preferably the catalytic cracking step is carried out in a riser reactor. Preferably this fluidized catalytic cracking reactor is part of a fluidized catalytic cracking (FCC) unit.

[0114] In one embodiment, where the organic solvent in the liquefaction step comprises one or more hydrocarbon compounds that also may suitable act as a fluid hydrocarbon co-feed, preferably a mixture of the liquefied product(s) and any organic solvent may be supplied to the fluidized catalytic cracking reactor. For example when a petroleum oil or a fraction thereof is used as a co-solvent in the liquefaction step, the fluid hydrocarbon co-feed as described herein may comprise or consist of such a co-solvent. In a further embodiment the organic solvent used in the liquefaction step is chosen from the fluid hydrocarbon co-feeds described above. Preferences for the fluid hydrocarbon co-feed are as described herein above.

[0115] In another preferred embodiment, the fluidized catalytic cracking reactor is a riser reactor and the fluid hydrocarbon co-feed is supplied to a riser reactor at a location downstream of the location where the liquefied product(s) is/are supplied to a riser reactor.

[0116] In a still further embodiment, a mixture of the liquefied product(s) and a first hydrocarbon co-feed (which may for example be the organic solvent when the organic solvent is chosen from the described fluid hydrocarbon co-feeds) is supplied to a riser reactor at a first location and a second fluid hydrocarbon co-feed is supplied to the riser reactor at a second location downstream of the first location. Preferences for the first and second fluid hydrocarbon co-feed are as described herein above.

[0117] By a riser reactor is herein understood an elongated essentially tube-shaped reactor suitable for carrying out catalytic cracking reactions. The elongated essentially tube-shaped reactor is preferably oriented in an essentially vertical manner.

[0118] Examples of suitable riser reactors are described in the Handbook titled “Fluid Catalytic Cracking technology and operations”, by Joseph W. Wilson, published by PennWell Publishing Company (1997), chapter 3, especially pages 101 to 112, herein incorporated by reference.

[0119] The riser reactor may be a so-called internal riser reactor or a so-called external riser reactor as described therein.

[0120] Most preferably the internal riser reactor is an essentially vertical essentially tube-shaped reactor, that may have an essentially vertical upstream end located outside a vessel and an essentially vertical downstream end located inside the vessel. The vessel is suitably a reaction vessel suitable for catalytic cracking reactions and/or a vessel that comprises one or more cyclone separators and/or swirl tubes. The internal riser reactor may be especially advantageous in the catalytic cracking step as it may be less prone to plugging, thereby increasing safety and hardware integrity.

[0121] The length of the riser reactor may vary widely. For practical purposes the riser reactor preferably has a length in the range from equal to or more than 10 meters, more preferably equal to or more than 15 meters and most preferably equal to or more than 20 meters, to equal to or less than 65 meters, more preferably equal to or less than 55 meters and most preferably equal to or less than 45 meters.

[0122] In a preferred embodiment the liquefied product(s) produced in the liquefaction step are supplied to a riser reactor, at the bottom of this riser reactor. This may advantageously result in in-situ water formation at the bottom of the reactor. The in-situ water formation may lower the hydrocarbon partial pressure and reduce second order hydrogen transfer reactions, thereby resulting in higher olefin yields. Preferably the hydrocarbon partial pressure is lowered to a pressure in the range from about 0.7 to 2.8 bar absolute (0.07 to 0.28 MegaPascal), more preferably about 1.2 to 2.8 bar absolute (0.12 to 0.28 MegaPascal).

[0123] It may be advantageous to also add a lift gas at the bottom of the riser reactor. Examples of such a liftgas include steam, vaporized oil and/or oil fractions, and mixtures thereof. Steam is most preferred as a lift gas from a practical perspective. However, the use of a vaporized oil and/or oil fraction (preferably vaporized liquefied petroleum gas, gasoline, diesel, kerosene or naphtha) as a liftgas may have the advantage that the liftgas can simultaneously act as a hydrogen donor and may prevent or reduce coke formation. Further if a fluid hydrocarbon co-feed is used as an organic solvent in the liquefaction step, also vaporized organic solvent may be used as a liftgas.

[0124] The fluidized catalytic cracking catalyst can be any catalyst known to the skilled person to be suitable for use in a cracking process. Preferably, the fluidized catalytic cracking catalyst comprises a zeolitic component. In addition, the fluidized catalytic cracking catalyst can contain an amorphous binder compound and/or a filler. Examples of the amorphous binder component include silica, alumina, titania, zirconia and magnesium oxide, or combinations of two or more of them. Examples of fillers include clays (such as kaolin).

[0125] The zeolite is preferably a large pore zeolite. The large pore zeolite includes a zeolite comprising a porous, crystalline aluminosilicate structure having a porous internal cell structure on which the major axis of the pores is in the range of about 0.62 nanometer to about 0.8 nanometer. The axes of zeolites are depicted in the ‘Atlas of Zeolite Structure Types’, of W. M. Meier, D. H. Olson, and Ch. Baerlocher, Fourth Revised Edition 1996, Elsevier, ISBN 0-444-10015-6. Examples of such large pore zeolites include FAU or faujasite, preferably synthetic faujasite, for example, zeolite Y or X, ultra-stable zeolite Y (USY), Rare Earth zeolite Y (=REY) and Rare Earth USY (REUSY). According to the present invention USY is preferably used as the large pore zeolite.

[0126] The fluidized catalytic cracking catalyst can also comprise a medium pore zeolite. The medium pore zeolite that can be used according to the present invention is a zeolite comprising a porous, crystalline aluminosilicate structure having a porous internal cell structure on which the major axis of the pores is in the range of about 0.45 nanometer to about 0.62 nanometer. Examples of such medium pore zeolites are of the MFI structural type, for example, ZSM-5; the MTW type, for example, ZSM-12; the TON structural type, for example, theta one; and the FER structural type, for example, ferrierite. According to the present invention, ZSM-5 is preferably used as the medium pore zeolite.

[0127] According to another embodiment, a blend of large pore and medium pore zeolites may be used. The ratio of the large pore zeolite to the medium pore size zeolite in the cracking catalyst is preferably in the range of 99:1 to 70:30, more preferably in the range of 98:2 to 85:15.

[0128] The total amount of the large pore size zeolite and/or medium pore zeolite that is present in the cracking catalyst is preferably in the range of about 5 wt % to about 40 wt %, more preferably in the range of about 10 wt % to about 30 wt %, and even more preferably in the range of about 10 wt % to about 25 wt % relative to the total mass of the fluidized catalytic cracking catalyst.

[0129] Preferably, the liquefied product(s) and any fluid hydrocarbon feed flow co-currently in the same direction. The fluidized catalytic cracking catalyst can be contacted in a cocurrent-flow, countercurrent-flow or cross-flow configuration with such a flow of the liquefied product(s) and optionally the fluid hydrocarbon feed. Preferably the catalytic cracking catalyst is contacted in a cocurrent flow configuration with a cocurrent flow of the liquefied product(s) and optionally the fluid hydrocarbon feed.

[0130] In a preferred embodiment the catalytic cracking step comprises:

a fluidized catalytic cracking step comprising contacting at least part of the final liquefied product with a fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C., to produce one or more cracked products and a spent fluidized catalytic cracking catalyst;

a separation step comprising separating the one or more cracked products from the spent fluidized catalytic cracking catalyst;

a regeneration step comprising regenerating spent fluidized catalytic cracking catalyst to produce a regenerated fluidized catalytic cracking catalyst, heat and carbon dioxide; and

a recycle step comprising recycling the regenerated fluidized catalytic cracking catalyst to the fluidized catalytic cracking step.

[0131] The fluidized catalytic cracking step is preferably carried out as described herein before.

[0132] The separation step is preferably carried out with the help of one or more cyclone separators and/or one or more swirl tubes. Suitable ways of carrying out the separation step are for example described in the Handbook titled "Fluid Catalytic Cracking; Design, Operation, and Troubleshooting of FCC Facilities" by Reza Sadeghbeigi, published by Gulf Publishing Company, Houston Tex. (1995), especially pages 219-223 and the Handbook "Fluid Catalytic Cracking technology and operations", by Joseph W. Wilson, published by PennWell Publishing Company (1997), chapter 3, especially pages 104-120, and chapter 6, especially pages 186 to 194, herein incorporated by reference.

[0133] In addition the separation step may further comprise a stripping step. In such a stripping step the spent fluidized catalytic cracking catalyst may be stripped to recover the products absorbed on the spent fluidized catalytic cracking catalyst before the regeneration step. These products may be recycled and added to a stream comprising one or more cracked products obtained from the catalytic cracking step.

[0134] The regeneration step preferably comprises contacting the spent fluidized catalytic cracking catalyst with an oxygen containing gas in a regenerator at a temperature of equal to or more than about 550° C. to produce a regenerated fluidized catalytic cracking catalyst, heat and carbon dioxide. During the regeneration coke, that can be deposited on the catalyst as a result of the fluidized catalytic cracking reaction, is burned off to restore the catalyst activity.

[0135] The oxygen containing gas may be any oxygen containing gas known to the skilled person to be suitable for use in a regenerator. For example the oxygen containing gas may be air or oxygen-enriched air. By oxygen enriched air is herein understood air comprising more than about 21 vol. % oxygen (O_2), more preferably air comprising equal to or more than about 22 vol. % oxygen, based on the total volume of air.

[0136] The heat produced in the exothermic regeneration step is preferably employed to provide energy for the endothermic catalytic cracking step. In addition the heat produced can be used to heat water and/or generate steam. The steam may be used elsewhere in the refinery, for example as a liftgas in a riser reactor.

[0137] Preferably the spent fluidized catalytic cracking catalyst is regenerated at a temperature in the range from equal to or more than about 575° C., more preferably from equal to or more than about 600° C., to equal to or less than about 950° C., more preferably to equal to or less than about 850° C. Preferably the spent fluidized catalytic cracking catalyst is regenerated at a pressure in the range from equal to or more than about 0.5 bar absolute to equal to or less than about 10 bar absolute (0.05 MegaPascal to 1 MegaPascal), more preferably from equal to or more than about 1.0 bar absolute to equal to or less than about 6 bar absolute (0.1 MegaPascal to 0.6 MegaPascal).

[0138] The regenerated fluidized catalytic cracking catalyst can be recycled to the fluidized catalytic cracking step. In a preferred embodiment a side stream of make-up fluidized catalytic cracking catalyst is added to the recycle stream to make-up for loss of fluidized catalytic cracking catalyst in the reaction zone and regenerator.

[0139] In the process according to the invention one or more cracked products are produced. In a preferred embodiment this/these one or more cracked products is/are subsequently fractionated to produce one or more product fractions.

[0140] Fractionation may be carried out in any manner known to the skilled person in the art to be suitable for fractionation of products from a catalytic cracking unit. For example the fractionation may be carried out as described in the Handbook titled "Fluid Catalytic Cracking technology and operations", by Joseph W. Wilson, published by PennWell Publishing Company (1997), pages 14 to 18, and chapter 8, especially pages 223 to 235, herein incorporated by reference.

[0141] In a further embodiment at least one of the one or more product fractions obtained by fractionation are subsequently hydrotreated with a source of hydrogen, preferably in the presence of a hydrotreatment catalyst to produce a hydrotreated product fraction. The hydrotreatment step may for example comprise hydrodeoxygenation, hydrodenitrogenation and/or hydrodesulphurization.

[0142] The one or more product fractions and/or the one or more hydrotreated product fractions and/or any fractions derived therefrom can conveniently be used as a biofuel component. Such a biofuel component may conveniently be blended with one or more other components to produce a biofuel. Examples of such one or more other components include anti-oxidants, corrosion inhibitors, ashless detergents, dehazers, dyes, lubricity improvers and/or mineral fuel components, but also conventional petroleum derived gasoline, diesel and/or kerosene fractions.

[0143] By a biofuel is herein understood a fuel that is at least party derived from a renewable energy source. The biofuel may advantageously be used in the engine of a transportation vehicle.

[0144] The examples serve described below further demonstrate certain aspects of the present invention. The examples are merely illustrative and not exhaustive, presented to provide a better understanding of embodiments of the present invention.

EXAMPLES

Example 1

[0145] About 30 grams of birch wood and 1.70 grams of palladium acetate ($Pd(OAc)_2$) were loaded into a Premex Batch autoclave of 300 ml equipped with electrical heating, stirrer, injection system, manometer and temperature recording.

[0146] Stirring was started (300 rpm) and the autoclave was closed. Stirring speed was increased to 750 rpm and a solution of water (84 g), acetic acid (36 g) and sulphuric acid (0.86 g) was injected. The autoclave was pressurised with hydrogen (H_2) to 4 MegaPascal (40 bar) and subsequently heated in 70 min to 200° C. Reactor pressure was subsequently increased to 8 MegaPascal (80 bar) by adding H_2. The reaction was continued for 60 min, occasionally H_2 was added to maintain the pressure at 8 MegaPascal. The reaction was stopped by rapid cooling to room temperature (20° C.), subsequently H_2 was vented and 143.2 g of a first total product (including liquid, tar, insoluble humins and catalyst) was collected. In a duplo experiment applying identical conditions a second total product (143.7 g) was prepared.

[0147] The first and second total product were combined. To the combined total products methyl-tetrahydrofuran (m-THF, 400 grams) was added. The mixture of methyl-tetrahydrofuran and total products was stirred for 10 minutes at room temperature (20° C.) and subsequently filtered over a P3 glass filter to produce a filtrate and a filter cake.

[0148] The filtrate was stored overnight (about 12 hours) to facilitate phase separation and produce a top organic layer and a bottom aqueous layer. The top organic layer was collected.

[0149] The filter cake on the P3 filter were washed with m-THF (300 g) to produce a m-THF solution. The m-THF solution was combined with the top organic layer. The m-THF was removed from the combination of top organic layer and m-THF solution by vacuum distillation at 80° C., 20 mbar (2 KiloPascal) to produce 25.1 grams of a liquefied product. To this liquefied product again 200 g m-THF was added and this solution was subsequently washed with 10 w % of $NaHCO_3$ (25 g) and water (25 g). The m-THF was again removed by vacuum distillation at 80° C., 20 mbar (2 KiloPascal) to produce 23.4 grams of a brownish black coloured viscous liquefied product.

[0150] The brownish black coloured viscous liquefied product was characterized by SEC(RI/UV) (size exclusion chromatography with UV and refractive index detectors), Gas Chromatography and ^{13}C-Nuclear Magnetic Resonance (^{13}C-NMR). Elemental analysis of carbon, hydrogen and oxygen resulted in C, 63.5 w % (±0.3), H, 7.89 w % (±0.1), 0 (by calculating the balance): 27.3 w % (±0.5). The brownish black coloured viscous liquefied product had a H/Ceff of 0.85. Total acid number (TAN) was determined to be (±5) mg KOH/g. The above brownish black coloured viscous liquefied product was used as a final liquefied product. A heavy feed mixture comprising long residue was used as a fluid hydrocarbon co-feed. The final liquefied product was blended with the fluid hydrocarbon co-feed to prepare a feed mixture containing a weight percentage of 20 wt % of the final liquefied product based on the total weight of final liquefied product and the fluid hydrocarbon co-feed. The feed mixture was injected into the fluidized catalyst bed of a MAT-5000 fluidized catalytic cracking unit. The fluidized catalyst bed contained 10 grams of FCC equilibrium catalyst containing ultra stable zeolite Y. The fluidized catalyst bed was kept at 520° C. and about 1 bar absolute (about 0.1 MegaPascal). The run included 7 experiments with 7 catalyst to feed weight ratios, namely catalyst/feed weight ratios of 3, 4, 5, 6, 6.5, 7 and 8.

[0151] When compared with a feed consisting of 100 wt % fluid hydrocarbon co-feed, the feed mixture of final liquefied product and fluid hydrocarbon co-feed is more reactive. The feed mixture of final liquefied product and fluid hydrocarbon co-feed shows a similar yield of valuable products (gasoline, light cycle oil and LPG) and a similar coke yield when compared to the reference feed. Detailed results are provided in Table 1.

[0152] The results in table 1 have been normalized and where applicable are calculated on a dry basis, i.e. without H_2O.

[0153] For the conversion calculation in table 1, first a corrected weight of the total feed was calculated by subtracting the weight of one water molecule for each oxygen atom that has not been converted into CO or CO2 from the feed. Conversion is subsequently defined as the weight in grams of drygas+LPG+gasoline+coke divided by the corrected weight in grams of the total feed. Hence, conversion=[Weight drygas+LPG+gasoline+coke]/[weight of the total feed−(weight of oxygen in feed−weight of oxygen in CO and CO_2)*18/16]*100%.

[0154] For the product yield calculation in table 1, first a corrected weight of the total feed is calculated by subtracting the weight of one water molecule for each oxygen atom that has not been converted into CO or CO_2 from the feed. Subsequently the product yield is defined as the weight in grams of the specific product divided by the corrected weight in grams of the total feed. In other words, the product yield distribution is on hydrocarbon basis. Hence, product yield for product X=[weight X]/[weight of the total feed−(weight of oxygen in feed−weight of oxygen in CO and CO_2)*18/16]*100%. As water could not be measured experimentally on the small scale of this example, it is calculated in table 1 from the measured oxygen content of the feed and correcting for the measured amounts of CO and CO2 formed. Assuming that there are no partially converted oxygenates in the product, this "assumed water yield" then gives the oxygen balance. Hence, water=[(weight of oxygen in the feed−weight of oxygen in CO and CO_2)*18/16]/[weight of the total feed]*100%.

TABLE 1

product after fluidized catalytic cracking (FCC) of a 100 wt % fluid hydrocarbon co-feed reference feed and product after FCC of a feed mixture consisting of 20 wt % final liquefied product and 80 wt % fluid hydrocarbon co-feed (at a constant cat/oil ratio of 3.0 and a temperature of 520° C.).

	100 wt % FHCF-reference	20 wt % liquefaction product and 80 wt % FHCF
Oxygen content in feed mixture (wt %)		6.5
Water (wt %)		6.9
Conversion at Cat/Oil 3 ratio	61.5	62.1
Gasoline yield (wt %)	45.1	44.2
LCO yield (wt %)	25.0	24.4
HCO yield (wt %)	7.3	7.0
Slurry oil yield (wt %)	6.1	6.1
Coke yield (wt %)	5.8	6.0
LPG yield (wt %)	9.0	10.0
Drygas yield (wt %)	1.6	1.9
CO_2 yield (on C basis)	0.1	0.3
CO yield (wt %) (on C basis)	0.1	0.2

FHCF = Fluid Hydrocarbon Co-Feed;
LCO = Light Cycle Oil;
HCO = heavy Cycle Oil,
LPG = liquefied Petroleum Gas.

Example 2

[0155] Furfural respectively furfuryl alcohol was used as an artificial representative of a final liquefied product. In addition a heavy feed mixture having a composition as illustrated in tables 2a and 2b was used as a fluid hydrocarbon co-feed.

TABLE 2a

Boiling range distribution of the fluid hydrocarbon feed as determined by gas chromatography according to ASTM D2887-06a.

wt %	° C.	wt %	° C.	wt %	° C.
IBP	240	34	410	68	476
2	281	36	414	70	481
4	306	38	417	72	486
6	321	40	421	74	492
8	333	42	425	76	498
10	342	44	428	78	504
12	351	46	432	80	511
14	358	48	435	82	519
16	365	50	438	84	527
18	371	52	442	86	548
20	377	54	445	88	563
22	382	56	449	90	585
24	387	58	453	92	n.d.
26	392	60	458	94	n.d.
28	397	62	462	96	n.d.
30	401	64	467	98	n.d.
32	405	66	471	FBP	n.d.

n.d: not determined

TABLE 2b

Element analyses of fluid hydrocarbon co-feed

Feed description.	[C] [wt %]	[H] [wt %]	[O] [wt %]	[S] [ppm]	[N] [ppm]
fluid hydrocarbon co-feed	86.65%	12.65%	0.00%	3360	2220

[0156] The furfural respectively furfuryl alcohol was blended with the fluid hydrocarbon co-feed to prepare a feed mixture containing a weight percentage of 20 wt % of furfural respectively furfuryl alcohol based on the total weight of the feed mixture. The feed mixture was injected into the fluidized catalyst bed of a MAT-5000 fluidized catalytic cracking unit. The fluidized catalyst bed contained 10 grams of FCC equilibrium catalyst containing ultra stable zeolite Y. The fluidized catalyst bed was kept at 520° C. and about 1 bar absolute (about 0.1 MegaPascal). The catalyst/feed weight ratio was 3.

[0157] The effective molar ratio of hydrogen to carbon (H/C_{eff}) of furfural respectively furfuryl alcohol is 0.0 respectively 0.4. By the effective molar ratio of hydrogen to carbon (H/C_{eff}) is understood the molar ratio of hydrogen to carbon after the theoretical removal of all moles of oxygen, present in the oil on a dry basis, via water production with hydrogen originally present, presuming no nitrogen or sulphur present ($H/C_{eff}=(H-2*O)/C$).

[0158] The feed mixture comprising furfural respectively furfuryl alcohol shows a slight decrease of valuable products (gasoline, light cycle oil and LPG) and a slight increase in coke yield when compared to the reference feed. Detailed results are provided in table 2c.

[0159] The below results in table 2c have been normalized and calculated on a dry basis, i.e. without H_2O.

[0160] For the conversion calculation, first a corrected weight of the total feed is calculated by subtracting the weight of one water molecule for each oxygen atom that has not been converted into CO or CO_2 from the feed. Conversion is subsequently defined as the weight in grams of drygas+LPG+gasoline+coke divided by the corrected weight in grams of the total feed. Hence, conversion=[Weight drygas+LPG+gasoline+coke]/[weight of the total feed−(weight of oxygen in feed−weight of oxygen in CO and CO_2)*18/16]*100%.

[0161] For the product yield calculation, first a corrected weight of the total feed is calculated by subtracting the weight of one water molecule for each oxygen atom that has not been converted into CO or CO_2 from the feed. Subsequently the product yield is defined as the weight in grams of the specific product divided by the corrected weight in grams of the total feed. In other words, the product yield distribution is on hydrocarbon basis. Hence, product yield for product X=[weight X]/[weight of the total feed−(weight of oxygen in feed−weight of oxygen in CO and CO_2)*18/16]*100%. As water could not be measured experimentally on this small scale, it is calculated from the measured oxygen content of the feed and correcting for the measured amounts of CO and CO_2 formed. Assuming that there are no partially converted oxygenates in the product, this "assumed water yield" then gives the oxygen balance. Hence, water=[(weight of oxygen in the feed−weight of oxygen in CO and CO_2)*18/16]/[weight of the total feed]*100%.

TABLE 2c

product after fluidized catalytic cracking (FCC) of a 100 wt % fluid hydrocarbon co-feed reference feed and product after FCC of a feed mixture consisting of 20 wt % furfural resp. furfuryl alcohol and 80 wt % fluid hydrocarbon co-feed (at a constant cat/oil ratio of 3.0 and a temperature of 520° C.)

	100 wt % FHCF-reference	20 wt % Furfural + 80 wt % FHCF	20 wt % Furfuryl alcohol + 80 wt % FHCF
Oxygen content in feed (wt %)	0.0	6.7	6.5
Conversion (%)	61.9	61.1	62.5
Gasoline yield (wt %)	45.1	40.9	41.7
LCO yield (wt %)	24.4	24.6	23.5
HCO yield (wt %)	7.4	7.3	6.8
Slurry oil yield (wt %)	6.2	6.2	6.0
Coke yield (wt %)	5.7	8.8	8.9
LPG yield (wt %)	9.5	9.5	10.0
Gasoline + LCO + LPG yield (wt %)	79.1	75.0	75.2
Drygas yield (wt %)	1.7	1.8	1.9
CO2 yield (wt % on C basis)	0.0	0.1	0.1
CO yield (wt % on C basis)	0.0	0.3	0.3

FHCF = Fluid Hydrocarbon Co-Feed;
LCO = Light Cycle Oil;
HCO = heavy Cycle Oil,
LPG = liquefied Petroleum Gas.

[0162] Example 2, further shows the advantage of co-feeding a complete final liquefied product, which is a mixture of several components, to the FCC unit, rather than a feed containing only furfural or furfuryl alcohol.

Example 3

[0163] Respectively tetrahydrofuran (THF), butanone and 2-butanol were used as an artificial representative of a final liquefied product. In addition a vacuum gas oil (VGO) was used as a fluid hydrocarbon co-feed.

[0164] The tetrahydrofuran (THF), butanone or 2-butanol respectively was blended with the fluid hydrocarbon co-feed to prepare a feed mixture containing a weight percentage of 20 wt % of tetrahydrofuran (THF), butanone or 2-butanol respectively, based on the total weight of the feed mixture. The feed mixture was injected into the fluidized catalyst bed of a MAT-5000 fluidized catalytic cracking unit. The fluidized catalyst bed contained 10 grams of FCC equilibrium catalyst containing ultra stable zeolite Y. The fluidized catalyst bed was kept at 550° C. and about 1 bar absolute (about 0.1 MegaPascal). The catalyst/feed weight ratio was 3.

[0165] The effective molar ratios of hydrogen to carbon (H/C_{eff}) of tetrahydrofuran (THF), butanone and 2-butanol respectively are 1.5, 1.5 and 2.0 respectively.

[0166] The feed mixture comprising respectively tetrahydrofuran (THF), butanone or 2-butanol shows a similar yield of valuable products (gasoline, light cycle oil and LPG) and for butanone and 2-butanol even a decrease in coke yield compared to the reference feed. Detailed results are provided in table 3.

TABLE 3

product after fluidized catalytic cracking (FCC) of a 100 wt % fluid hydrocarbon co-feed reference feed and product after FCC of a feed mixture consisting of 20 wt % THF, butanone or 2-butanol respectively and 80 wt % fluid hydrocarbon co-feed (at aconstant cat/oil ratio of 3.0 and a temperature of 550° C.)

	100 wt % FHCF-reference*	20 wt % THF + 80 wt % FHCF*	20 wt % Butanone + 80 wt % FHCF*	20 wt % 2-Butanol + 80 wt % FHCF*
Oxygen content in feed (wt %)	0.0	4.3	4.4	4.4
Conversion (%)	59.1	61.9	60.6	63.7
Gasoline yield (wt %)	40.7	37.0	39.3	39.8
LCO yield (wt %)	28.7	25.9	27.4	25.4
HCO yield (wt %)	7.0	6.7	6.8	6.2
Slurry oil yield (wt %)	5.2	5.4	5.1	4.7
Coke yield (wt %)	3.9	5.6	4.0	3.2
LPG yield (wt %)	11.8	15.7	14.5	18.2
Gasoline + LCO + LPG yield (wt %)	81.2	78.6	81.2	83.4
Drygas yield (wt %)	2.8	3.7	2.8	2.5
CO2 yield (wt % on C basis)	0.00	0.01	0.01	0.00
CO yield (wt % on C basis)	0.00	0.03	0.00	0.00

FHCF = Fluid Hydrocarbon Co-Feed;
LCO = Light Cycle Oil;
HCO = heavy Cycle Oil,
PG = liquefied Petroleum Gas.

[0167] The above results in table 3 have been normalized and calculated on a dry basis, i.e. without H_2O.

[0168] For the conversion calculation, first a corrected weight of the total feed is calculated by subtracting the weight of one water molecule for each oxygen atom that has not been converted into CO or CO_2 from the feed. Conversion is subsequently defined as the weight in grams of drygas+LPG+gasoline+coke divided by the corrected weight in grams of the total feed. Hence, conversion=[Weight drygas+LPG+gasoline+coke]/[weight of the total feed−(weight of oxygen in feed−weight of oxygen in CO and CO_2)*18/16]*100%.

[0169] For the product yield calculation, first a corrected weight of the total feed is calculated by subtracting the weight of one water molecule for each oxygen atom that has not been converted into CO or CO_2 from the feed. Subsequently the product yield is defined as the weight in grams of the specific product divided by the corrected weight in grams of the total feed. In other words, the product yield distribution is on hydrocarbon basis. Hence, product yield for product X=[weight X]/[weight of the total feed−(weight of oxygen in feed−weight of oxygen in CO and CO_2)*18/16]*100%. As water could not be measured experimentally on this small scale, it is calculated from the measured oxygen content of the feed and correcting for the measured amounts of CO and CO_2 formed. Assuming that there are no partially converted oxygenates in the product, this "assumed water yield" then gives the oxygen balance. Hence, water=[(weight of oxygen in the feed−weight of oxygen in CO and CO_2)*18/16]/[weight of the total feed]*100%.

[0170] Further modifications and alternative embodiments of various aspects of the invention will be apparent to those skilled in the art in view of this description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the general manner of carrying out the invention. It is to be understood that the forms of the invention shown and described herein are to be taken as the presently preferred embodiments. Elements and materials may be substituted for those illustrated and described herein, parts and processes may be reversed, and certain features of the invention may be utilized independently, all as would be apparent to one skilled in the art after having the benefit of this description of the invention. Changes may be made in the elements described herein without departing from the spirit and scope of the invention as described in the following claims

What is claimed is:

1. A method for conversion of a cellulosic material comprising

a liquefaction step to produce a final liquefied product, the liquefaction step comprising:

contacting a cellulosic material with a liquid solvent at a temperature of equal to or more than about 200° C.; or

contacting a cellulosic material with a liquid solvent at a temperature of equal to or more than about 100° C. in the presence of a catalyst; and

a catalytic cracking step to produce at least one cracked product, the catalytic cracking step comprising contacting at least part of the final liquefied product with a fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C.

2. The method of claim **1**, wherein the liquid solvent comprises water and/or an organic solvent.

3. The method of claim **1**, wherein the liquefaction step comprises simultaneously contacting the cellulosic material with an organic solvent, a source of hydrogen, an acid catalyst and a hydrogenation catalyst at a temperature of equal to or more than about 150° C.

4. The method of claim **1**, wherein the liquefaction step comprises contacting the cellulosic material with an organic solvent in the presence of an acid catalyst at a temperature of equal to or more than about 150° C. to produce an intermediate liquefied product; and subsequently hydrotreating the intermediate liquefied product with a source of hydrogen in the presence of a hydrotreatment catalyst to produce a final liquefied product.

5. The method of claim **1**, wherein the liquid solvent is an organic solvent and wherein the process further comprises a separation step, wherein at least a portion of the final liquefied product produced in the liquefaction step is separated from at least part of the organic solvent.

6. The method of claim **5** wherein the separated portion of the organic solvent is used in the liquefaction step.

7. The method of claim **1**, wherein the catalytic cracking step comprises contacting at least part of the final liquefied product and a fluid hydrocarbon co-feed with the fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C.

8. The method of claim **7**, wherein the fluid hydrocarbon co-feed comprises at least one of a straight run (atmospheric) gas oil, a flashed distillate, a vacuum gas oil (VGO), a light cycle oil, a heavy cycle oil, a hydrowax, a coker gas oil, a gasoline, a naphtha, a diesel, a kerosene, an atmospheric residue (“long residue”), a vacuum residue (“short residue”), and any combination thereof.

9. The method of claim **1**, wherein the liquefaction step comprises contacting a cellulosic material with an organic solvent at a temperature of equal to or more than about 100° C. in the presence of a catalyst, wherein the organic solvent comprises a fraction of a petroleum oil; and wherein the catalytic cracking step comprises contacting a mixture of at least part of the final liquefied product and the fraction of a petroleum oil with a fluidized catalytic cracking catalyst in a fluidized catalytic cracking reactor at a temperature of equal to or more than about 400° C.

10. The method of claim **9**, wherein the liquefaction step comprises simultaneously contacting the cellulosic material with the fraction of a petroleum oil, with a source of hydrogen, and with a hydrogenation catalyst at a temperature of equal to or more than about 150° C.

11. The method of claim **9**, wherein a further organic solvent is generated in-situ during the liquefaction step.

12. The method of claim **1**, wherein the liquefaction step comprises simultaneously contacting the cellulosic material with a liquid solvent, with a source of hydrogen, with an acid catalyst and with a hydrogenation catalyst at a temperature of equal to or more than about 150° C.; and wherein the catalytic cracking step comprises contacting at least part of the final liquefied product with a fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C.

13. The method of claim **12**, wherein the liquid solvent is water or a solvent mixture comprising an organic solvent and water.

14. The method of claim **1**, wherein the final liquefied product or part thereof comprises one, two or more compounds chosen from the group consisting of gamma-valerolactone and/or levulinic acid; tetrahydrofufuryl and/or tetrahydropyranyl; furfural and/or hydroxymethylfurfural; mono- and/or di-alcohols and/or mono- and/or di-ketones; and/or guaiacol and/or syringol components.

15. The method of claim **1**, wherein the process further comprises:

a fractionation step comprising fractionating the at least one cracked product to produce at least one product fraction.

16. The method of claim **15**, wherein the process further comprises:

a hydrotreatment step comprising hydrotreating the at least one product fraction with a source of hydrogen to produce at least one hydrotreated product fraction.

17. A biofuel component comprising the at least one product fraction or any product derived from the at least one product fraction produced in claim **15**.

18. A biofuel component comprising the at least one hydrotreated product fraction or any product derived from the at least one hydrotreated product fraction produced in claim **16**.

19. A process for the production of a biofuel comprising blending the biofuel component of claim **17** with one or more other components to produce a biofuel.

20. A process for the production of a biofuel comprising blending the biofuel component of claim **18** with one or more other components to produce a biofuel.

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