A process for making a distillate product and one or more C2-C4 olefins from a FCC feedstock containing a cellulosic material and a hydrocarbon co-feed is provided.
PROCESS FOR MAKING A DISTILLATE PRODUCT AND/OR C2-C4 OLEFINs

The present application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/583,678, filed Jan. 6, 2012, the entire disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

The invention relates to a process for making a distillate product and/or C2-C4 olefins.

BACKGROUND OF THE INVENTION

The fluidized catalytic cracking (FCC) of heavy hydrocarbons to produce lower boiling hydrocarbon products such as gasoline is well known in the art. FCC processes have been around since the 1940’s. Typically, a FCC unit or process includes at least a riser reactor, a catalyst separator and a regenerator. A feedstock is introduced into the riser reactor wherein it is contacted with hot FCC catalyst from the regenerator. The mixture of the feedstock and FCC catalyst passes through the riser reactor and into the catalyst separator wherein the hydrocarbon product is separated from the FCC catalyst. The separated hydrocarbon product passes from the catalyst separator to a downstream system for further separation and the separated catalyst passes to the regenerator where the coke deposited on the FCC catalyst during the cracking reaction is burned off the catalyst to provide a regenerated catalyst. The resulting regenerated catalyst is used as the aforementioned hot FCC catalyst and is mixed with the FCC feedstock that is introduced into the riser reactor.

Many FCC processes and systems are designed so as to provide for a high conversion of the FCC feedstock to products having boiling temperatures in the gasoline boiling range. There are situations, however, when it is desirable to provide for the high conversion of the FCC feedstock to lower olefins, such as C2-C4 olefins, and/or to a distillate product, which distillate product may comprise products having boiling temperatures in the diesel boiling range—as opposed to products having boiling temperatures in the gasoline boiling range.

US2006/0231461 describes a process for making middle distillate and lower olefins. In this process a dense phase reactor, or fixed fluidized bed reactor is used between the catalyst regenerator and the riser reactor of a FCC process or unit to provide for an improved middle distillate yield and for enhanced selectivity towards the production of lower olefins. The dense phase reactor is used to provide for the cracking of a gasoline feedstock to yield lower olefins and for the conditioning of the catalyst so that this catalyst is more suitable for the production of a middle distillate product in the riser reactor.

It would be desirable to produce such middle distillate product and such lower olefins in a sustainable manner.

Without wishing to be bound by any kind of theory, some may consider that carbon is present in the atmosphere as CO2 and that photoautotrophs like plants, algae and some bacteria fix this inorganic carbon to organic carbon (such as for example carbohydrates) using sunlight for energy. Over geological time frames (>10^9 years) organic matter (plant materials) is fossilized to provide petroleum, natural gas and coal. It is stated that when consuming these fossil resources to make polymers, chemicals & fuel the carbon is released back into the atmosphere as CO2 in a short time frame of 1-10 years. In this case, it is argued that the rate at which biomass is converted to fossil resources is in total imbalance with the rate at which fossil resources are consumed and liberated. However, when using annually renewable crops or biomass as the feedstocks for manufacturing our carbon based polymers, chemicals and fuels, the rate at which CO2 is fixed equals the rate at which it is consumed and liberated. Using annually renewable carbon feedstocks allows for sustainable development of carbon based materials and for control and even reduction of CO2 emissions to help meet global CO2 emission standards under the Kyoto protocol.

It would be an advancement in the art to provide processes that may help to create sustainable CO2 emissions or even reduce CO2 emissions from a refinery and/or to provide processes that can be beneficial in a CO2 capture and trade scheme.

WO2008/127956 describes a system comprising a riser reactor comprising a gas oil feedstock and a first catalyst under catalytic cracking conditions to yield a riser reactor product comprising a cracked gas oil product and a first used catalyst; an intermediate reactor comprising at least a portion of the cracked gas oil product and a second catalyst under high severity conditions to yield a cracked intermediate reactor product and a second used catalyst, wherein the intermediate reactor feedstock comprises at least one of a fatty acid and a fatty acid ester. This fatty acid and/or fatty acid ester can for example be obtained plant oils, such as for example palm oil, coconut oil, corn oil, soya oil, safflower oil, sunflower oil, linseed oil, olive oil and peanut oil and/or animal fats.

A disadvantage of the process as described in WO2008/127956, however, is that the use of plant oils and/or animal fats as an FCC feedstock may compete with their use as food.

SUMMARY OF THE INVENTION

It has now been found that such an FCC process can be obtained by feeding a cellulosic material, such as for example pyrolysis oil and/or wood, in the right location into the FCC process.

Accordingly, in an embodiment, a process for making a distillate product and one or more C2-C4 olefins is provided comprising:

a) contacting a FCC feedstock with a FCC catalyst at a temperature of at least 400° C. in a riser reactor to produce a distillate product and a spent FCC catalyst, wherein the FCC feedstock comprises a cellulosic material and a hydrocarbon co-feed;
b) separating at least a portion of the distillate product from the spent FCC catalyst;
c) regenerating the spent FCC catalyst to produce a regenerated FCC catalyst;
d) contacting an intermediate reactor feedstock with at least a portion of the regenerated FCC catalyst at a temperature of at least 500° C. in an intermediate reactor to produce one or more C2-C4 olefins and a used regenerated FCC catalyst;
e) separating at least a portion of the one or more C2-C4 olefins from the used regenerated catalyst; and
f) providing at least a portion of the used regenerated FCC catalyst as FCC catalyst in step a).

In another embodiment, a process for the preparation of a biofuel and/or a biochemical is provided comprising:

a) contacting a FCC feedstock with a FCC catalyst at a temperature of at least 400° C. in a riser reactor to produce a
distillate product and a spent FCC catalyst, wherein the FCC feedstock comprises a cellulosic material and a hydrocarbon co-feed;
b) separating at least a portion of the distillate product from the spent FCC catalyst;
c) regenerating the spent FCC catalyst to produce a regenerated FCC catalyst;
d) contacting an intermediate reactor feedstock with at least a portion of the regenerated FCC catalyst at a temperature of at least 500° C. in an intermediate reactor to produce one or more C2-C4 olefins and a used regenerated FCC catalyst;
e) separating at least a portion of the one or more C2-C4 olefins from the used regenerated catalyst;
f) providing at least a portion of the used regenerated FCC catalyst as FCC catalyst in step a); and
g) blending at least a portion of the distillate product and/or at least a portion of the one or more C2-C4 olefins with one or more other components to produce a biofuel and/or a biochemical.

[0018] Accordingly, in an embodiment provides a process for making a distillate product and one or more C2-C4 olefins comprising:
a) contacting a FCC feedstock with a FCC catalyst at a temperature of equal to or more than 400° C. in a riser reactor to produce a distillate product and a spent FCC catalyst, wherein the FCC feedstock comprises a cellulosic material and a hydrocarbon co-feed;
b) separating at least part of the distillate product from the spent FCC catalyst;
c) regenerating the spent FCC catalyst to produce a regenerated FCC catalyst;
d) contacting an intermediate reactor feedstock with at least part of the regenerated FCC catalyst at a temperature of equal to or more than 500° C. in an intermediate reactor to produce one or more C2-C4 olefins and a used regenerated FCC catalyst;
e) separating at least part of the one or more C2-C4 olefins from the used regenerated catalyst;
f) using at least part of the used regenerated FCC catalyst as FCC catalyst in step a).

[0019] Without wishing to be bound by any kind of theory, it is believed that when cellulosic materials (such as solid cellulosic material and/or pyrolysis oil) are catalytically cracked, much more coke is formed than when vegetable oils and/or animal fat are catalytically cracked. Therefore, if cellulosic materials, such as solid cellulosic material and/or pyrolysis oil, were fed to the intermediate reactor—similar to the fatty acids and/or fatty acid esters in WO2008/127956—excessive coke would form on the catalyst and the used catalyst could no longer be used for the production of any distillate product in the riser reactor.

[0020] However, it was found that the cellulosic material(s) can be used as a feedstock in the process for the making of a distillate product and one or more C2-C4 olefins, when the cellulosic material(s) is fed into the riser reactor instead of the intermediate reactor and when the cellulosic material(s) are fed together with a hydrocarbon co-feed.

[0021] Operating an FCC process in a mode for the production of a distillate product and one or more C2-C4 olefins—rather than a mode for the production of a gasoline product—further has the advantage that a lower temperature can be used in the riser reactor, thereby further reducing coke formation due to the cellulosic material feed. Operating at such lower temperature may result in lower yields of C3 and/or C4 hydrocarbon products, such as for example propane, propene, butanes and/or butenes. In addition, operating at such lower temperature may result in a more olefinic gasoline that may be more difficult to blend with other components in a fuel. Conveniently, however, the process according to the invention allows one to optionally recycle any olefinic gasoline, made as a product in the riser reactor, as a feed to the intermediate reactor in step d) of the process. In this intermediate reactor such olefinic gasoline can advantageously be converted into C3 and/or C4 hydrocarbon products and a blendable gasoline.

[0022] Hence, the process of the present invention advantageously allows one to use a non-edible renewable energy source, such as a cellulosic material, as a feedstock in an FCC process for the making of a distillate product and one or more C2-C4 olefins.

[0023] In step a) of the process according to the invention a FCC feedstock is contacted with a FCC catalyst at a temperature of equal to or more than 400° C., in a riser reactor to produce a distillate product and a spent FCC catalyst.
The Fluidized Catalytic Cracking (FCC) feedstock can comprise one or more cellulosic material(s). Preferably the FCC feedstock comprises a solid cellulosic material, a pyrolysis oil derived from cellulosic material, and/or a mixture thereof. In an especially preferred embodiment the FCC feedstock comprises one or more material(s) chosen from the group of non-edible solid cellulosic material, pyrolysis oil and/or mixtures thereof. By a non-edible material is herein understood a material that is not suitable for human consumption.

By a cellulosic material is herein understood and defined as a material comprising cellulose, hemicellulose, lignocellulose and/or lignin; a material derived therefrom; and/or mixtures of such materials. For example, pyrolysis oil may be considered a liquid material derived from a cellulosic material. More preferably the cellulosic material comprises lignocellulose or a material derived thereof. Such a material that comprises lignocellulose is also referred to as a lignocellulose material. Preferably, the cellulosic material is a solid cellulosic material or a liquid or gaseous material derived of such a solid cellulosic material. Most preferably the cellulosic material is a solid cellulosic material, a pyrolysis oil derived (produced) from cellulosic material, and/or a mixture thereof.

Preferably the cellulosic material is not a material used for human food production. Examples of suitable cellulosic materials include aquatic plants and algae, agricultural waste and/or forestry waste and/or paper waste and/or plant material obtained from domestic waste and/or sugar processing residues and/or mixtures thereof. Examples of suitable cellulosic 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 straw, barley straw, rye straw and oat straw; grasses; forestry products and/or forestry residues such as wood and wood-related materials such as wood chips, sawdust, bark or the needles of trees; waste paper; sugar processing residues such as bagasse and beet pulp; or mixtures thereof.

More preferably the cellulosic material is a solid cellulosic material selected from the group consisting of wood, sawdust, straw, grass, bagasse, corn stover and/or mixtures thereof. These solid cellulosic materials are advantageous as they do not compete with human food production and are therefore considered more sustainable.

The cellulosic material may also be a material derived from the above materials, for example liquid and gaseous materials derived from the above cellulosic material by pyrolysis, (hydro-)liquefaction (also sometimes referred to as solvolysis), torrefaction or other treatments. More preferably the cellulosic material is a, optionally torrefied, solid cellulosic material or a pyrolysis oil.

By a pyrolysis oil is herein understood an oil obtained by pyrolysis of a cellulosic material. The pyrolysis oil may be upgraded by hydrotreatment and/or hydrodeoxygenation (for example to substantially reduce the oxygen content of the pyrolysis oil). Preferably, however, an essentially untreated pyrolysis oil is used which has not or essentially not been upgraded by hydrotreatment and/or hydrodeoxygenation, as such hydrotreatment and/or hydrodeoxygenation can advantageously be avoided in the processes according to the invention. The pyrolysis oil may comprise a “whole” pyrolysis oil or a part thereof.

By pyrolysis is herein understood the thermal decomposition of a, preferably solid, cellulosic material at a temperature of equal to or more than 350° C. The concentration of oxygen is preferably less than the concentration required for complete combustion. More preferably the pyrolysis is carried out in the essential absence of non-in-situ generated oxygen. A limited amount of oxygen may be generated in-situ during the pyrolysis process. Preferably pyrolysis is carried out in an oxygen-poor, preferably an oxygen-free, atmosphere. More preferably pyrolysis is carried out in an atmosphere containing equal to or less than 5 vol. % oxygen, more preferably equal to or less than 1 vol. % oxygen and most preferably equal to or less than 0.1 vol. % oxygen. In a most preferred embodiment pyrolysis is carried out in the essential absence of oxygen.

The pyrolysis temperature is preferably equal to or more than 350° C, more preferably equal to or more than 400° C and most preferably equal to or more than 450° C. The pyrolysis temperature is further preferably equal to or less than 800° C, more preferably equal to or less than 700° C and most preferably equal to or less than 650° C.

The pyrolysis pressure may vary widely. For practical purposes a pressure in the range from 0.01 to 0.5 MPa (MegaPascal), more preferably in the range from 0.1 to 0.2 MPa is preferred. Most preferred is an atmospheric pressure (about 0.1 MPa).

By torrefying or torrefaction is herein understood the treatment of the solid cellulosic material at a temperature in the range from equal to or more than 200° C to equal to or less than 350° C in the essential absence of a catalyst and in an oxygen-poor, preferably an oxygen-free, atmosphere. By an oxygen-poor atmosphere is understood an atmosphere containing equal to or less than 15 vol. % oxygen, preferably equal to or less than 10 vol. % oxygen and more preferably equal to or less than 5 vol. % oxygen. By an oxygen-free atmosphere is understood an atmosphere where oxygen is essentially absent.

Torrefying of a solid cellulosic material is preferably carried out at a temperature of more than 200° C, more preferably at a temperature equal to or more than 210° C, still more preferably at a temperature equal to or more than 220° C, yet more preferably at a temperature equal to or more than 230° C. In addition torrefying of a solid cellulosic material is preferably carried out at a temperature less than 350° C, more preferably at a temperature equal to or less than 330° C, still more preferably at a temperature equal to or less than 310° C, yet more preferably at a temperature equal to or less than 300° C.

Torrefaction of any solid cellulosic material is preferably carried out in the essential absence of oxygen. More preferably the torrefaction is carried under an inert atmosphere, containing for example inert gases such as nitrogen, carbon dioxide and/or steam; and/or under a reducing atmosphere in the presence of a reducing gas such as hydrogen, gaseous hydrocarbons such as methane and ethane or carbon monoxide.

Any torrefaction may be carried out at a wide range of pressures. Preferably, however, the torrefaction is carried out at atmospheric pressure (about 0.1 MPa). In addition, the torrefaction may be carried out batchwise or continuously.

The torrefied solid cellulosic material has a higher energy density, a higher mass density and greater flowability, making it easier to transport, pelletize and/or store. Being more brittle, it may be easier reduced into smaller particles.

If the cellulosic material comprises a solid cellulosic material, the process according to the invention preferably
comprises an additional step wherein the particle size of such solid cellulosic material is reduced before using it as part of the FCC feedstock in step a).

[0039] Preferably any solid cellulosic material used as part of the FCC feedstock in step a) is a micronized solid cellulosic material. By a micronized solid cellulosic material is herein understood a solid cellulosic material that has a particle size distribution with a mean particle size in the range from equal to or more than 5 micrometer to equal to or less than 5000 micrometer, as measured with a laser scattering particle size distribution analyzer.

[0040] The particle size of any solid cellulosic material, can optionally be reduced before or after such solid cellulosic material is torrefied. Such a particle size reduction may for example be especially advantageous when such solid cellulosic material comprises wood or torrefied wood. The particle size of any, optionally torrefied, solid cellulosic material can be reduced in any manner known to the skilled person to be suitable for this purpose. Suitable methods for particle size reduction include crushing, grinding and/or milling. The particle size reduction may for example be achieved by means of a ball mill, hammer mill, (knife) shredder, chipper, knife grid, or cutter.

[0041] Preferably any solid cellulosic material used in the FCC feedstock in step a) has a particle size distribution where the mean particle size lies in the range from equal to or more than 5 micrometer (micron), more preferably equal to or more than 10 micrometer, even more preferably equal to or more than 20 micrometer, and most preferably equal to or more than 100 micrometer to equal to or less than 500,000 micrometer, more preferably equal to or less than 1000 micrometer and most preferably equal to or less than 500 micrometer.

[0042] For practical purposes the particle size distribution and mean particle size of the solid cellulosic material can be determined with a Laser Scattering Particle Size Distribution Analyzer, preferably a Horiba LA950, according to the ISO 13320 method titled “Particle size analysis—Laser diffraction methods”.

[0043] In addition to the cellulosic material, the FCC feedstock also comprises a hydrocarbon co-feed (herein also referred to as hydrocarbon feed). The hydrocarbon co-feed comprises one or more material(s) other than the cellulosic material described above. The hydrocarbon co-feed hence comprises one or more material(s) other than for example a solid cellulosic material; a pyrolysis oil; or a mixture thereof.

[0044] By a hydrocarbon feed is herein understood a feed that contains one or more hydrocarbon compounds. By a hydrocarbon compound is herein understood a compound that contains both hydrogen and carbon and preferably consists of hydrogen and carbon. Preferably the hydrocarbon co-feed is a fluid hydrocarbon co-feed. By a fluid hydrocarbon co-feed is herein understood a hydrocarbon co-feed that is not in a solid state when contacted with the FCC catalyst. The hydrocarbon co-feed is preferably fed via a feed nozzle into the riser reactor in an essentially liquid state, in an essentially gaseous state or in a partially liquid-partially gaseous state. For hydrocarbon co-feeds that are highly viscous, it may therefore be advantageous to preheat such feeds before entering the feed nozzle. The hydrocarbon co-feed is preferably in a gaseous state when contacted with the catalytic cracking catalyst. When entering the riser reactor in an essentially or partially liquid state, the fluid hydrocarbon co-feed preferably vaporizes upon entry and preferably is contacted in a gaseous state with the FCC catalyst and/or the cellulosic material.

[0045] The hydrocarbon co-feed can for example be any non-solid hydrocarbon co-feed known to the skilled person to be suitable as a feed for a catalytic cracking unit. The 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 Fischer-Tropsch oil (sometimes referred to as a synthetic oil) and/or a mixture thereof.

[0046] The hydrocarbon co-feed may also be a hydrocarbon co-feed from a renewable source, such as for example a vegetable oil.

[0047] In one embodiment the 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. Such oils are sometimes also referred to as mineral oils and preferably the hydrocarbon co-feed is therefore a mineral hydrocarbon co-feed. By a mineral hydrocarbon co-feed is understood a hydrocarbon co-feed that comprises or is derived from a mineral oil.

[0048] More preferably the hydrocarbon co-feed comprises a fraction of a, preferably conventional, crude oil or renewable oil. Preferred hydrocarbon co-feeds include straight run (atmospheric) gas oils, flashed distillate, vacuum gas oils (VGO), coker gas oils, diesel, gasoline, kerosene, naphtha, liquefied petroleum gases, atmospheric residue (“long residue”) and vacuum residue (“shor residue”) and/or mixtures thereof. Most preferably the hydrocarbon co-feed comprises a long residue and/or VGO.

[0049] The composition of the hydrocarbon co-feed may vary widely. The hydrocarbon co-feed may for example contain paraffins, olefins and aromatics. By paraffins both normal-, cyclo- and branched-paraffins are understood.

[0050] In a preferred embodiment the hydrocarbon co-feed comprises one or more paraffins, for example in the range from equal to or more than 20 wt % to equal to or less than 100 wt % of one or more paraffins, preferably in the range from equal to or more than 50 wt % of one or more paraffins, more preferably from equal to or more than 70 wt % of one or more paraffins, most preferably from equal to or more than 90 wt %, to equal to or less than 100 wt % of one or more paraffins, based on the total weight of the hydrocarbon co-feed. Such a hydrocarbon co-feed comprising one or more paraffins is herein also referred to as a paraffinic hydrocarbon co-feed.

[0051] For practical purposes the paraffin content of all hydrocarbon co-feeds having an initial boiling point of at least 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 hydrocarbon co-feeds the paraffin content of the hydrocarbon co-feed can be measured by means of comprehensive multi-dimensional gas chromatography (GC×GC), as described in P. J. Schoenmakers, J. T., M. M. Oomen, J. Blomberg, W. Genmit, G. van Velzen, J. Chromatogr. A, 892 (2000) p. 29 and further.

[0052] Examples of paraffinic hydrocarbon co-feeds include so-called Fischer-Tropsch derived hydrocarbon

In a preferred embodiment the hydrocarbon co-feed comprises equal to or more than 11 wt % elemental hydrogen, more preferably equal to or more than 12 wt % elemental hydrogen (i.e. hydrogen atoms), based on the total weight of the 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 12.2 wt %, allows the hydrocarbon co-feed to act as a cheap hydrogen donor in the catalytic cracking process. A particularly preferred hydrocarbon co-feed having an elemental hydrogen content of equal to or more than 12.5 wt % is Fischer-Tropsch derived waxoy raffinate. Such Fischer-Tropsch derived waxoy raffinate may for example comprise about 85 wt % of elemental carbon and 15 wt % of elemental hydrogen.

The weight ratio of the cellulosic material to hydrocarbon co-feed may vary widely.

The weight ratio of hydrocarbon co-feed to cellulosic material 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 hydrocarbon co-feed to cellulosic material 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 hydrocarbon co-feed and the cellulosic material are preferably being fed to the catalytic cracking reactor in a weight ratio within the above ranges. If the cellulosic material is a solid cellulosic material, the amount of solid cellulosic material, based on the total weight of the FCC feedstock, is preferably equal to or less than 30 wt %, more preferably equal to or less than 20 wt %, most preferably equal to or less than 10 wt % and even more preferably equal to or less than 5 wt %.

For practical purposes the amount of any solid cellulosic material present, based on the total weight of the FCC feedstock, is preferably equal to or more than 0.1 wt %, more preferably equal to or more than 1 wt %.

When the cellulosic material comprises a pyrolysis oil, the feed supplied to the catalytic cracking reactor may preferably comprise in the range from equal to or more than 5 wt %, more preferably from equal to or more than 10 wt % to equal to or less than 95 wt %, more preferably equal to or less than 99 wt % of such pyrolysis oil based on the total weight of the FCC feedstock.

Preferably the combination of the, preferably solid, cellulosic material and the hydrocarbon co-feed has an overall molar ratio of hydrogen to carbon (H/C) of equal to or more than 1.1 (1.1/1), more preferably of equal to or more than 1.2 (1.2/1), most preferably of equal to or more than 1.3 (1.3/1). For practical purposes the FCC feedstock may for example have an overall molar ratio of hydrogen to carbon (H/C) in the range from equal to or more than 1.1 (1.1/1) to equal to or less than 2.15 (2.15/1).

The hydrocarbon co-feed and the cellulosic material can be mixed prior to entry into the riser reactor or they can be added separately, at the same location or at different locations to the riser reactor.

In one embodiment the hydrocarbon co-feed and the cellulose material are not mixed together prior to entry into the riser reactor. In this embodiment the hydrocarbon co-feed and the cellulosic material may be fed simultaneously (that is at one location) to the riser reactor, and optionally mixed upon entry of the riser reactor; or, alternatively, the hydrocarbon co-feed and the cellulosic material may be added separately (at different locations) to the riser reactor. Riser reactors can have multiple feed inlet nozzles. The cellulosic material and the hydrocarbon co-feed can therefore be processed in the riser reactor even if both components are not miscible by feeding each component through a separate feed inlet nozzle.

When the cellulosic material is a solid cellulosic material, such solid cellulosic material is preferably supplied to the riser reactor at a location upstream of the location where the hydrocarbon co-feed is supplied to the riser reactor. Without wishing to be bound by any kind of theory it is believed that this allows the solid cellulosic material to be contacted with the FCC catalyst first; allowing the solid cellulose material to be converted into an intermediate oil product and allowing this intermediate oil product to be at least partly and preferably wholly vaporized before the FCC catalyst is quenched by addition of a hydrocarbon co-feed. Further supply of the solid cellulosic material upstream of the hydrocarbon co-feed allows for longer residence times for the solid cellulose material (when compared to the residence time for the hydrocarbon co-feed), making it possible to use a solid cellulosic material with a particle size distribution having a mean particle size of equal to or more than 2000 micrometer.

In another embodiment the hydrocarbon co-feed and the cellulosic material are mixed together prior to entry into a riser reactor to provide a feed mixture comprising the hydrocarbon co-feed and the cellulosic material. The feed mixture may be prepared just before entry to a riser reactor or it may optionally be held in a stirred feed vessel before being forwarded to a riser reactor.

The fluidized catalytic cracking (FCC) catalyst preferably comprises a zeolite (also sometimes referred to as a crystalline aluminosilicate), preferably dispersed in an amorphous matrix component. For example the FCC catalyst may comprise amorphous silica alumina and a zeolite. In addition, the FCC catalyst preferably comprises a binder and/or a filter.

In a preferred embodiment the FCC catalyst includes a so-called "large pore" zeolite. By a "large pore" zeolite is herein understood 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 0.62 nanometer to 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.

In a preferred embodiment the FCC catalyst includes a zeolite chosen from the group consisting of Y zeolites, ultrastable Y zeolites (USY), ZSM zeolites, zeolite beta, zeolite L, offretite, mordenite, faujasite (including synthetic faujasite), and zeolite omega, Rare earth zeolite Y (~REY) and Rare earth USY (REUSY).

If the FCC catalyst comprises a Y-type zeolite, such a Y-type zeolite preferably comprises an overall silica-to-alumina mole ratio of more than 3.6, more preferably an overall silica-to-alumina mole ratio of between about 3.0 and about 6.0.
[0066] The FCC catalyst can also comprise a so-called medium pore zeolite in addition to the above mentioned zeolites. By a "medium pore" zeolite is herein understood 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 0.45 nanometer to 0.62 nanometer.

[0067] Hence, in addition to the above mentioned zeolites, the FCC catalyst preferably includes a zeolite chosen from the group consisting of MFI type zeolites (such as for example ZSM-5); MTW type zeolites (such as for example ZSM-12); MTT type zeolites (such as for example ZSM-23) the TON type zeolites (such as for example zeolite theta one or ZSM-22); and the FER structural type, for example, ferrierite. Of these MFI type zeolites, preferably ZSM-5, are most preferred.

[0068] In a preferred embodiment the FCC catalyst comprises zeolite Y or ultrastable zeolite Y (USY) in combination with an MFI type zeolite such as ZSM-5.

[0069] If the FCC catalyst comprises both a large pore zeolite and a medium pore zeolite, the ratio of the large pore zeolite to the medium pore size zeolite in the FCC catalyst is preferably in the range of 99:1 to 70:30, more preferably in the range of 98:2 to 85:15.

[0070] In a preferred embodiment the stability and/or acidity of a zeolite used in the FCC catalyst can be increased by exchanging the zeolite with hydrogen ions, ammonium ions, polyvalent metal cations, such as rare earth-containing cations, magnesium cations or calcium cations, or a combination of hydrogen ions, ammonium ions and polyvalent metal cations, thereby lowering the sodium content until it is less than about 0.8 weight percent, preferably less than about 0.5 weight percent and or less than about 0.3 weight percent, calculated as Na₂O.

[0071] The FCC catalyst further preferably comprises an amorphous matrix component. Examples of such an amorphous matrix include amorphous silica-alumina, amorphous silica, amorphous alumina, amorphous titania, amorphous zirconia and amorphous magnesium oxide, or combinations of two or more of these.

[0072] In addition the FCC catalyst may comprise binders and/or fillers. An example of a binder is silica sol. Examples of fillers include natural or synthetic clays, pillared or delaminated clays, or mixtures of one or more of these. Examples of clays which may be present in the FCC catalyst include kaolin, hectorite, sepiolite and attapulgite.

[0073] The total amount of zeolite that is present in the FCC catalyst is preferably in the range of 5 wt% to 50 wt%, more preferably in the range of 10 wt% to 30 wt%, and even more preferably in the range of 10 wt% to 25 wt% relative to the total mass of the FCC catalyst, whilst the remainder is preferably amorphous matrix component, binder and/or filler.

[0074] By a riser reactor is herein understood an elongated essentially tube-shaped reactor. Such reactors are suitable for carrying out catalytic cracking reactions. The elongated essentially tube-shaped reactor is preferably oriented in an essentially vertical manner.


[0076] The riser reactor may be a so-called internal riser reactor or a so-called external riser reactor as described therein.

[0077] 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 is especially advantageous when at least part of the feed comprises a solid cellulosic material or a pyrolysis oil. The solid cellulosic material may be converted in-situ into a pyrolysis oil. Without wishing to be bound to any kind of theory it is believed that an internal riser reactor may reduce polymerization of any olefins formed, thereby reducing plugging risks and maintenance or service requirements.

[0078] When an external riser reactor is used, it may be advantageous to use an external riser reactor with a curve or low velocity zone at its upper end as for example illustrated in the Handbook titled “Fluid Catalytic Cracking technology and operations”, by Joseph W. Wilson, published by PennWell Publishing Company (1997), chapter 3, FIG. 3-7, herein incorporated by reference. It has been advantageously found that a part of the catalytic cracking catalyst may deposit in the curve or low velocity zone, thereby forming a protective layer against corrosion by any residual solid cellulosic material particles and/or any oxygen-containing hydrocarbons contained in a pyrolysis oil.

[0079] It may be advantageous to 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/or any mixtures of these. 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. In an especially preferred embodiment both steam as well as vaporized oil and/or a vaporized oil fraction (preferably vaporized liquefied petroleum gas, vaporized gasoline, diesel, kerosene or naphtha) are used as liftgas.

[0080] When the cellulosic material is a solid cellulosic material and this solid cellulosic material is introduced at the bottom of the riser reactor, it can be advantageous to increase the residence time of the cellulosic material at that part of the riser reactor by increasing the diameter of the riser reactor at the bottom. Hence in a preferred embodiment the riser reactor comprises a riser reactor pipe and a bottom section, which bottom section has a larger diameter than the riser reactor pipe, and wherein a solid cellulosic material is supplied to the riser reactor in the bottom section.

[0081] The bottom section having the larger diameter may for example have the form of a lift pot.

[0082] Preferably the total average residence time of the cellulosic material in the riser reactor lies in the range from equal to or more than 1.0 seconds, more preferably from equal to or more than 1.5 seconds, still more preferably from equal to or more than 2.0 seconds to equal to or less than 5.0 seconds, preferably to equal to or less than 4.0 seconds, most preferably to equal to or less than 2.5 seconds. Residence time as referred to in this patent application is based on the vapour residence at outlet conditions, that is, residence time includes
not only the residence time of a specified feed (such as the FCC feedstock) but also the residence time of its conversion products.

[0083] Preferably the temperature in the riser reactor, where the FCC feedstock is contacted with the FCC catalyst, lies in the range from equal to or more than 400°C, more preferably from equal to or more than 450°C, still more preferably from equal to or more than 480°C, to equal to or less than 800°C, more preferably to equal to or less than 700°C, still more preferably to equal to or less than 600°C, and most preferably to equal to or less than 550°C.

[0084] Preferably the pressure in the riser reactor ranges from equal to or more than 0.05 MPa to equal to or less than 1 MPa, more preferably from equal to or more than 0.1 MPa to equal to or less than 0.6 MPa.

[0085] The weight ratio of FCC catalyst to FCC feedstock (that is the total FCC feedstock of all catalytic materials and hydrocarbon co-feed) will herein also be referred to as catalyst feed ratio (catalyst:feed ratio). This catalyst to feed weight ratio preferably lies in the range from equal to or more than 1:1, more preferably from equal to or more than 2:1 and most preferably from equal to or more than 3:1 to equal to or less than 150:1, more preferably to equal to or less than 100:1, most preferably to equal to or less than 50:1.

[0086] In step a) preferably one or more hydrocarbon products, compounds and a spent FCC catalyst may be produced. The one or more hydrocarbon product(s) comprise at least a distillate product, but may also include one or more other product(s). By a hydrocarbon product is herein understood a product comprising one or more hydrocarbon compounds.

[0087] In step b) such one or more hydrocarbon product(s) —which hydrocarbon product(s) comprise least part of the distillate product—can be separated from the spent FCC catalyst.

[0088] Step b) (also referred to herein as 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 SadeghiBeigi, published by Gulf Publishing Company, Houston Tex. (1995), especially pages 219-223 and the Handbook “Fluid Catalytic Cracking Technology and Operations”, by Joseph W. Wilke, published by PennWell Publishing Company (1997), chapter 3, especially pages 104-120, and chapter 6, especially pages 186 to 194, herein incorporated by reference. The cyclone separators are preferably operated at a velocity in the range from 18 to 80 meters/second, more preferably at a velocity in the range from 25 to 55 meters/second.

[0089] Step b) may further comprise stripping of the spent FCC catalyst. In such a stripping step the spent FCC catalyst may be stripped to recover any products absorbed on the spent FCC catalyst before forwarding the spent FCC catalyst to the regeneration in step c). These products may be recycled and/or added to the one or more hydrocarbon product(s) obtained from step a).

[0090] In a preferred embodiment the one or more hydrocarbon product(s) obtained in step a) and/or step b) are subsequently fractionated to produce one or more product fractions.

[0091] 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 reactor. 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), chapter 8, especially pages 223 to 235, herein incorporated by reference.

[0092] The one or more hydrocarbon product(s) are preferably obtained as gaseous hydrocarbon products from step (a) and/or step (b). These gaseous hydrocarbon products can subsequently be separated into various gas and liquid products in one or more fractionation units.

[0093] Preferably a cooler and/or fractionator is used to cool the gaseous hydrocarbon products obtained from step (a) and to condense any heavy liquid products. The fractionator preferably comprises a distillation tower, which distillation tower comprising a bottom section (sometimes referred to as flash zone) at the bottom of the tower; a heavy cycle oil (HCO) section, a light cycle oil (LCO) section and a top section.

[0094] In the light cycle oil (LCO) section of the distillation tower the distillate product may be separated from the remainder of the hydrocarbon products. By a distillate product is herein preferably understood a hydrocarbon-compound-containing composition of which at least 80 wt %, more preferably at least 90 wt % has a boiling temperature at 0.1 MPa in the range from equal to or more than 221°C to less equal to or less than 370°C.

[0095] From the top section of the distillation tower, naphtha products (herein also referred to as gasoline-containing products) and so-called dry gas can be withdrawn. By naphtha product(s) or gasoline-containing-product(s) are herein preferably understood hydrocarbon-compound-containing compositions of which at least 80 wt %, more preferably at least 90 wt % has a boiling temperature at 0.1 MPa in the range from equal to or more than 30°C to less than 221°C.

[0096] Step c) (also referred to herein as regeneration step) preferably comprises regenerating the spent FCC catalyst in a regenerator to produce a regenerated FCC catalyst. More preferably step c) comprises contacting the spent FCC catalyst with an oxygen-containing gas in a regenerator at a temperature of equal to or more than 550°C to produce a regenerated FCC catalyst, heat and carbon dioxide. During the regeneration coke, that can be deposited on the FCC catalyst as a result of the catalytic cracking reaction(s) in step a) and/or step d), is burned off and/or the catalyst activity.

[0097] Preferably the catalyst regenerates comprises an essentially vertical-arranged, essentially cylindrical vessel that defines the regeneration zone and wherein the spent FCC catalyst is maintained as a fluidized bed by the upward passage of the oxygen-containing gas, such as air.

[0098] Preferably the spent FCC catalyst is regenerated at a temperature in the range from equal to or more than 575°C, more preferably from equal to or more than 600°C, to equal to or less than 950°C, more preferably to equal to or less than 850°C. In a most preferred embodiment the temperature within the regeneration zone is preferably maintained in the range of from equal to or more than 620°C to equal to or less than 780°C, and more preferably in the range of from equal to or more than 670°C to equal to or less than 750°C. Preferably the spent FCC catalyst is regenerated at a pressure in the range from equal to or more than 0.05 MPa to equal to or less than 1 MPa, more preferably from equal to or more than 0.1 MPa to equal to or less than 0.6 MPa.

[0099] The residence time of the spent FCC catalyst within the regeneration zone is preferably in the range of from equal
to or more than 1 minute to equal to or less than 6 minutes, and more preferably from equal to or more than 2 minutes to equal to or less than 4 minutes. The coke content on the regenerated FCC catalyst is less than the coke content on the spent FCC catalyst. Preferably the coke content on the regenerated FCC catalyst is equal to or less than 0.5 wt. %, based on the total weight of the regenerated FCC catalyst. More preferably the coke content of the regenerated FCC catalyst lies in the range of from equal to or more than 0.01 wt. % to equal to or less than 0.5 wt. % based on the total weight of the regenerated FCC catalyst. Most preferably the coke concentration on the regenerated FCC catalyst lies in the range of equal to or more than 0.01 wt. % to equal to or less than 0.1 wt. %, based on the total weight of the regenerated FCC catalyst.

[0100] In a preferred embodiment a side stream of fresh FCC catalyst is added to the regenerator to make-up for possible losses of the FCC catalyst in the process, such as for example possible losses of FCC catalyst in any cyclone(s) after the reactor(s) and/or the regenerator. In addition the side stream of fresh FCC catalyst may be used to replace part of the spent FCC catalyst with fresh FCC catalyst to make-up for any loss in catalyst activity in the process. If part of the spent FCC catalyst is replaced by fresh FCC catalyst, such part of the spent FCC catalyst is preferably equal to or less than 10 wt %, more preferably equal to or less than 5 wt % and most preferably equal to or less than 1 wt %, based on the total weight of catalyst present in the regenerator.

[0101] By a fresh FCC catalyst is herein understood an FCC catalyst that has not been used yet in a fluidized catalytic cracking reaction.

[0102] 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 21 vol. % oxygen (O₂), more preferably air comprising equal to or more than 22 vol. % oxygen, based on the total volume of air.

[0103] Any heat produced in the exothermic regeneration step is preferably employed to provide energy for feed vaporization and the endothermic catalytic cracking in step a) and/or step d). In addition the heat produced can be used to heat water to generate steam. The steam may be used elsewhere, for example as a liftgas in the riser reactor.

[0104] In a preferred embodiment step c) further comprises separating the produced regenerated FCC catalyst from any side-products produced in the regeneration, such as for example carbon dioxide. Preferably such separation is carried out with the help of one or more cyclone separators and/or swirl tubes.

[0105] The regenerated FCC catalyst is at least partly forwarded to step d).

[0106] In step d) at least part of the regenerated FCC catalyst is contacted with an intermediate reactor feedstock in an intermediate reactor at a temperature of equal to or more than 500°C to produce one or more C2-C4 olefins and a used regenerated FCC catalyst.

[0107] The intermediate reactor feedstock is preferably a feedstock comprising one or more hydrocarbon compounds of which one or more hydrocarbon compounds at least 80 wt %, more preferably at least 90 wt % has a boiling temperature at 0.1 MPa of equal to or below 221°C, more preferably equal to or below 204°C. More preferably the intermediate reactor feedstock is a feedstock comprising one or more hydrocarbon compounds of which hydrocarbon compounds at least 80 wt %, more preferably at least 90 wt % has a boiling temperature at 0.1 MPa in the range from equal to or more than 30°C to less than 221°C, more preferably in the range from equal to or more than 32°C to equal to or less than 204°C.

[0108] Examples of refinery streams that may be used as the intermediate reactor feedstock include the so-called naphtha products described herein above. Such naphtha products can for example be formed by one or more fraction(s) of the products of a fluidized catalytic cracking reactor, of which fraction(s) at least 80 wt %, more preferably at least 90 wt % boils in the range from equal to or more than 30°C to less than 221°C.

[0109] Examples of naphtha products include light-lighercycle oil (LLCO), sometimes also referred to as heavy-catalytically-cracked gasoline (HCCG) or heavy-catalytically-cracked naphtha; catalytically-cracked gasoline (CCG, sometimes also referred to as heart-cut gasoline or catalytically-cracked naphtha); and a light catalytically-cracked gasoline (LCCG, sometimes also referred to as catalytically-cracked tops or light catalytically-cracked naphtha).

[0110] Further examples of refinery streams that may be used as the intermediate reactor feedstock include, coker gasoline, visbreaker gasoline, light straight run gasoline, heavy straight run gasoline, raffinates, hydroxwaxes, Fischer-Tropsch waxes and/or mixtures of these.

[0111] In an especially preferred embodiment the intermediate reactor feedstock comprises a product produced in the riser reactor in step a), for example a gasoline-containing product or naphtha product produced in the riser reactor of step a). Hence preferably step a) comprises contacting a FCC feedstock with a FCC catalyst at a temperature of equal to or more than 400°C. In a riser reactor to produce a gasoline-containing product, a distillate product and a spent FCC catalyst; and at least part of the gasoline-containing product is used as an intermediate reactor feedstock in step d).

[0112] In a preferred embodiment the intermediate reactor feedstock comprises one or more olefins, for example comprising in the range from equal to or more than 20 wt % of one or more olefins, more preferably equal to or more than 45 wt % of one or more olefins, to equal to or less than 65 wt % of one or more olefins, more preferably equal to or less than 55 wt % of one or more olefins, based on the total weight of intermediate reactor feedstock. By an olefin is herein understood a hydrocarbon compound wherein two or more carbon atoms are bound to another carbon atom by a double bond. Preferably such olefins contained in the intermediate reactor feedstock are C5-olefins. By C5-olefins are herein understood olefins having equal to or more than 5 carbon atoms. Examples of such C5-olefins include pentenes, pentadienes, hexenes, and hexadienes. An example of such an olefin-containing intermediate reactor feedstock is an olefin-containing naphtha product (for example catalytically cracked gasoline). Preferably the intermediate reactor feedstock is therefore a naphtha product (also referred to herein as gasoline-containing product) comprising in the range from equal to or more than 20 wt % to equal to or less than 65 wt % of one or more olefins, based on the total weight of naphtha product. Such a naphtha product comprising one or more olefins may be difficult to blend with other fuel components. The process according to the invention can conveniently convert such an olefin-containing naphtha product into a blendable gasoline component and one or more C2-C4 olefins.
[0113] In a preferred embodiment the present invention therefore also provides a process for the preparation of a biofuel and/or a biochemical, comprising
a) contacting a FCC feedstock with a FCC catalyst at a temperature of equal to or more than 400°C in a riser reactor to produce a distillate product, a spent FCC catalyst, and optionally a first gasoline-containing-product, wherein the FCC feedstock comprises a cellulosic material and a hydrocarbon co-feed;
b) separating at least part of the distillate product from the spent FCC catalyst;
c) regenerating the spent FCC catalyst to produce a regenerated FCC catalyst;
d) contacting an intermediate reactor feedstock, which intermediate reactor feedstock may optionally comprise the first gasoline-containing-product, with at least part of the regenerated FCC catalyst at a temperature of equal to or more than 500°C in an intermediate reactor to produce a used regenerated FCC catalyst, one or more C2-C4 olefins and a second gasoline-containing-product, which second gasoline-containing-product comprises one or more hydrocarbon compounds, and wherein at least 80 wt % of such one or more hydrocarbon compounds has a boiling temperature at 0.1 MPa in the range from equal to or more than 30°C to less than 221°C;
e) separating at least part of the second gasoline-containing-product and at least part of the one or more C2-C4 olefins from the used regenerated catalyst;
f) using at least part of the used regenerated FCC catalyst as FCC catalyst in step a); wherein at least part of the first gasoline-containing-product or at least part of the second gasoline-containing-product is blended with one or more other components to prepare a biofuel and/or a biochemical.

[0114] In addition the intermediate reactor feedstock may comprise further biological feed components such as vegetable oils, used cooking oil, animal fat and/or mixtures thereof. Such vegetable oils, used cooking oil and/or animal fat may optionally be upgraded or pretreated, for example by means of a hydrotreatment (including for example hydrogenation and/or hydrodeoxygenation). Suitable plant oils (vegetable oils) include for example rapeseed oil, palm oil, coconut oil, corn oil, soya oil, safflower oil, sunflower oil, linseed oil, olive oil and peanut oil. Suitable animal fats include for example pork lard, beef fat, mutton fat and chicken fat. If any biological feed component is present, such biological feed component is preferably present in the intermediate reactor feedstock in an amount of equal to or more than 1 wt % to equal to or less than 40 wt %, more preferably from equal to or more than 5 wt % to equal to or less than 30 wt %, most preferably from equal to or more than 10 wt % to equal to or less than 20 wt %, based on the total weight of the intermediate reactor feedstock.

[0115] The intermediate reactor is preferably an intermediate reactor comprising a fluidized catalyst. More preferably the intermediate reactor is a fluidized bed reactor or a riser reactor. In case the intermediate reactor is a riser reactor, the intermediate reactor in step d) could be referred to as the second riser reactor, since the riser reactor in step a) would form the first riser reactor. When the intermediate reactor is a fluidized bed reactor it is preferably a so-called dense phase reactor, dense bed reactor or a fixed fluidized bed reactor.

[0116] If the intermediate reactor is a fluidized bed reactor, this fluidized bed reactor can for example comprise a vessel that defines a fluidized bed reaction zone. Regenerated FCC catalyst may be contained in this reaction zone where it may be fluidized by the introduction of the intermediate reactor feedstock and, optionally, steam.

[0117] If the intermediate reactor is a riser reactor, the riser reactor may for example be any type or riser reactor as described for step a), including for example an internal or external riser reactor and/or a riser reactor including a liftgas. If a liftgas is used, any liftgas as mentioned for step a) may be used, but steam may be most preferred as a liftgas.

[0118] Preferably the temperature in the intermediate reactor, where the intermediate reactor feedstock is contacted with the regenerated FCC catalyst, lies in the range from equal to or more than 500°C, more preferably from equal to or more than 550°C, and most preferably equal to or more than 550°C to equal to or less than 900°C, more preferably to equal to or less than 850°C, still more preferably to equal to or less than 800°C and most preferably to equal to or less than 750°C.

[0119] In a preferred embodiment the temperature in the intermediate reactor in step d) is higher than the temperature in the riser reactor in step a).

[0120] Preferably the pressure in the intermediate reactor ranges from equal to or more than 0.05 MPa (MegaPascal) to equal to or less than 1 MPa, more preferably from equal to or more than 0.1 MPa to equal to or less than 0.6 MPa.

[0121] In a preferred embodiment the intermediate reactor feedstock and steam are simultaneously fed into the reaction zone of the intermediate reactor to be contacted with the regenerated FCC catalyst. The use of steam as a co-feed or liftgas may advantageously improve selectivity towards C2-C4 olefins. When steam is used, the weight ratio of steam to intermediate reactor feedstock lies preferably in the range of equal to or more than 0.1:1 to equal to or less than 15:1. More preferably, the weight ratio of steam to intermediate reactor feedstock lies in the range of from 0.2:1 to 10:1.

[0122] In step d) preferably one or more hydrocarbon products and a used regenerated FCC catalyst may be produced. The one or more hydrocarbon product(s) comprise at least one or more C2-C4 olefins, but may also include one or more other hydrocarbon product(s).

[0123] In step (e) one or more hydrocarbon product(s) can be separated from the used regenerated FCC catalyst in any manner known to the person skilled in the art. For example, the used regenerated FCC catalyst may be separated from the one or more hydrocarbon products in the same manner as the one or more hydrocarbon product(s)—which hydrocarbon product(s) may comprise least part of the distillate—can be separated from the spent FCC catalyst in step (b). For example such separation can be carried out with the help of one or more cyclone separators and/or one or more swirl tubes. In addition, a stripping step may be incorporated in step (e), wherein the used regenerated FCC catalyst may be stripped to recover any products absorbed on the used regenerated FCC catalyst before using at least part of the used regenerated FCC catalyst as FCC catalyst in step (a). These products may be recycled and/or added to the one or more hydrocarbon product(s) obtained in step (d).

[0124] In a preferred embodiment the one or more hydrocarbon product(s) obtained in step (d) are subsequently cooled and/or fractionated to produce one or more product fractions, one of which would be the one or more C2-C4 olefins.

[0125] By olefins are herein preferably understood hydrocarbon compounds having one or more unsaturated bond(s). By C2-C4 olefins are herein understood olefins having in the
range from equal to or more than 2 to equal to or less than 4 carbon atoms. Preferably the C2-C4 olefins are olefins chosen from the group consisting of ethene, propene, 1-butene, 2-butene, butadiene and methyl-propene. Most preferred olefins are ethene and propene.

[0126] In step f) at least part of the used regenerated FCC catalyst is recycled and used as FCC catalyst in step a).

[0127] Advantageously the regenerated FCC catalyst is partially deactivated during step d) prior to using the used regenerated FCC catalyst in the riser reactor in step a). What is meant by partial deactivation is that the used regenerated FCC catalyst will contain a higher concentration of coke than the regenerated FCC catalyst. The use of such partially deactivated catalyst (i.e. the already partially coked catalyst comprising) in step a) advantageously allows one to operate at a lower temperature and lower catalyst activity such that the desired distillate product can be made in higher yields. The coke concentration on the used regenerated FCC catalyst is greater than the coke concentration on the regenerated FCC catalyst, but it is less than that of the separated spent FCC catalyst. Preferably, the coke content of the used regenerated FCC catalyst is in the range of from equal to or more than 0.1 wt. % to equal to or less than 1 wt. %, and more preferably, from equal to or more than 0.1 wt. % to equal to or less than 0.6 wt. %.

[0128] The amount of regenerated FCC catalyst produced in step c) that is provided to the intermediate reactor in step d) may vary extensively and may for example lie in the range from equal to or more than 1 wt. % to equal to or less than 100 wt. %, based on the total weight of regenerated FCC catalyst produced in step c). More preferably the amount of regenerated FCC catalyst produced in step c) that is provided to the intermediate reactor in step d) may lie in the range from equal to or more than 10 wt. %, still more preferably equal to or more than 50 wt. % to equal to or less than 100 wt. %, possibly equal to or less than 90 wt. %, based on the total weight of regenerated FCC catalyst produced in step c).

[0129] To assist in providing for the control of the process conditions within the riser reactor in step a) and/or to provide for the desired product mix, the regenerated FCC catalyst produced in step c) can be divided into at least a first portion that is passed to the intermediate reactor in step d) and a second portion that is passed to the riser reactor in step a). In such a case the second portion preferably comprises equal to or less than 50 wt. %, based on the total weight of regenerated FCC catalyst produced in step c). If a second portion is present, the second portion more preferably lies in the range from equal to or more than 10 wt. % to equal to or less than 50 wt. %, based on the total weight of the FCC catalyst produced in step c).

[0130] The one or more hydrocarbon product(s), such as for example the distillate product and/or the one or more C2-C4 olefins, obtained in the process according to the invention may advantageously be used to produce one or more biofuel components and/or one or more biochemical components.

[0131] For example, the C2-C4 olefins produced according to the invention may advantageously be used to produce bio-polymers, such as for example biological polypropylene and/or biological polyethylene.

[0132] The distillate product produced according to the invention may advantageously be used as a biofuel component or it may undergo further process steps to be converted into a biofuel component.

[0133] The biofuel components and/or biochemical components produced according to the process of the present invention will have increased levels of carbon-14 isotope and are advantageously more sustainable than their conventional counterparts.

[0134] In one embodiment at least part of the distillate product produced in the process of the invention is hydrotreated before being used as a biofuel component. Such hydrotreatment may include for example hydrosulfurization, hydrodeoxygenation, hydrodenitrogenation and/or hydrogenation. In a preferred embodiment the distillate product produced is hydrodeoxygenated.

[0135] The hydrotreatment (such as the hydrodeoxygenation) preferably comprises contacting the distillate product with hydrogen in the presence of a hydrotreatment catalyst (such as a hydrodeoxygenation catalyst) at a temperature in the range from equal to or more than 200°C, preferably equal to or more than 250°C, to equal to or less than 450°C, preferably equal to or less than 400°C; at a total pressure in the range of equal to or more than 1 MPa to equal to or less than 35 MPa; and/or a partial hydrogen pressure in the range of equal to or more than 0.2 MPa to equal to or less than 35 MPa.

[0136] Any hydrodeoxygenation catalyst used can be any type of hydrodeoxygenation catalyst known by the person skilled in the art to be suitable for this purpose. The hydrodeoxygenation catalyst preferably comprises a catalyst support and one or more active elements. The active elements may include metals such as Nickel (Ni), Chromium (Cr), Molybdenum (Mo), and Tungsten (W), Cobalt (Co), Platinum (Pt), Palladium (Pd), Rhodium (Rh), Ruthenium (Ru), Iridium (Ir), Osmium (Os), Copper (Cu), iron (Fe), Zinc (Zn), Gallium (Ga), Indium (In) and Vanadium (V) in elementary form, alloys or mixtures of one or more thereof such as:

[0137] Preferably the hydrodeoxygenation catalyst is a catalyst comprising Ruthenium, Rhenium, Cobalt, Nickel, Copper, Tungsten and/or alloys or mixtures of Ruthenium, Rhenium, Cobalt, Nickel, Tungsten and/or Copper, such as for example Rh—Co and/or Ni—Cu, on a catalyst carrier that is inert at the reaction conditions. The carrier preferably may comprise a refractory oxide or mixtures thereof, preferably alumina, amorphous silica-alumina, titania or silica, ceria, zirconia, or it may comprise an inert component such as carbon or silicon carbide or carbon. Carriers that were found inert are ZrO2, CeO2, Ce2O3, and/or mixtures thereof such as CeO2—ZrO2, silicon carbide and/or carbon. In some cases it may be advantageous to use a sulphided hydrodeoxygenation catalyst. If a sulphided hydrodeoxygenation catalyst is used, the catalyst may be sulphided in-situ or ex-situ. In the case of in-situ sulphiding, a sulphur source, usually hydrogen sulphide or a hydrogen sulphide precursor, is preferably supplied to the catalyst during operation of the hydrodeoxygenation process. Most preferred are hydrodeoxygenation catalysts comprising rhodium on alumina(Rh/Al2O3), rhodium on silica (Rh/SiO2), rhodium on zirconia (Rh/ZrO2), rhodium-cobalt on alumina (RhCo/Al2O3), rhodium-cobalt on silica (RhCo/SiO2), rhodium-cobalt on zirconia (RhCo/ZrO2), nickel on alumina(Ni/Al2O3), nickel on silica (Ni/SiO2), nickel on zirconia (Ni/ZrO2), nickel-copper on alumina (NiCu/Al2O3), nickel-copper on silica (NiCu/SiO2), nickel-copper on zirconia (NiCu/ZrO2), nickel-tungsten on alumina (NiW/Al2O3), nickel-tungsten on silica (NiW/SiO2), nickel-tungsten on zirconia (NiW/ZrO2), cobalt on alumina (Co/Al2O3), cobalt on silica (Co/SiO2), cobalt on zirconia...
(Co/ZrO₂), cobalt-molybdenum on silica (CoMo/SiO₂), cobalt-molybdenum on zirconia (CoMo/ZrO₂), cobalt-molybdenum on alumina (CoMo/Al₂O₃).

[0138] The biofuel component and/or biochemical component can be blended with one or more other components to produce a biofuel and/or a biochemical. Examples of one or more other components with which the biofuel component and/or biochemical component may be blended include antioxidants, corrosion inhibitors, ashless detergents, dehazers, dyes, lubricity improvers and/or mineral fuel components, but also conventional petroleum derived gasoline, diesel and/or kerosene fractions.

[0139] By a biofuel respectively a biochemical is herein understood a fuel or a chemical that is at least party derived from a renewable energy source.

[0140] In FIG. 1 one embodiment according to the invention is illustrated. In FIG. 1, a FCC feedstock comprising cellulosic material and hydrocarbon co-feed (102) and steam (104) are introduced into the bottom of a first riser reactor (106). In the bottom of the first riser reactor (106), the FCC feedstock (102) and the steam (104) are mixed with “fresh” regenerated FCC catalyst (108) and used regenerated FCC catalyst (110). In the first reactor riser (106) the FCC feedstock (102) is catalytically cracked to produce one or more hydrocarbon products comprising distillate and a spent FCC catalyst. The mixture of one or more hydrocarbon products, spent FCC catalyst, steam, and any residual non-cracked FCC feedstock is forwarded from the top of the first riser reactor (106) into a reactor vessel (112), comprising a first cyclone separator (114) closely coupled with a second cyclone separator (116). One or more products (118) are retrieved via the top of the second cyclone separator (116) and optionally forwarded to a fractionator (not shown). Spent FCC catalyst is retrieved from the bottom of the cyclone separators (114 and 116) and forwarded to a stripper (120) where further hydrocarbon products are stripped off the spent FCC catalyst.

[0141] The spent and stripped FCC catalyst (122) is forwarded to a regenerator (124), where the spent and stripped FCC catalyst is contacted with air (126) to produce a regenerated FCC catalyst (108). A first part of the regenerated FCC catalyst (108a) is recycled to the bottom of the first riser reactor (106). A second part of the regenerated FCC catalyst (108b) is forwarded to the bottom of a intermediate riser reactor (130). In the bottom of the intermediate riser reactor (130) the second part of the regenerated FCC catalyst (108b) is contacted with an intermediate reactor feedstock (132) consisting of gasoline, and a second stream of steam (134). In the intermediate riser reactor (130) the intermediate reactor feedstock (132) is catalytically cracked to produce one or more hydrocarbon products comprising C2-C4 olefins and a used regenerated FCC catalyst. The mixture of one or more hydrocarbon products, used regenerated FCC catalyst, steam, and any residual non-cracked intermediate reactor feed is forwarded from the top of the intermediate riser reactor (130) into a second reactor vessel (136), comprising a first cyclone separator (138) closely coupled with a second cyclone separator (140). One or more products (142) are retrieved via the top of the second cyclone separator (140) and optionally forwarded to a fractionator (not shown). Used regenerated FCC catalyst is retrieved from the bottom of the cyclone separators (138 and 140) and forwarded to a stripper (144) where further hydrocarbon products are stripped off the used regenerated FCC catalyst. Subsequently the stripped used regenerated FCC catalyst is recycled to the bottom of the first riser reactor (106) as FCC catalyst stream (110).

What is claimed is:
1. A process for making a distillate product and one or more C2-C4 olefins comprising:
a) contacting a FCC feedstock with a FCC catalyst at a temperature of at least 400°C in a riser reactor to produce a distillate product and a spent FCC catalyst, wherein the FCC feedstock comprises a cellulosic material and a hydrocarbon co-feed;
b) separating at least a portion of the distillate product from the spent FCC catalyst;
c) regenerating the spent FCC catalyst to produce a regenerated FCC catalyst;
d) contacting an intermediate reactor feedstock with at least a portion of the regenerated FCC catalyst at a temperature of at least 500°C in an intermediate reactor to produce one or more C2-C4 olefins and a used regenerated FCC catalyst;
e) separating at least a portion of the one or more C2-C4 olefins from the used regenerated catalyst; and
f) providing at least a portion of the used regenerated FCC catalyst as FCC catalyst in step a).
2. The process of claim 1 wherein the FCC feedstock comprises a hydrocarbon co-feed and at least one cellulosic material selected from the group consisting of a solid cellulosic material, a pyrolysis oil derived from cellulosic material, and a mixture thereof.
3. The process of claim 1 wherein the hydrocarbon co-feed comprises at least 8 wt % elemental hydrogen, based on the total weight of the hydrocarbon co-feed on a dry basis.
4. The process of claim 1 wherein the hydrocarbon co-feed comprises in the range from at least 20 wt % to at most 100 wt % of at least one paraffin, based on the total weight of the hydrocarbon co-feed.
5. The process of claim 1 wherein the combination of the cellulosic material and the hydrocarbon co-feed has an overall molar ratio of hydrogen to carbon (H/C) of equal to or more than 1.1 (1.1/1).
6. The process of claim 1 wherein the cellulosic material is a solid cellulosic material and said solid cellulosic material is supplied to the riser reactor at a location upstream of the location where the hydrocarbon co-feed is supplied to the riser reactor.
7. The process of claim 1 wherein the FCC catalyst comprises zeolite Y or ultrastable zeolite Y (USY) in combination with an MFI type zeolite.
8. The process of claim 1 wherein step a) comprises contacting a FCC feedstock with a FCC catalyst at a temperature of at least 400°C in a riser reactor to produce a gasoline-containing product, a distillate product and a spent FCC catalyst; and wherein at least a portion of the gasoline-containing product is provided as an intermediate reactor feedstock in step d).
9. The process of claim 1 wherein at least 85 wt % of the hydrocarbon co-feed comprises in the range from at least 20 wt % to at most 65 wt % of one or more olefins, based on the total weight of intermediate reactor feedstock.
10. The process of claim 9 wherein the one or more olefins are one or more C5-olefins.
11. The process of claim 1 wherein an intermediate reactor feedstock in step d) comprises one or more hydrocarbon compounds, and at least 80 wt % of said one or more hydro-
carbon compounds has a boiling temperature at 0.1 MPa in the range from at least 30°C to less than 221°C.

12. The process of claim 1 wherein the temperature in step a) is higher than the temperature in step d).

13. The process of claim 1 wherein the intermediate reactor feedstock comprise further biological feed components.

14. A process for the preparation of a biofuel and/or a biochemical, comprising

a) contacting a FCC feedstock with a FCC catalyst at a temperature of at least 400°C. in a riser reactor to produce a distillate product and a spent FCC catalyst, wherein the FCC feedstock comprises a cellulosic material and a hydrocarbon co-feed;
b) separating at least a portion of the distillate product from the spent FCC catalyst;
c) regenerating the spent FCC catalyst to produce a regenerated FCC catalyst;
d) contacting an intermediate reactor feedstock with at least a portion of the regenerated FCC catalyst at a temperature of at least 500°C. in an intermediate reactor to produce one or more C2-C4 olefins and a used regenerated FCC catalyst;
e) separating at least a portion of the one or more C2-C4 olefins from the used regenerated catalyst;
f) providing at least a portion of the used regenerated FCC catalyst as FCC catalyst in step a); and
g) blending at least a portion of the distillate product and/or at least a portion of the one or more C2-C4 olefins with one or more other components to produce a biofuel and/or a biochemical.

15. The process of claim 14 wherein the FCC feedstock comprises a hydrocarbon co-feed and at least one cellulosic material selected from the group consisting of a solid cellulosic material, a pyrolysis oil derived from cellulosic material, and a mixture thereof.

16. The process of claim 14 wherein the temperature in step a) is higher than the temperature in step d).

17. A process for the preparation of a biofuel and/or a biochemical, comprising

a) contacting a FCC feedstock with a FCC catalyst at a temperature of at least 400°C. in a riser reactor to produce a distillate product and a spent FCC catalyst, wherein the FCC feedstock comprises a cellulosic material and a hydrocarbon co-feed;
b) separating at least a portion of the distillate product from the spent FCC catalyst;
c) regenerating the spent FCC catalyst to produce a regenerated FCC catalyst;
d) contacting an intermediate reactor feedstock with at least a portion of the regenerated FCC catalyst at a temperature of at least 500°C. in an intermediate reactor to produce a used regenerated FCC catalyst, one or more C2-C4 olefins and a gasoline-containing-product, said gasoline-containing-product comprises one or more hydrocarbon compounds, wherein at least 80 wt % of such one or more hydrocarbon compounds has a boiling temperature at 0.1 MPa in the range from equal to or more than 30°C to less than 221°C.;
e) separating at least a portion of the gasoline-containing-product and at least a portion of the one or more C2-C4 olefins from the used regenerated catalyst;
f) providing at least a portion of the used regenerated FCC catalyst as FCC catalyst in step a); and
g) blending at least a portion of the distillate product and/or at least a portion of the gasoline-containing-product with one or more other components to produce a biofuel and/or a biochemical.

18. The process of claim 17 wherein the FCC feedstock comprises a hydrocarbon co-feed and at least one cellulosic material selected from the group consisting of a solid cellulosic material, a pyrolysis oil derived from cellulosic material, and a mixture thereof.

19. The process of claim 17 wherein the temperature in step a) is higher than the temperature in step d).