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(54) **GREEN FLUID CATALYTIC CRACKING PROCESS**

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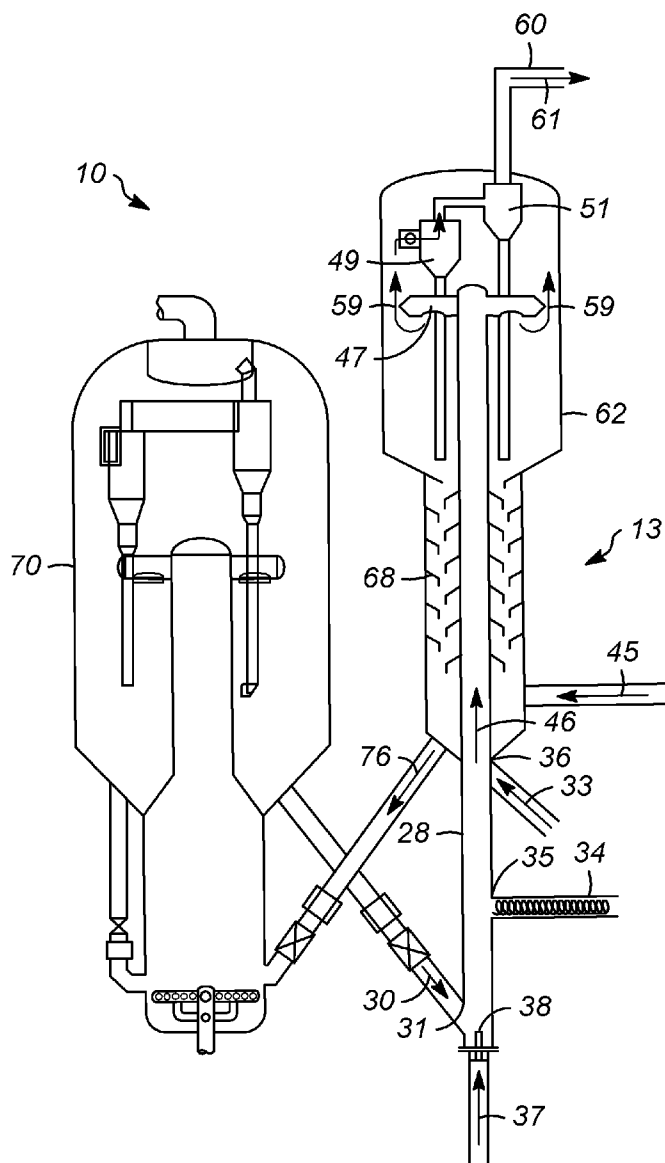
(57) **ABSTRACT**

A process and apparatus for co-processing a hydrocarbon feedstock and a renewable biomass feedstock are described. Solid particles of biomass are introduced into the riser reactor zone and mixed with catalyst. The hydrocarbon feed stock is also introduced into the riser reactor zone. The solid particles of biomass react in the presence of the catalyst and are converted into oxygenated hydrocarbons, while the hydrocarbon reacts in the presence of the catalyst to form hydrocarbon products having a lower boiling point than the feedstock.

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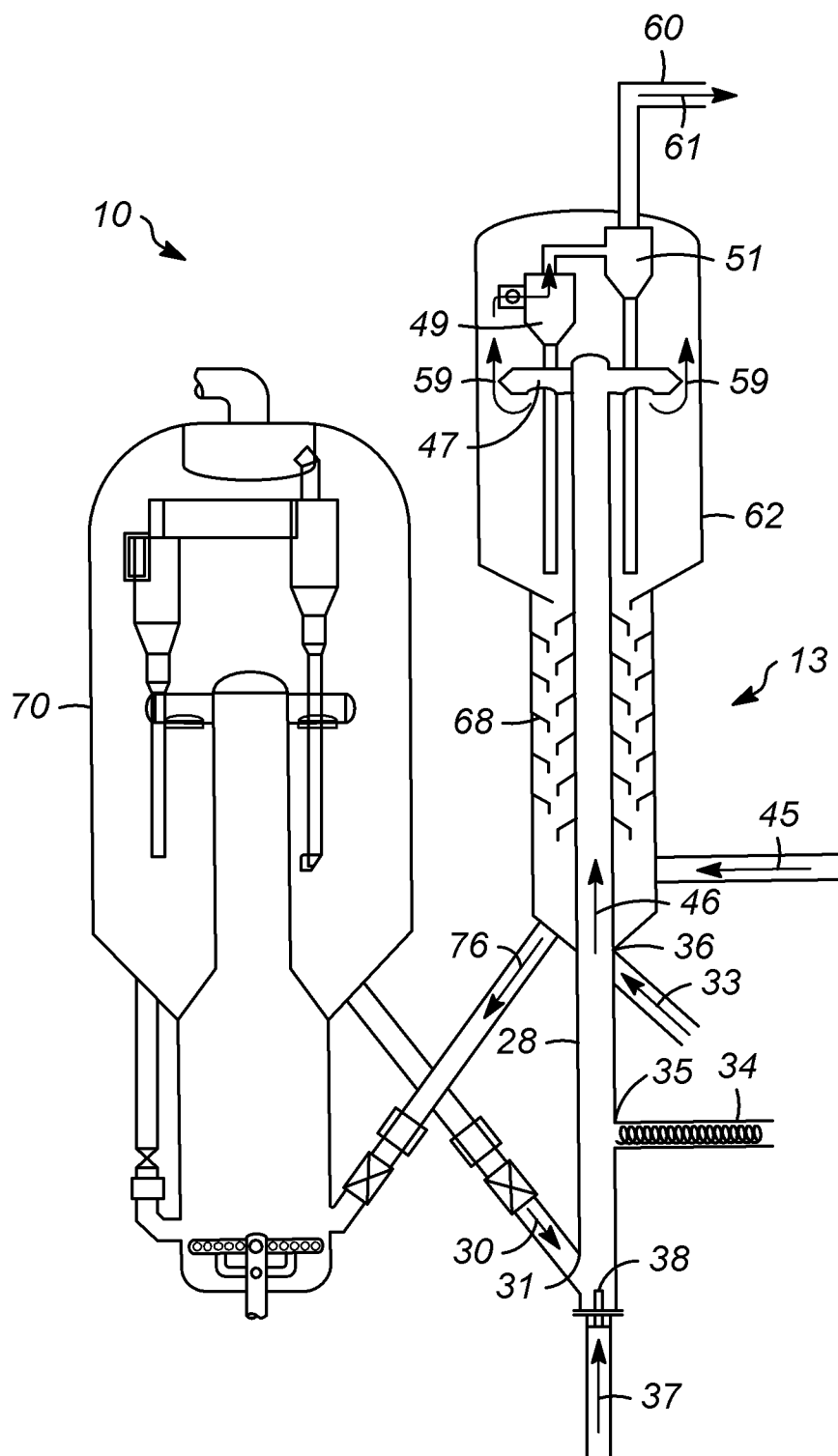


FIG. 1

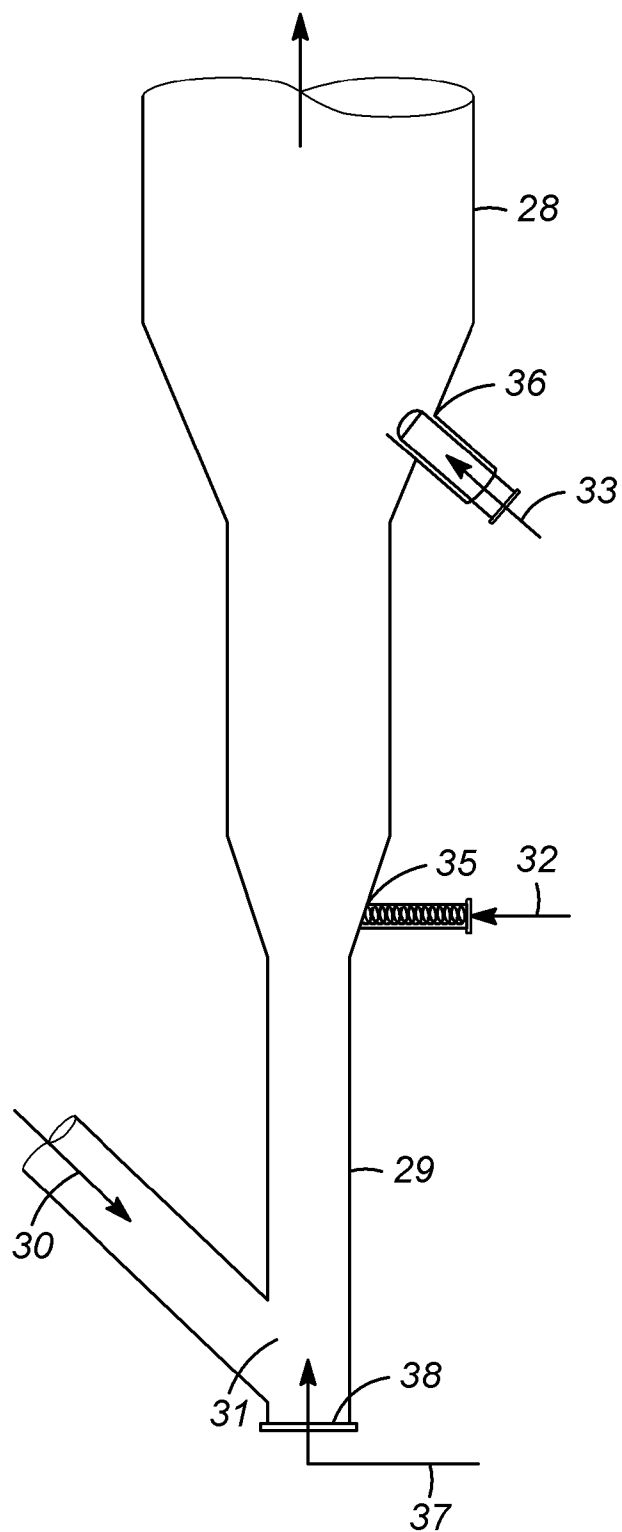


FIG. 2

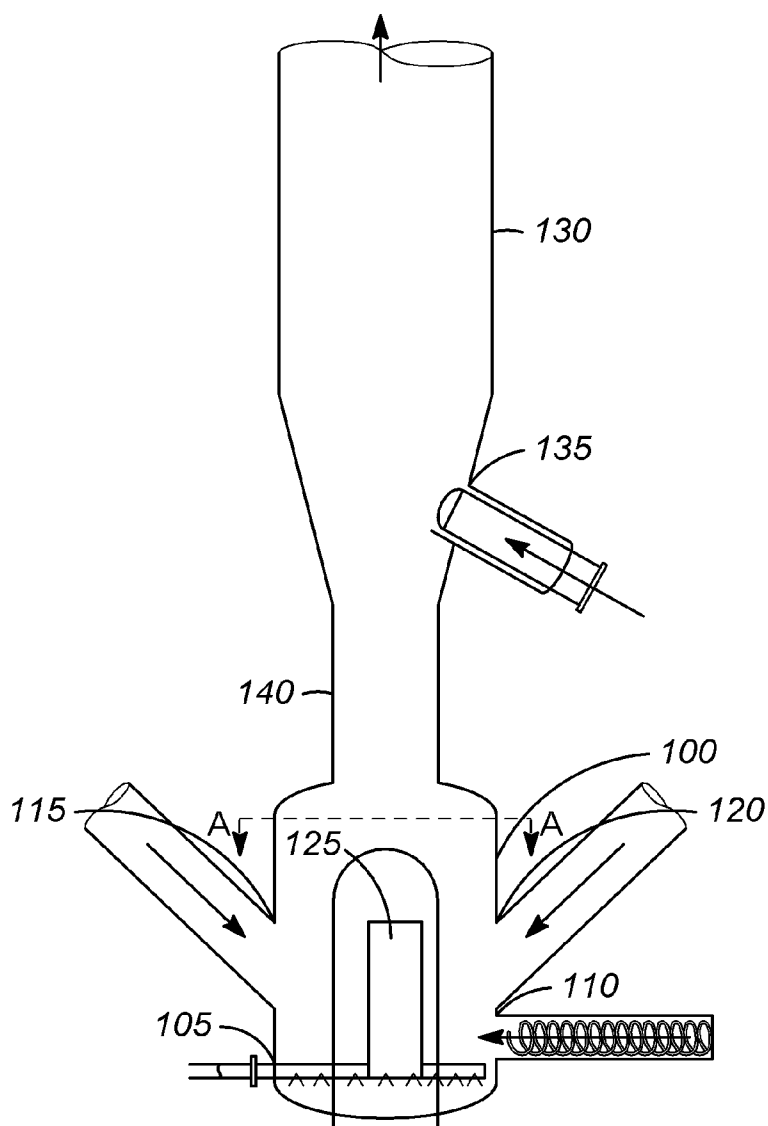


FIG. 3

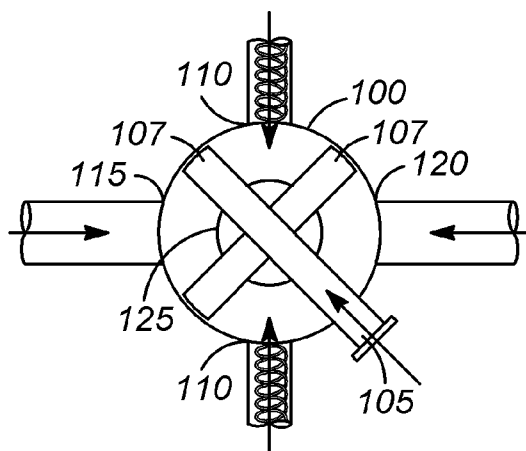


FIG. 4

GREEN FLUID CATALYTIC CRACKING PROCESS

BACKGROUND OF THE INVENTION

[0001] Transportation fuels derived from biomass have greatly reduced greenhouse gas emissions compared to fuels derived from petroleum. In addition, biomass is a renewable resource. Therefore, an economical process to utilize biomass as a feedstock is desirable.

[0002] However, the capital and operating costs associated with converting biomass feedstock to transportation fuel are high because the processes generally require multiple steps. One typical process involves pyrolysis followed by catalytic pyrolysis in separate, sequential process units.

[0003] US 2013/045683 describes a process in which a liquid thermally produced from biomass is introduced into a petroleum conversion unit, such as a fluid catalytic cracker, a coker, a hydrocracker, or hydrotreater, for coprocessing with a petroleum feed.

[0004] US 2013/0068997 describes a process in which solid biomass is introduced into a reactor and is agitated by a gas sufficient to reduce the size of the biomass particles so that the plurality of biomass particles can be substantially characterized by individual sizes below 1.5 mm. The biomass particles are then liquefied and co-processed with a petroleum feed.

[0005] Therefore, there is a need for improved processes for converting biomass to transportation fuels.

SUMMARY OF THE INVENTION

[0006] One aspect of the invention is a process for coprocessing a hydrocarbon feedstock and a renewable biomass feedstock. In one embodiment, the process includes introducing a lift gas into a fluid catalytic cracking riser reactor zone. A catalyst is introduced into the riser reactor zone at a point downstream of where the lift gas is introduced. Solid particles of the biomass feedstock are injected into the riser reactor zone. The hydrocarbon feedstock is introduced into the riser reactor zone. The solid particles of the biomass feedstock are mixed with the catalyst, the solid particles of the biomass feedstock reacting in the presence of the catalyst to form biomass products comprising gas, vapor, and char, and the gas and vapor biomass products further reacting in the presence of the catalyst to form oxygenated hydrocarbon products. The hydrocarbon feedstock is mixed with the catalyst, the hydrocarbon feedstock reacting in the presence of the catalyst to form hydrocarbon products having a lower boiling point than a boiling point of the hydrocarbon feedstock. The oxygenated hydrocarbon products from the biomass feedstock, the hydrocarbon products from the hydrocarbon feedstock, or both are recovered. The solid particles of biomass feedstock are injected into the riser reactor zone at a point upstream of where the hydrocarbon feedstock is introduced and at or downstream of the point where the catalyst is introduced, or at a point downstream of where the hydrocarbon feedstock and the catalyst are introduced.

[0007] Another aspect of the invention is a riser reactor zone. In one embodiment, the riser reactor zone includes a riser reactor; a chamber at the bottom of the riser reactor, the chamber having a lift gas inlet, a biomass inlet, and a catalyst inlet; and a hydrocarbon inlet in the riser reactor, the hydrocarbon inlet being positioned downstream of the chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 illustrates one embodiment of a fluid catalytic cracking process of the present invention.

[0009] FIG. 2 illustrates the riser reactor of FIG. 1.

[0010] FIG. 3 illustrates another embodiment of a riser reactor with a chamber useful in the process of the present invention.

[0011] FIG. 4 is a cross section of the chamber illustrated in FIG. 3.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Processes and apparatus for coprocessing biomass with a hydrocarbon feedstock in a fluid catalytic cracking (FCC) unit have been developed. By coprocessing biomass feedstock along with typical hydrocarbon derived feedstock, some of the specialized equipment in a biomass pyrolysis unit can be eliminated, and some equipment required by both processes can be shared. Because the biomass is directly introduced into the FCC reactor, a separate biomass pyrolysis unit is not required. Consequently, the capital and operating costs are similar to the cost of an FCC unit, but much less than the cost of separate pyrolysis and catalytic pyrolysis units. It also allows the oxygenated hydrocarbon products from the biomass and hydrocarbon products from the hydrocarbon feedstock to share the fractionation and gas concentration equipment. In addition, the process can be easily retrofitted into many existing FCC units.

[0013] The biomass is converted into oxygenated hydrocarbon products having a lower oxygen content than those formed by pyrolysis and catalytic pyrolysis units. Thermal pyrolysis oil typically contains about 30 to 50 wt % oxygen and about 20 to 30 wt % water with high acidity (TAN greater than 150). Oil from a catalytic process typically contains less than about 5 wt % oxygen and less than 1 wt % water. The goal of the present process is to produce a product using biomass that has very low oxygen content. With the present process, it is expected that an oxygen content of less than about 4 wt % can be obtained, or less than about 3 wt %, or less than about 2 wt %, or less than about 1 wt %, or less than about 0.75 wt %, or less than about 0.5 wt %, or less than about 0.3 wt %, or less than about 0.2 wt %.

[0014] The oxygenated hydrocarbon product from the biomass is thus more valuable than products made using the prior art processes because: 1) it is more stable in storage and transportation; 2) it is fully miscible with hydrocarbon; 3) it has a higher energy content; and 4) and it is from a renewable resource.

[0015] The hydrocarbon feed is converted to hydrocarbon products having a lower boiling point than the feed. Examples of the hydrocarbon products include, but are not limited to, propane, butane, light naphtha, heavy naphtha, cycle oil, and the like.

[0016] FCC is a well-known process for the conversion of relatively high boiling point hydrocarbons to lower boiling point hydrocarbons in the heating oil or gasoline (or lighter) range. FCC units generally have one or more reaction chambers. A hydrocarbon stream is contacted in the reaction chamber(s) with a particulate cracking catalyst that is maintained in a fluidized state under conditions that are suitable for the conversion of the relatively high boiling point hydrocarbons to lower boiling point hydrocarbons.

[0017] FIGS. 1 and 2 illustrate one embodiment of the FCC process 10 of the present invention. The FCC unit includes a

vertical conduit or riser 28. The lift gas 37 is introduced into the riser 28 through nozzle 38, and the particulate cracking catalyst 30 may be introduced into the riser 28 at a catalyst outlet 31.

[0018] The biomass can be dried to minimize the amount of water that has to be processed in the fractionation system. The biomass is typically dried to less than about 20% moisture, or less than 10%, or between about 4% and about 8%, although higher moisture content can be used. In the present process, the moisture content is not critical because the product has low solubility in water, and it separates easily from the water. The water poses a heat and vapor load on the system, but not a product quality problem. In contrast, the moisture content is critical in the thermal pyrolysis process of biomass because the water in the biomass adds to the water that comes from the conversion of the biomass. All of the water ends up in the liquid product, diluting the energy content of the product and reducing its value. In addition, if the moisture content of the product exceeds about 30%, the product will separate into two immiscible phases, an aqueous phase of limited value and a viscous, low value organic phase.

[0019] The biomass is then ground to a size appropriate for rapid heat transfer from the catalyst in the riser to the biomass particles, typically in the range of about 0.5 mm to about 6 mm, with up to about 0.5 wt % outside this range. Size ranges larger than this increase the likelihood and frequency of bridging in the biomass feed system or plugging in the auger.

[0020] The ground biomass particles 32 are injected through nozzles at the biomass inlet 35 into the reactor riser 28 by an appropriate system, such as a pressurized auger.

[0021] In some embodiments, the biomass inlet 35 is located upstream of the hydrocarbon inlet 36 in the reactor riser 28 but downstream of the catalyst inlet 31 and the catalyst acceleration zone 29. In an alternate embodiment, the biomass inlet 35 is located downstream of the hydrocarbon inlet 36 and the catalyst inlet 31. In another embodiment, the biomass inlet 35 is located at the bottom of the riser 28 at or near the level of the lift gas inlet 38 and upstream of the catalyst inlet 31 and the hydrocarbon inlet.

[0022] The biomass 32 mixes with the hot catalyst 30 in the riser reactor 28. The hot catalyst 30 thermally decomposes the biomass 32 into gas, vapor, and char. The vapor and gas are further converted by the catalyst 31 to valuable products. The holocellulose and the lignin in the biomass thermally depolymerize, and the phenolic monomers from the lignin and the sugar monomers from the holocellulose react within the catalyst to form oxygenated hydrocarbons having a much lower oxygen content than can be achieved by pyrolysis alone. The hot catalyst 30 and partially converted biomass products then meet with the atomized hydrocarbon feed 33 which is introduced at hydrocarbon feed inlet 36. The hydrocarbon feed 33 reacts over the catalyst 30 to form hydrocarbon products, such as cracked hydrocarbons.

[0023] Catalytic cracking of the mixture 46 of the hydrocarbon feed stream 33, the biomass feed 32, and the lift gas 37 produces an effluent 59 that includes spent particulate cracking catalyst 76 and a gaseous component 61. The gaseous component 61 includes products from the reactions in the riser 28, as described above. In accordance with an embodiment, the spent particulate cracking catalyst 76 and the gaseous component 61 are separated. In this embodiment, and as shown in FIG. 1, the gaseous component 61 of the effluent 59 is separated from the spent particulate cracking catalyst 76 in a separator vessel 62, and the gaseous component 61 may be

vented from the separator vessel 62 via a product line 60. Various separation schemes are known in the art for separating the spent particulate catalyst 76 and the gaseous component 61. In one embodiment, bulk separation is accomplished by passing the effluent 59 through a tee disengager 47, followed by passing the effluent through a primary cyclone 49 and secondary cyclone 51 to complete the separation. Although multiple sets of cyclones are generally used, only one set of the primary cyclone 49 and the secondary cyclone 51 is shown. The spent particulate cracking catalyst 76 falls downward to a stripper 68, where stripping steam 45 is introduced and combined with the spent particulate cracking catalyst 76. A catalyst regenerator 70 is in fluid communication with the separator vessel 62 and with the riser 28. The spent particulate cracking catalyst 76 that is separated from the gaseous component 61 is introduced into the catalyst regenerator 70 from the stripper 68, and coke is removed from the spent particulate cracking catalyst 76 in the catalyst regenerator 70. The catalyst regenerator 70 passes regenerated particulate catalyst 30 to the riser 28.

[0024] The gaseous component 61 from the cracking zone is typically processed through a product recovery section, not shown. Methane, ethane, ethylene, propane, propylene, light naphtha, heavy naphtha, cycle oil and slurry oil are all potentially part of the first slate of products recovered from the cracking zone. The exact products derived from the catalytic cracking process depend on the feedstock selected, the exact process conditions, the cracking catalyst selected, the downstream processes that are available and the current, relative economic value of the products.

[0025] The cracking zone can be operated at any useful process conditions. Temperatures generally range from about 470° C. to about 600° C. The reactor temperature can be adjusted to maximize the desired products from the process. For example, the lowest-boiling products, such as propylene, are maximized at the highest reactor temperature, and the intermediate boiling range products, such as naphtha, are maximized at lower temperatures. Pressures typically vary between about 69 KPa and about 280 KPa. Variations in these conditions are due to differences in feedstock, catalyst and process equipment.

[0026] Residence time for the catalytic cracker feedstock in contact with the cracking catalyst in the riser is typically from about 0.1 to 5 seconds, or 0.5 to 3 seconds, or less than or equal to 2 seconds. The exact residence time depends upon the catalytic cracker feedstock quality, the specific catalyst, and the desired product distribution. Short residence time assures that the desired products are not converted to undesirable products by further reaction. The diameter and height of the riser may be varied and/or diluents such as steam or lift gas may be added to the riser to obtain the desired residence time.

[0027] As is known to those of skill in the art, riser reactors can be upflow units, as illustrated, or downflow units (not shown).

[0028] Suitable biomass feedstocks include, but are not limited to, lignin, plant parts, fruits, vegetables, plant processing waste, wood chips, chaff, grains, grasses, corn and corn husks, weeds, aquatic plants, hay, recycled and non-recycled paper and paper products, and any cellulose-containing biological material or material of biological origin.

[0029] Suitable hydrocarbon feedstocks include, but are not limited to, petroleum products such as Vacuum Gas Oil (VGO), Hydrotreated VGO, Atmospheric Distillation Col-

umn Bottoms, Demetallized Oil, Deasphalted Oil, Hydrocracker Main Column Bottoms, Fischer-Tropsch liquids derived from renewable or non-renewable feedstocks, triglycerides of vegetable or animal origin, and the like.

[0030] In other embodiments as shown in FIGS. 3-4, the ground biomass particles are injected into a chamber 100. FIG. 3 is drawn to show the relative vertical positions of the connections. It does not accurately show the position of the biomass inlets because they would be perpendicular to the plane of FIG. 3.

[0031] The lift gas enters the chamber 100 through lift gas inlet 105. The biomass is injected into the chamber 100 through biomass inlet 110, while the regenerated catalyst enters through regenerated catalyst inlet 115. In some embodiments, spent particulate cracking catalyst is recycled to the riser. In this case, the spent particulate cracking catalyst can be introduced into the chamber 100 through spent catalyst inlet 120. Recycle of the spent particulate cracking catalyst is described in U.S. Pat. No. 5,597,537, which is incorporated herein by reference. The chamber 100 can include a baffle 125 to aid mixing, if desired. The use of baffles is described in U.S. Pat. No. 8,323,477, which is incorporated herein by reference. The hot catalyst and the biomass mix together in the chamber 100 at controlled temperature, velocity, and residence time to ensure sufficient thermal decomposition of the biomass step and begin the conversion step to valuable products. The mixture of catalyst and biomass is carried upward by the lift gas to mix with the hydrocarbon feedstock which enters the riser reactor 130 through the hydrocarbon inlet 135.

[0032] As shown, the chamber 100 is below the hydrocarbon feed inlet 135 in the riser reactor 130 and below the catalyst acceleration zone 140.

[0033] FIG. 4 is a cross-section of the chamber 100 shown in FIG. 3. The lift gas flows from the lift gas inlet 105 through the lift gas distributor 107 which has holes in the bottom through which the lift gas enters the chamber 100. The hot catalyst from the regeneration zone enters the chamber 100 through the regeneration catalyst inlet 115, while the spent particulate cracking catalyst enters chamber 100 on the opposite side through the spent catalyst inlet 120. The biomass feed inlets 110 are on opposite sides of the chamber 100 and offset from the regeneration catalyst inlet 115 and the spent catalyst inlet 120 by 90 degrees (measured in the horizontal plane). The number of biomass feed nozzles will depend on the unit capacity.

[0034] The biomass and catalyst inlets are desirably arranged to provide the greatest distance possible between inlets. For example, if there are two inlets (one biomass inlet and one catalyst inlet, for example), they are desirably positioned 180 degrees from each other. If there are three inlets, they are desirably 120 degrees from each other, while if there are four inlets, they are located 90 degrees from each other.

[0035] There can be one or more lift gas inlets, one or more catalyst inlets (regenerated and/or spent), one or more biomass inlets, and one or more hydrocarbon inlets in any of the embodiments.

[0036] The biomass feed rate is typically a small fraction of the hydrocarbon feed rate, which ensures proper conversion of the biomass without deactivating the catalyst before it contacts the hydrocarbon feed. The amount of biomass will typically be less than about 20 wt % of the total amount of biomass feedstock and hydrocarbon feedstock, generally in the range of about 0.1 wt % to about 20 wt %, or about 0.1 wt % to about 15 wt %, or about 0.1 wt % to about 10 wt %, or

about 0.1 wt % to about 5 wt %, or about 0.1 wt % to about 2 wt %, 1 wt % to about 20 wt %, or about 1 wt % to about 15 wt %, or about 1 wt % to about 10 wt %, or about 1 wt % to about 5 wt %.

[0037] The mass ratio of catalyst to total feed (i.e., biomass and hydrocarbon) is typically at least about 4:1, or at least about 5:1, or at least about 7:1, or at least about 10:1, or at least about 15:1, or at least about 20:1, or at least about 24:1, or in the range of about 4:1 to about 24:1, about 4:1 to about 20:1, or about 4:1 to about 15:1, or about 4:1 to about 10:1, or about 4:1 to about 7:1.

[0038] The mass ratio of catalyst to hydrocarbon feed is typically about 4:1 to about 12:1 without spent catalyst recirculation, and up to 25:1 with spent catalyst recirculation.

[0039] Any of the well-known catalysts that are used in the art of fluidized catalytic cracking, such as an active amorphous clay-type catalyst and/or a high activity, crystalline zeolite, may be used. Zeolite catalysts are preferred over amorphous catalysts because of their much-improved selectivity to desired products. In one embodiment, the catalyst includes a large pore zeolite, such as a Y-type zeolite, an active alumina material, a binder material, including either silica or alumina or a clay such as kaolin. In another embodiment, the catalyst includes a medium or smaller pore zeolite catalyst exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48, and other similar materials. U.S. Pat. No. 3,702,886 describes ZSM-5. Other suitable medium or smaller pore zeolites include ferrierite, erionite, and ST-5, developed by Petroleos de Venezuela, S.A. The catalyst preferably disperses the medium or smaller pore zeolite on a matrix including a binder material such as silica or alumina and an inert filler material such as kaolin. The catalyst may also include some other active material such as beta zeolite.

[0040] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A process for co-processing a hydrocarbon feedstock and a renewable biomass feedstock comprising:

introducing a lift gas into a fluid catalytic cracking riser reactor zone;

introducing a catalyst into the riser reactor zone at a point downstream of where the lift gas is introduced;

injecting solid particles of the biomass feedstock into the riser reactor zone;

introducing the hydrocarbon feedstock into the riser reactor zone;

mixing the solid particles of the biomass feedstock with the catalyst, the solid particles of the biomass feedstock reacting in the presence of the catalyst to form biomass products comprising gas, vapor, and char, and the gas

and vapor biomass products further reacting in the presence of the catalyst to form oxygenated hydrocarbon products;

mixing the hydrocarbon feedstock with the catalyst, the hydrocarbon feedstock reacting in the presence of the catalyst to form hydrocarbon products having a lower boiling point than a boiling point of the hydrocarbon feedstock; and

recovering the oxygenated hydrocarbon products, the hydrocarbon products, or both;

wherein the solid particles of biomass feedstock are injected into the riser reactor zone at a point upstream of where the hydrocarbon feedstock is introduced and at or downstream of the point where the catalyst is introduced, or at a point downstream of where the hydrocarbon feedstock and the catalyst are introduced.

2. The process of claim 1 wherein the solid particles of biomass feedstock are injected using a pressurized auger.

3. The process of claim 1 wherein introducing the catalyst into the riser reactor zone comprises introducing regenerated catalyst from a regeneration zone into the riser reactor zone.

4. The process of claim 3 further comprising:

separating the catalyst from the oxygenated hydrocarbon products and the hydrocarbon products in a separation zone of the riser reactor zone; and

regenerating at least a portion of the separated catalyst in the regeneration zone to form the regenerated catalyst.

5. The process of claim 1 wherein a ratio of an amount of the biomass feedstock to an amount of the hydrocarbon feedstock is less than about 20%.

6. The process of claim 1 wherein a ratio of an amount of catalyst to an amount of total feedstock is at least about 4 to 1.

7. The process of claim 1 wherein a temperature in the riser reactor zone is in a range of about 470° C. to about 600° C.

8. The process of claim 1 wherein mixing the solid particles of the biomass feedstock with the catalyst comprises mixing the solid particles of the biomass feedstock with the catalyst in a chamber, the chamber having a catalyst inlet and a biomass inlet.

9. The process of claim 8 wherein the chamber further comprises a baffle for mixing the solid particles of the biomass feedstock with the catalyst.

10. The process of claim 1, wherein the solid particles of the biomass feedstock have a particle size of about 6 mm.

11. The process of claim 1, wherein the catalyst comprises a zeolitic catalyst.

12. The process of claim 1, further comprising drying the biomass feedstock to a moisture content of less than about 20% before injecting the solid particles of the biomass feedstock into the riser reactor zone.

13. A process for co-processing a hydrocarbon feedstock and a renewable biomass feedstock comprising:

introducing a lift gas into a chamber in a fluid catalytic cracking riser reactor zone;

introducing a catalyst into the chamber at a point downstream of where the lift gas is introduced;

injecting solid particles of the biomass feedstock into the chamber;

mixing the solid particles of the biomass feedstock with the catalyst, the solid particles of the biomass feedstock reacting in the presence of the catalyst to form biomass products comprising gas, vapor, and char, and the gas and vapor biomass products further reacting in the presence of the catalyst to form oxygenated hydrocarbon products;

introducing the hydrocarbon feedstock into the riser reactor zone downstream of the chamber;

mixing the hydrocarbon feedstock with the catalyst, the hydrocarbon feedstock reacting in the presence of the catalyst to form hydrocarbon products having a lower boiling point than a boiling point of the hydrocarbon feedstock; and

recovering the oxygenated hydrocarbon products, the hydrocarbon products, or both.

14. The process of claim 13 wherein the solid particles of biomass feedstock are injected using a pressurized auger.

15. The process of claim 13 further comprising:

separating the catalyst from the oxygenated hydrocarbon products and the hydrocarbon products in a separation zone of the riser reactor zone; and

regenerating at least a portion of the separated catalyst in a regeneration zone; and

wherein introducing the catalyst into the chamber comprises introducing the regenerated catalyst into the chamber.

16. The process of claim 13 wherein a ratio of an amount of catalyst to an amount of total feedstock is at least about 4 to 1.

17. The process of claim 13 wherein a temperature in the riser reactor zone is in a range of about 470° C. to about 600° C.

18. The process of claim 13 wherein the chamber has at least one catalyst inlet and at least one biomass inlet.

19. The process of claim 18 wherein the mixing chamber further comprises a baffle for mixing the solid particles of the biomass feedstock with the catalyst.

20. A riser reactor zone comprising:

a riser reactor;

a chamber at one end of the riser reactor, the chamber having at least one lift gas inlet, at least one biomass inlet, and at least one catalyst inlet;

a hydrocarbon inlet in the riser reactor, the hydrocarbon inlet being downstream of the chamber.

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