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(54) Title: INTEGRATED HYDROPROCESSING, STEAM PYROLYSIS CATALYTIC CRACKING PROCESS TO PRODUCE PETROCHEMICALS FROM CRUDE OIL
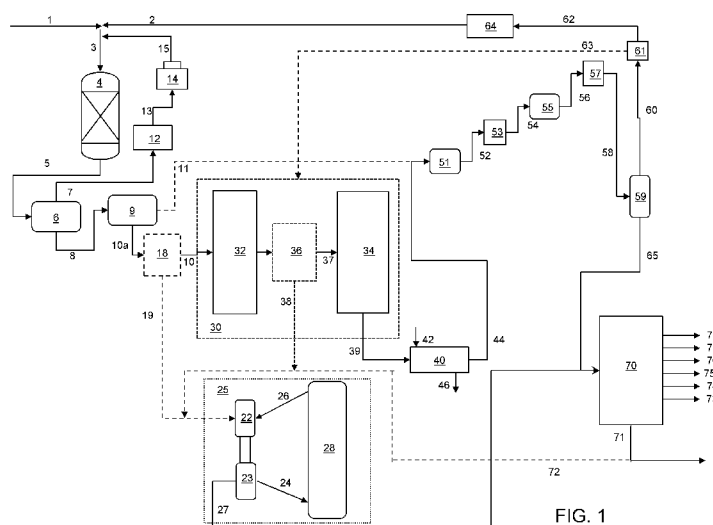
FIG. 1

(57) Abstract: An integrated hydrotreating, steam pyrolysis and catalytic cracking process for the production of olefins and aromatic petrochemicals from a crude oil feedstock is provided. Crude oil and hydrogen are charged to a hydroprocessing zone under conditions effective to produce a hydroprocessed effluent, which is thermally cracked in the presence of steam in a steam pyrolysis zone to produce a mixed product stream. Heavy components are catalytically cracked, which are derived from one or more of the hydroprocessed effluent, a heated stream within the steam pyrolysis zone, or the mixed product stream catalytically cracking. Catalytically cracked products are produced, which are combined with the mixed product stream and the combined stream is separated, and olefins and aromatics are recovered as product streams.

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INTEGRATED HYDROPROCESSING, STEAM PYROLYSIS AND CATALYTIC CRACKING PROCESS TO PRODUCE PETROCHEMICALS FROM CRUDE OIL

RELATED APPLICATIONS

[01]   This application claims the benefit of priority of U.S. Provisional Patent Application Nos. 61/613,315 filed March 20, 2012 and 61/785,913 filed March 14, 2013, which are incorporated by reference herein.

BACKGROUND OF THE INVENTION

Field of the Invention

[02]   The present invention relates to an integrated hydroprocessing, steam pyrolysis and fluidized catalytic cracking process to produce petrochemicals such as olefins and aromatics.

Description of Related Art

[03]   The lower olefins (i.e., ethylene, propylene, butylene and butadiene) and aromatics (i.e., benzene, toluene and xylene) are basic intermediates which are widely used in the petrochemical and chemical industries. Thermal cracking, or steam pyrolysis, is a major type of process for forming these materials, typically in the presence of steam, and in the absence of oxygen. Feedstocks for steam pyrolysis can include petroleum gases and distillates such as naphtha, kerosene and gas oil. The availability of these feedstocks is usually limited and requires costly and energy-intensive process steps in a crude oil refinery.

[04]   Studies have been conducted using heavy hydrocarbons as a feedstock for steam pyrolysis reactors. A major drawback in conventional heavy hydrocarbon pyrolysis operations is coke formation. For example, a steam cracking process for heavy liquid hydrocarbons is disclosed in United States Patent Number 4,217,204 in which a mist of molten salt is introduced

into a steam cracking reaction zone in an effort to minimize coke formation. In one example using Arabian light crude oil having a Conradson carbon residue of 3.1% by weight, the cracking apparatus was able to continue operating for 624 hours in the presence of molten salt. In a comparative example without the addition of molten salt, the steam cracking reactor became clogged and inoperable after just 5 hours because of the formation of coke in the reactor.

[05]   In addition, the yields and distributions of olefins and aromatics using heavy hydrocarbons as a feedstock for a steam pyrolysis reactor are different than those using light hydrocarbon feedstocks. Heavy hydrocarbons have a higher content of aromatics than light hydrocarbons, as indicated by a higher Bureau of Mines Correlation Index (BMCI). BMCI is a measurement of aromaticity of a feedstock and is calculated as follows:

$$BMCI = 87552/VAPB + 473.5 * (sp.\ gr.) - 456.8 \qquad (1)$$

where:

VAPB = Volume Average Boiling Point in degrees Rankine and

sp. gr. = specific gravity of the feedstock.

[06]   As the BMCI decreases, ethylene yields are expected to increase. Therefore, highly paraffinic or low aromatic feeds are usually preferred for steam pyrolysis to obtain higher yields of desired olefins and to avoid higher undesirable products and coke formation in the reactor coil section.

[07]   The absolute coke formation rates in a steam cracker have been reported by Cai et al., "Coke Formation in Steam Crackers for Ethylene Production," *Chem. Eng. & Proc.*, vol. 41, (2002), 199 – 214. In general, the absolute coke formation rates are in the ascending order of olefins > aromatics > paraffins, where olefins represent heavy olefins

[08]   To be able to respond to the growing demand of these petrochemicals, other type of feeds which can be made available in larger quantities, such as raw crude oil, are attractive to producers. Using crude oil feeds will minimize or eliminate the likelihood of the refinery being a bottleneck in the production of these necessary petrochemicals.

SUMMARY OF THE INVENTION

[09]   The system and process herein provides a steam pyrolysis zone integrated with a hydroprocessing zone to permit direct processing of feedstocks including crude oil feedstocks to produce petrochemicals including olefins and aromatics.

[10]   An integrated hydroprocessing, steam pyrolysis and catalytic cracking process for the production of olefins and aromatic petrochemicals from a crude oil feedstock is provided. Crude oil and hydrogen are charged to a hydroprocessing zone under conditions effective to produce an effluent having a reduced content of contaminants, an increased paraffincity, reduced Bureau of Mines Correlation Index, and an increased American Petroleum Institute gravity. Hydroprocessed effluent is thermally cracked in the presence of steam in a steam pyrolysis zone to produce a mixed product stream. Heavy components are catalytically cracked, which are derived from one or more of the hydroprocessed effluent, a heated stream within the steam pyrolysis zone, or the mixed product stream from steam cracking. Catalytically cracked products are produced, which are combined with the mixed product stream and the combined stream is separated, and olefins and aromatics are recovered as product streams.

[11]   As used herein, the term "crude oil" is to be understood to include whole crude oil from conventional sources, including crude oil that has undergone some pre-treatment. The term crude

oil will also be understood to include that which has been subjected to water-oil separations; and/or gas-oil separation; and/or desalting; and/or stabilization.

[12]   Other aspects, embodiments, and advantages of the process of the present invention are discussed in detail below. Moreover, it is to be understood that both the foregoing information and the following detailed description are merely illustrative examples of various aspects and embodiments, and are intended to provide an overview or framework for understanding the nature and character of the claimed features and embodiments. The accompanying drawings are illustrative and are provided to further the understanding of the various aspects and embodiments of the process of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[13]   The invention will be described in further detail below and with reference to the attached drawings where:

[14]   FIG. 1 is a process flow diagram of an embodiment of an integrated process described herein;

[15]   FIGs. 2A-2C are schematic illustrations in perspective, top and side views of a vapor-liquid separation device used in certain embodiments of the integrated process described herein;

[16]   FIGs. 3A-3C are schematic illustrations in section, enlarged section and top section views of a vapor-liquid separation device in a flash vessel used in certain embodiments of a the integrated process described herein;

[17]   FIG. 4 is a generalized diagram of a downflow fluidized catalytic cracking reactor system; and

[18]   FIG. 5 is a generalized diagram of a riser fluidized catalytic cracking reactor system.

DETAILED DESCRIPTION OF THE INVENTION

[19]   A process flow diagram including integrated hydroprocessing, steam pyrolysis and catalytic cracking processes is shown in FIG. 1.   The integrated system generally includes a selective hydroprocessing zone, a steam pyrolysis zone, a fluidized catalytic cracking zone and a product separation zone.

[20]   The selective hydroprocessing zone generally includes a hydroprocessing reaction zone 4 having an inlet for receiving a mixture 3 of crude oil feed 1, hydrogen 2 recycled from the steam pyrolysis product stream, and make-up hydrogen as necessary (not shown).   Hydroprocessing reaction zone 4 further includes an outlet for discharging a hydroprocessed effluent 5.

[21]   Reactor effluents 5 from the hydroprocessing reaction zone 4 are cooled in a heat exchanger (not shown) and sent to a high pressure separator 6.   The separator tops 7 are cleaned in an amine unit 12 and a resulting hydrogen rich gas stream 13 is passed to a recycling compressor 14 to be used as a recycle gas 15 in the hydroprocessing reactor. A bottoms stream 8 from the high pressure separator 6, which is in a substantially liquid phase, is cooled and introduced to a low pressure cold separator 9, where it is separated into a gas stream and a liquid stream 10a. Gases from low pressure cold separator include hydrogen, H_2S, NH_3 and any light hydrocarbons such as C_1-C_4 hydrocarbons.   Typically these gases are sent for further processing such as flare processing or fuel gas processing. According to certain embodiments of the process and system herein, hydrogen and other hydrocarbons are recovered from stream 11 by combining it with steam cracker products 44 as a combined feed to the product separation zone. All or a portion of liquid stream 10a serves as the hydroprocessed cracking feed to the steam pyrolysis zone 30.

[22]   Steam pyrolysis zone 30 generally comprises a convection section 32 and a pyrolysis section 34 that can operate based on steam pyrolysis unit operations known in the art, i.e., charging the thermal cracking feed to the convection section in the presence of steam.

[23]   In certain embodiments, a vapor-liquid separation zone 36 is included between sections 32 and 34. Vapor-liquid separation zone 36, through which the heated cracking feed from the convection section 32 passes and is fractioned, can be a flash separation device, a separation device based on physical or mechanical separation of vapors and liquids or a combination including at least one of these types of devices.

[24]   In additional embodiments, a vapor-liquid separation zone 18 is included upstream of section 32. Stream 10a is fractioned into a vapor phase and a liquid phase in vapor-liquid separation zone 18, which can be a flash separation device, a separation device based on physical or mechanical separation of vapors and liquids or a combination including at least one of these types of devices.

[25]   Useful vapor-liquid separation devices are illustrated by, and with reference to FIGs. 2A-2C and 3A-3C. Similar arrangements of vapor-liquid separation devices are described in U.S. Patent Publication Number 2011/0247500 which is incorporated herein by reference in its entirety. In this device vapor and liquid flow through in a cyclonic geometry whereby the device operates isothermally and at very low residence time (in certain embodiments less than 10 seconds), and with a relatively low pressure drop (in certain embodiments less than 0.5 bars). In general vapor is swirled in a circular pattern to create forces where heavier droplets and liquid are captured and channeled through to a liquid outlet as liquid residue which can be passed to the fluidized catalytic cracking zone, and vapor is channeled through a vapor outlet. In embodiments in which a vapor-liquid separations device 36 is provided, the liquid phase 38 is

discharged as residue and the vapor phase is the charge 37 to the pyrolysis section 34. In embodiments in which a vapor-liquid separation device 18 is provided, the liquid phase 19 is discharged as the residue and the vapor phase is the charge 10 to the convection section 32. The vaporization temperature and fluid velocity are varied to adjust the approximate temperature cutoff point, for instance in certain embodiments compatible with the residue fuel oil blend, e.g. about 540°C.

[26]   In the process herein, all rejected residuals or bottoms recycled, e.g., streams 19, 38 and 72, have been subjected to the hydroprocessing zone and contain a reduced amount of heteroatom compounds including sulfur-containing, nitrogen-containing and metal compounds as compared to the initial feed. All or a portion of these residual streams can be charged to the fluidized catalytic cracking zone 25 for processing as described herein.

[27]   A quenching zone 40 is also integrated downstream of the steam pyrolysis zone 30 and includes an inlet in fluid communication with the outlet of steam pyrolysis zone 30 for receiving mixed product stream 39, an inlet for admitting a quenching solution 42, an outlet for discharging the quenched mixed product stream 44 to the separation zone and an outlet for discharging quenching solution 46.

[28]   In general, an intermediate quenched mixed product stream 44 is converted into intermediate product stream 65 and hydrogen 62. The recovered hydrogen is purified in and used as recycle hydrogen stream 2 in the hydroprocessing reaction zone. Intermediate product stream 65 is generally fractioned into end-products and residue in separation zone 70, which can be one or multiple separation units, such as plural fractionation towers including de-ethanizer, de-propanizer, and de-butanizer towers as is known to one of ordinary skill in the art. For example, suitable apparatus are described in "Ethylene," Ullmann's Encyclopedia of Industrial

Chemistry, Volume 12, Pages 531 – 581, in particular Fig. 24, Fig 25 and Fig. 26, which is incorporated herein by reference.

[29]   Product separation zone 70 is in fluid communication with the product stream 65 and includes plural products 73-78, including an outlet 78 for discharging methane, an outlet 77 for discharging ethylene, an outlet 76 for discharging propylene, an outlet 75 for discharging butadiene, an outlet 74 for discharging mixed butylenes, and an outlet 73 for discharging pyrolysis gasoline. Additionally pyrolysis fuel oil 71 is recovered, e.g., as a low sulfur fuel oil blend to be further processed in an off-site refinery. A portion 72 of the discharged pyrolysis fuel oil can be charged to the fluidized catalytic cracking zone 25 (as indicated by dashed lines). Note that while six product outlets are shown along with the hydrogen recycle outlet and the bottoms outlet, fewer or more can be provided depending, for instance, on the arrangement of separation units employed and the yield and distribution requirements.

[30]   Fluidized catalytic cracking zone 25 generally includes one or more reaction sections in which the charge and an effective quantity of fluidized cracking catalyst are introduced. In addition, steam can be integrated with the feed to atomize or disperse the feed into the fluidized catalytic cracking reactor. The charge to fluidized catalytic cracking zone 25 includes all or a portion of bottoms 19 from vapor-liquid separation zone 18 or all or a portion of bottoms 38 from vapor-liquid separation section 36. Additionally as described herein all or a portion 72 of pyrolysis fuel oil 71 from product separation zone 70 can be combined as the charge to fluidized catalytic cracking zone 25.

[31]   In addition, fluidized catalytic cracking zone 25 includes a regeneration section in which cracking catalysts that have become coked, and hence access to the active catalytic sites becomes limited or nonexistent, are subjected to high temperatures and a source of oxygen to combust the

accumulated coke and steam to strip heavy oil adsorbed on the spent catalyst. While arrangements of certain FCC units are described herein with respect to FIGs. 4 and 5, one of ordinary skill in the art will appreciate that other well-known FCC units can be employed.

[32]   In certain embodiments, fluidized catalytic cracking zone 25 operates under conditions that promote formation of olefins while minimizing olefin-consuming reactions, such as hydrogen-transfer reactions. In certain embodiments, fluidized catalytic cracking zone 25 can be categorized as a high-severity fluidized catalytic cracking system.

[33]   In a process employing the arrangement shown in FIG. 1, a crude oil feedstock 1 is admixed with an effective amount of hydrogen 2 and 15 (and optionally make-up hydrogen, not shown), and the mixture 3 is charged to the inlet of selective hydroprocessing reaction zone 4 at a temperature in the range of from 300°C to 450°C. In certain embodiments, hydroprocessing reaction zone 4 includes one or more unit operations as described in commonly owned United States Patent Publication Number 2011/0083996 and in PCT Patent Application Publication Numbers WO2010/009077, WO2010/009082, WO2010/009089 and WO2009/073436, all of which are incorporated by reference herein in their entireties. For instance, a hydroprocessing reaction zone can include one or more beds containing an effective amount of hydrodemetallization catalyst, and one or more beds containing an effective amount of hydroprocessing catalyst having hydrodearomatization, hydrodenitrogenation, hydrodesulfurization and/or hydrocracking functions. In additional embodiments hydroprocessing reaction zone 4 includes more than two catalyst beds. In further embodiments hydroprocessing reaction zone 4 includes plural reaction vessels each containing catalyst beds, e.g. of different function.

[34] Hydroprocessing reaction zone 4 operates under parameters effective to hydrodemetallize, hydrodearomatize, hydrodenitrogenate, hydrodesulfurize and/or hydrocrack the crude oil feedstock. In certain embodiments, hydroprocessing is carried out using the following conditions: operating temperature in the range of from 300°C to 450°C; operating pressure in the range of from 30 bars to 180 bars; and a liquid hour space velocity (LHSV) in the range of from 0.1 h^{-1} to 10 h^{-1}. Notably, using crude oil as a feedstock in the hydroprocessing reaction zone 4 advantages are demonstrated, for instance, as compared to the same hydroprocessing unit operation employed for atmospheric residue. For instance, at a start or run temperature in the range of 370°C to 375°C with a deactivation rate of around 1°C/month. In contrast, if residue were to be processed, the deactivation rate would be closer to about 3°C/month to 4°C/month. The treatment of atmospheric residue typically employs pressure of around 200 bars whereas the present process in which crude oil is treated can operate at a pressure as low as 100 bars. Additionally to achieve the high level of saturation required for the increase in the hydrogen content of the feed, this process can be operated at a high throughput when compared to atmospheric residue. The LHSV can be as high as 0.5 h^{-1} while that for atmospheric residue is typically 0.25 h^{-1}. An unexpected finding is that the deactivation rate when processing crude oil is going in the inverse direction from that which is usually observed. Deactivation at low throughput (0.25 hr^{-1}) is 4.2°C/month and deactivation at higher throughput (0.5 hr^{-1}) is 2.0°C/month. With every feed which is considered in the industry, the opposite is observed. This can be attributed to the washing effect of the catalyst.

[35] Reactor effluents 5 from the hydroprocessing reaction zone 4 are cooled in an exchanger (not shown) and sent to a high pressure cold or hot separator 6. Separator tops 7 are cleaned in an amine unit 12 and the resulting hydrogen rich gas stream 13 is passed to a recycling

compressor 14 to be used as a recycle gas 15 in the hydroprocessing reaction zone 4. Separator bottoms 8 from the high pressure separator 6, which are in a substantially liquid phase, are cooled and then introduced to a low pressure cold separator 9. Remaining gases, stream 11, including hydrogen, H_2S, NH_3 and any light hydrocarbons, which can include C_1-C_4 hydrocarbons, can be conventionally purged from the low pressure cold separator and sent for further processing, such as flare processing or fuel gas processing. In certain embodiments of the present process, hydrogen is recovered by combining stream 11 (as indicated by dashed lines) with the cracking gas, stream 44 from the steam cracker products.

[36] In certain embodiments the bottoms stream 10a is the feed 10 to the steam pyrolysis zone 30. In further embodiments, bottoms 10a from the low pressure separator 9 are sent to separation zone 18 wherein the discharged vapor portion is the feed 10 to the steam pyrolysis zone 30. The vapor portion can have, for instance, an initial boiling point corresponding to that of the stream 10a and a final boiling point in the range of about 350°C to about 600°C. Separation zone 18 can include a suitable vapor-liquid separation unit operation such as a flash vessel, a separation device based on physical or mechanical separation of vapors and liquids or a combination including at least one of these types of devices. Certain embodiments of vapor-liquid separation devices, as stand-alone devices or installed at the inlet of a flash vessel, are described herein with respect to FIGs. 2A-2C and 3A-3C, respectively.

[37] The steam pyrolysis feed 10 contains a reduced content of contaminants (i.e., metals, sulfur and nitrogen), an increased paraffinicity, reduced BMCI, and an increased American Petroleum Institute (API) gravity. The steam pyrolysis feed 10, which contains an increased hydrogen content as compared to the feed 1, is conveyed to the inlet of a convection section 32 of steam pyrolysis zone 30 in the presence of an effective amount of steam, e.g., admitted via a

steam inlet. In the convention section 32 the mixture is heated to a predetermined temperature, e.g., using one or more waste heat streams or other suitable heating arrangement. In certain embodiments the mixture is heated to a temperature in the range of from 400°C to 600°C and material with a boiling point below the predetermined temperature is vaporized.

[38]   The heated mixture of the light fraction and additional steam is passed to the pyrolysis section 34 to produce a mixed product stream 39. In certain alternative embodiments the heated mixture from section 32 is passed to the vapor-liquid separation section 36 to reject a portion 38 as a low sulfur fuel oil component suitable for use as an FCC feedstock in certain embodiments, or in certain embodiments for use as a pyrolysis fuel oil blend component (not shown).

[39]   The steam pyrolysis zone 30 operates under parameters effective to crack feed 10 into desired products including ethylene, propylene, butadiene, mixed butenes and gasoline and fuel oil. In certain embodiments, steam cracking is carried out using the following conditions: a temperature in the range of from 400°C to 900°C in the convection section and in the pyrolysis section; a steam-to-hydrocarbon ratio in the convection section in the range of 0.3:1 to 2:1; and a residence time in the convection section and in the pyrolysis section in the range of from 0.05 seconds to 2 seconds.

[40]   In certain embodiments, the vapor-liquid separation section 36 includes one or a plurality of vapor liquid separation devices 80 as shown in FIGs. 2A-2C. The vapor liquid separation device 80 is economical to operate and maintenance free since it does not require power or chemical supplies. In general, device 80 comprises three ports including an inlet port 82 for receiving a vapor-liquid mixture, a vapor outlet port 84 and a liquid outlet port 86 for discharging and the collection of the separated vapor and liquid phases, respectively. Device 80 operates based on a combination of phenomena including conversion of the linear velocity of the

incoming mixture into a rotational velocity by the global flow pre-rotational section, a controlled centrifugal effect to pre-separate the vapor from liquid, and a cyclonic effect to promote separation of vapor from the liquid. To attain these effects, device 80 includes a pre-rotational section 88, a controlled cyclonic vertical section 90 and a liquid collector/settling section 92.

[41]   As shown in FIG. 2B, the pre-rotational section 88 includes a controlled pre-rotational element between cross-section (S1) and cross-section (S2), and a connection element to the controlled cyclonic vertical section 90 and located between cross-section (S2) and cross-section (S3). The vapor liquid mixture coming from inlet 82 having a diameter (D1) enters the apparatus tangentially at the cross-section (S1). The area of the entry section (S1) for the incoming flow is at least 10% of the area of the inlet 82 according to the following equation:

$$\frac{\pi * \left([D1]\right)^2}{4} \tag{2}$$

[42]   The pre-rotational element 88 defines a curvilinear flow path, and is characterized by constant, decreasing or increasing cross-section from the inlet cross-section S1 to the outlet cross-section S2. The ratio between outlet cross-section from controlled pre-rotational element (S2) and the inlet cross-section (S1) is in certain embodiments in the range of $0.7 \leq S2/S1 \leq 1.4$.

[43]   The rotational velocity of the mixture is dependent on the radius of curvature (R1) of the center-line of the pre-rotational element 88 where the center-line is defined as a curvilinear line joining all the center points of successive cross-sectional surfaces of the pre-rotational element 88. In certain embodiments the radius of curvature (R1) is in the range of $2 \leq R1/D1 \leq 6$ with opening angle in the range of $150° \leq \alpha R1 \leq 250°$.

[44]   The cross-sectional shape at the inlet section S1, although depicted as generally square, can be a rectangle, a rounded rectangle, a circle, an oval, or other rectilinear, curvilinear or a combination of the aforementioned shapes. In certain embodiments, the shape of the cross-

section along the curvilinear path of the pre-rotational element 88 through which the fluid passes progressively changes, for instance, from a generally square shape to a rectangular shape. The progressively changing cross-section of element 88 into a rectangular shape advantageously maximizes the opening area, thus allowing the gas to separate from the liquid mixture at an early stage and to attain a uniform velocity profile and minimize shear stresses in the fluid flow.

[45]   The fluid flow from the controlled pre-rotational element 88 from cross-section (S2) passes section (S3) through the connection element to the controlled cyclonic vertical section 90. The connection element includes an opening region that is open and connected to, or integral with, an inlet in the controlled cyclonic vertical section 90. The fluid flow enters the controlled cyclonic vertical section 90 at a high rotational velocity to generate the cyclonic effect. The ratio between connection element outlet cross-section (S3) and inlet cross-section (S2) in certain embodiments is in the range of $2 \leq S3/S1 \leq 5$.

[46]   The mixture at a high rotational velocity enters the cyclonic vertical section 90. Kinetic energy is decreased and the vapor separates from the liquid under the cyclonic effect. Cyclones form in the upper level 90a and the lower level 90b of the cyclonic vertical section 90. In the upper level 90a, the mixture is characterized by a high concentration of vapor, while in the lower level 90b the mixture is characterized by a high concentration of liquid.

[47]   In certain embodiments, the internal diameter D2 of the cyclonic vertical section 90 is within the range of $2 \leq D2/D1 \leq 5$ and can be constant along its height, the length (LU) of the upper portion 90a is in the range of $1.2 \leq LU/D2 \leq 3$, and the length (LL) of the lower portion 90b is in the range of $2 \leq LL/D2 \leq 5$.

[48]   The end of the cyclonic vertical section 90 proximate vapor outlet 84 is connected to a partially open release riser and connected to the pyrolysis section of the steam pyrolysis unit.

The diameter (DV) of the partially open release is in certain embodiments in the range of $0.05 \leq$ DV/D2 ≤ 0.4.

[49]   Accordingly, in certain embodiments, and depending on the properties of the incoming mixture, a large volume fraction of the vapor therein exits device 80 from the outlet 84 through the partially open release pipe with a diameter DV. The liquid phase (e.g., residue) with a low or non-existent vapor concentration exits through a bottom portion of the cyclonic vertical section 90 having a cross-sectional area S4, and is collected in the liquid collector and settling pipe 92.

[50]   The connection area between the cyclonic vertical section 90 and the liquid collector and settling pipe 92 has an angle in certain embodiments of 90°. In certain embodiments the internal diameter of the liquid collector and settling pipe 92 is in the range of $2 \leq D3/D1 \leq 4$ and is constant across the pipe length, and the length (LH) of the liquid collector and settling pipe 92 is in the range of $1.2 \leq LH/D3 \leq 5$. The liquid with low vapor volume fraction is removed from the apparatus through pipe 86 having a diameter of DL, which in certain embodiments is in the range of $0.05 \leq DL/D3 \leq 0.4$ and located at the bottom or proximate the bottom of the settling pipe.

[51]   In certain embodiments, a vapor-liquid separation device 18 or 36 is provided similar in operation and structure to device 80 without the liquid collector and settling pipe return portion. For instance, a vapor-liquid separation device 180 is used as inlet portion of a flash vessel 179, as shown in FIGs 3A-3C. In these embodiments the bottom of the vessel 179 serves as a collection and settling zone for the recovered liquid portion from device 180.

[52]   In general a vapor phase is discharged through the top 194 of the flash vessel 179 and the liquid phase is recovered from the bottom 196 of the flash vessel 179. The vapor-liquid separation device 180 is economical to operate and maintenance free since it does not require power or chemical supplies. Device 180 comprises three ports including an inlet port 182 for

receiving a vapor-liquid mixture, a vapor outlet port 184 for discharging separated vapor and a liquid outlet port 186 for discharging separated liquid. Device 180 operates based on a combination of phenomena including conversion of the linear velocity of the incoming mixture into a rotational velocity by the global flow pre-rotational section, a controlled centrifugal effect to pre-separate the vapor from liquid, and a cyclonic effect to promote separation of vapor from the liquid. To attain these effects, device 180 includes a pre-rotational section 188 and a controlled cyclonic vertical section 190 having an upper portion 190a and a lower portion 190b. The vapor portion having low liquid volume fraction is discharged through the vapor outlet port 184 having a diameter (DV). Upper portion 190a which is partially or totally open and has an internal diameter (DII) in certain embodiments in the range of 0.5<DV/DII<1.3. The liquid portion with low vapor volume fraction is discharged from liquid port 186 having an internal diameter (DL) in certain embodiments in the range of 0.1<DL/DII<1.1. The liquid portion is collected and discharged from the bottom of flash vessel 179.

[53] In order to enhance and to control phase separation, generally by depressing the boiling points of the hydrocarbons and reducing coke formation, heating steam is added to the feed to the vapor-liquid separation device 80 or 180. The feeds can also be heated by conventional heat exchangers as is known to those of ordinary skill in the art. The temperature of the feed to device 80 or 180 is adjusted so that the desired residue fraction is discharged as the liquid portion, e.g., in the range of about 350°C to about 600°C.

[54] While the various members of the vapor-liquid separation devices are described separately and with separate portions, it will be understood by one of ordinary skill in the art that apparatus 80 or apparatus 180 can be formed as a monolithic structure, e.g., it can be cast or molded, or it can be assembled from separate parts, e.g., by welding or otherwise attaching

separate components together which may or may not correspond precisely to the members and portions described herein.

[55]   The vapor-liquid separation devices described herein can be designed to accommodate a certain flow rate and composition to achieve desired separation, e.g., at 540°C. In one example, for a total flow rate of 2002 m^3/day at 540°C and 2.6 bar, and a flow composition at the inlet of 7% liquid, 38% vapor and 55% steam with a density of 729.5 kg/m^3, 7.62 kg/m^3 and 0.6941 kg/m^3, respectively, suitable dimensions for device 80 (in the absence of a flash vessel) includes D1 =5.25 cm ; S1 =37.2 cm^2; S1=S2=37.2 cm^2; S3= 100 cm^2; αR1 =213°; R1 = 14.5 cm; D2= 20.3 cm; LU=27 cm; LL= 38 cm; LH= 34 cm; DL= 5.25 cm; DV= 1.6 cm; and D3= 20.3 cm. For the same flow rate and characteristics, a device 180 used in a flash vessel includes D1= 5.25 cm; DV = 20.3 cm; DL= 6 cm; and DII= 20.3 cm.

[56]   It will be appreciated that although various dimensions are set forth as diameters, these values can also be equivalent effective diameters in embodiments in which the components parts are not cylindrical.

[57]   Mixed product stream 39 is passed to the inlet of quenching zone 40 with a quenching solution 42 (e.g., water and/or pyrolysis fuel oil) introduced via a separate inlet to produce a quenched mixed product stream 44 having a reduced temperature, e.g., of about 300°C, and spent quenching solution 46 is discharged. The gas mixture effluent 39 from the cracker is typically a mixture of hydrogen, methane, hydrocarbons, carbon dioxide and hydrogen sulfide. After cooling with water or oil quench, mixture 44 is compressed in a multi-stage compressor zone 51, typically in 4-6 stages to produce a compressed gas mixture 52. The compressed gas mixture 52 is treated in a caustic treatment unit 53 to produce a gas mixture 54 depleted of hydrogen sulfide and carbon dioxide. The gas mixture 54 is further compressed in a compressor zone 55, and the

resulting cracked gas 56 typically undergoes a cryogenic treatment in unit 57 to be dehydrated, and is further dried by use of molecular sieves.

[58]   The cold cracked gas stream 58 from unit 57 is passed to a de-methanizer tower 59, from which an overhead stream 60 is produced containing hydrogen and methane from the cracked gas stream. The bottoms stream 65 from de-methanizer tower 59 is then sent for further processing in product separation zone 70, comprising fractionation towers including de-ethanizer, de-propanizer and de-butanizer towers.   Process configurations with a different sequence of de-methanizer, de-ethanizer, de-propanizer and de-butanizer can also be employed.

[59]   According to the processes herein, after separation from methane at the de-methanizer tower 59 and hydrogen recovery in unit 61, hydrogen 62 having a purity of typically 80-95 vol% is obtained. Recovery methods in unit 61 include cryogenic recovery (e.g., at a temperature of about −157°C). Hydrogen stream 62 is then passed to a hydrogen purification unit 64, such as a pressure swing adsorption (PSA) unit to obtain a hydrogen stream 2 having a purity of 99.9%+, or a membrane separation units to obtain a hydrogen stream 2 with a purity of about 95%. The purified hydrogen stream 2 is then recycled back to serve as a major portion of the requisite hydrogen for the hydroprocessing reaction zone. In addition, a minor proportion can be utilized for the hydrogenation reactions of acetylene, methylacetylene and propadiene (not shown).   In addition, according to the processes herein, methane stream 63 can optionally be recycled to the steam cracker to be used as fuel for burners and/or heaters (as indicated by dashed lines).

[60]   The bottoms stream 65 from de-methanizer tower 59 is conveyed to the inlet of product separation zone 70 to be separated into methane, ethylene, propylene, butadiene, mixed butylenes, gasoline and fuel oil discharged via plural outlets 78, 77, 76, 75, 74 and 73, respectively. Pyrolysis gasoline generally includes C5-C9 hydrocarbons, and aromatics including

benzene, toluene and xylene can be extracted from this cut. Hydrogen is passed to an inlet of hydrogen purification zone 64 to produce a high quality hydrogen gas stream 2 that is discharged via its outlet and recycled to the inlet of hydroprocessing zone 4. Pyrolysis fuel oil is discharged via outlet 71 (e.g., materials boiling at a temperature higher than the boiling point of the lowest boiling C10 compound, known as a "C10+" stream) which can be used as a pyrolysis fuel oil blend, e.g., a low sulfur fuel oil blend to be further processed in an off-site refinery. Further, as shown herein, fuel oil 72 (which can be all or a portion of pyrolysis fuel oil 9), can be introduced to the fluidized catalytic cracking zone 25.

[61] All or a portion of one or more of the unvaporized heavy liquid fraction 19 from separation zone 18, the rejected portion 38 from vapor-liquid separation zone 36 and the pyrolysis fuel oil 72 from product separation zone 70, are processed in fluidized catalytic cracking zone 25 (as indicated by dashed lines for streams 19, 38 and 72). As shown in FIG. 1, a high-severity FCC unit operation is schematically shown. As described further herein, fluidized catalytic cracking zone 25 can in certain embodiments include conventional FCC operations or high-severity operations, for instance, in the form of riser systems or downflow systems. All or a portion of one or more of streams 19, 38 and 72 are introduced to the catalyst and feed mixing zone 22 where it is mixed with the hot regenerated catalyst introduced through line 26. Effective operating conditions, for instance in conjunction with a high severity fluidized catalytic cracking system, includes a reaction zone temperature from between about 530°C to 700°C, an effective catalyst/oil ratio is in the range of from 10:1 to about 40:1, and an effective residence time of the mixture in the downflow reaction zone is from about 0.2 seconds to about 2 seconds. Suitable fluid catalytic cracking can be determined in conjunction with any catalyst conventionally used in FCC processes, e.g., zeolites, silica-alumina, carbon monoxide burning promoter additives,

bottoms cracking additives, light olefin-producing additives and any other catalyst additives routinely used in the FCC process. The preferred cracking zeolites in the FCC process are zeolites Y, REY, USY, and RE-USY. For enhanced light olefins production from naphtha cracking, ZSM-5 zeolite crystal or other pentasil type catalyst structure can be used.

[62]   The reaction product stream is recovered via line 27 after rapid separation of catalyst from the product in a separation device 70. The spent catalyst is discharged through transfer line 24 and admitted to a catalyst regenerator zone 25. The regenerated catalyst is raised to a catalysts hopper for stabilization and then conveyed to the mixing zone through line 26. The hot regenerated catalyst provides heat for the endothermic cracking reaction in the reactor vessel.

[63]   The steam pyrolysis zone post-quench and separation effluent stream 65 and the post-separation effluent stream 27 from the fluidized catalytic cracking section is separated in a series of separation units 70 to produce the principal products 73-78, including methane, ethane, ethylene, propane, propylene, butane, butadiene, mixed butenes, gasoline, and fuel oil. The hydrogen stream 62 is passed through a hydrogen purification unit 64 to form a high quality hydrogen gas 2 for admixture with the feed to the hydroprocessing unit 4.

[64]   In certain embodiments, hydroprocessing or hydrotreating processes can increase the paraffin content (or decrease the BMCI) of a feedstock by saturation followed by mild hydrocracking of aromatics, especially polyaromatics. When hydrotreating a crude oil, contaminants such as metals, sulfur and nitrogen can be removed by passing the feedstock through a series of layered catalysts that perform the catalytic functions of demetallization, desulfurization and/or denitrogenation.

    a.   In one embodiment, the sequence of catalysts to perform hydrodemetallization (HDM) and hydrodesulfurization (HDS) is as follows: The catalyst in the HDM

section are generally based on a gamma alumina support, with a surface area of about $140 - 240$ m^2/g. This catalyst is best described as having a very high pore volume, e.g., in excess of 1 cm^3/g. The pore size itself is typically predominantly macroporous. This is required to provide a large capacity for the uptake of metals on the catalysts surface and optionally dopants. Typically the active metals on the catalyst surface are sulfides of Nickel and Molybdenum in the ratio Ni/Ni+Mo < 0.15. The concentration of Nickel is lower on the HDM catalyst than other catalysts as some Nickel and Vanadium is anticipated to be deposited from the feedstock itself during the removal, acting as catalyst. The dopant used can be one or more of phosphorus (see, e.g., United States Patent Publication Number US 2005/0211603 which is incorporated by reference herein), boron, silicon and halogens. The catalyst can be in the form of alumina extrudates or alumina beads. In certain embodiments alumina beads are used to facilitate un-loading of the catalyst HDM beds in the reactor as the metals uptake will be ranged between from 30 to 100 % at the top of the bed.

b. An intermediate catalyst can also be used to perform a transition between the HDM and HDS function. It has intermediate metals loadings and pore size distribution. The catalyst in the HDM/HDS reactor is essentially alumina based support in the form of extrudates, optionally at least one catalytic metal from group VI (e.g., molybdenum and/or tungsten), and/or at least one catalytic metals from group VIII (e.g., nickel and/or cobalt). The catalyst also contains optionally at least one dopant selected from boron, phosphorous, halogens and silicon. Physical properties include a surface area of about $140 - 200$ m^2/g, a pore volume

of at least 0.6 cm^3/g and pores which are mesoporous and in the range of 12 to 50 nm.

c. The catalyst in the HDS section can include those having gamma alumina based support materials, with typical surface area towards the higher end of the HDM range, e.g. about ranging from 180 – 240 m^2/g. This required higher surface for HDS results in relatively smaller pore volume, e.g., lower than 1 cm^3/g. The catalyst contains at least one element from group VI, such as molybdenum and at least one element from group VIII, such as nickel. The catalyst also comprises at least one dopant selected from boron, phosphorous, silicon and halogens. In certain embodiments cobalt is used to provide relatively higher levels of desulfurization. The metals loading for the active phase is higher as the required activity is higher, such that the molar ratio of Ni/Ni+Mo is in the range of from 0.1 to 0.3 and the (Co+Ni)/Mo molar ratio is in the range of from 0.25 to 0.85.

d. A final catalyst (which could optionally replace the second and third catalyst) is designed to perform hydrogenation of the feedstock (rather than a primary function of hydrodesulfurization), for instance as described in Appl. Catal. A General, 204 (2000) 251. The catalyst will be also promoted by Ni and the support will be wide pore gamma alumina. Physical properties include a surface area towards the higher end of the HDM range, e.g., 180 – 240 m^2/g. This required higher surface for HDS results in relatively smaller pore volume, e.g., lower than 1 cm^3/g.

[65] In certain embodiments, a fluidized catalytic cracking zone 25 is constructed and arranged using a downflow reactor that operates under conditions that promote formation of

olefins and that minimize olefin-consuming reactions, such as hydrogen-transfer reactions. FIG. 4 is a generalized process flow diagram of an FCC unit 200 which includes a downflow reactor and can be used in the hybrid system and process according to the present invention. FCC unit 200 includes a reactor/separator 210 having a reaction zone 214 and a separation zone 216. FCC unit 200 also includes a regeneration zone 218 for regenerating spent catalyst.

[66]   In particular, a charge 220 is introduced to the reaction zone, in certain embodiments also accompanied by steam or other suitable gas for atomization of the feed, and with an effective quantity of heated fresh or hot regenerated solid cracking catalyst particles from regeneration zone 218 is also transferred, e.g., through a downwardly directed conduit or pipe 222, commonly referred to as a transfer line or standpipe, to a withdrawal well or hopper (not shown) at the top of reaction zone 214. Hot catalyst flow is typically allowed to stabilize in order to be uniformly directed into the mix zone or feed injection portion of reaction zone 214.

[67]   All or a portion of one or more of streams 19, 38 and 71, serve as the charge to the FCC unit 200, alone or in combination with an additional feed (not shown). The charge is injected into a mixing zone through feed injection nozzles typically situated proximate to the point of introduction of the regenerated catalyst into reaction zone 214. These multiple injection nozzles result in the catalyst and oil mixing thoroughly and uniformly. Once the charge contacts the hot catalyst, cracking reactions occur. The reaction vapor of hydrocarbon cracked products, unreacted feed and catalyst mixture quickly flows through the remainder of reaction zone 214 and into a rapid separation zone 216 at the bottom portion of reactor/separator 210. Cracked and uncracked hydrocarbons are directed through a conduit or pipe 224 to a conventional product recovery section known in the art.

[68]   If necessary for temperature control, a quench injection can be provided near the bottom of reaction zone 214 immediately before the separation zone 216. This quench injection quickly reduces or stops the cracking reactions and can be utilized for controlling cracking severity and allows for added process flexibility.

[69]   The reaction temperature, i.e., the outlet temperature of the downflow reactor, can be controlled by opening and closing a catalyst slide valve (not shown) that controls the flow of regenerated catalyst from regeneration zone 218 into the top of reaction zone 214. The heat required for the endothermic cracking reaction is supplied by the regenerated catalyst. By changing the flow rate of the hot regenerated catalyst, the operating severity or cracking conditions can be controlled to produce the desired yields of light olefinic hydrocarbons and gasoline.

[70]   A stripper 232 is also provided for separating oil from the catalyst, which is transferred to regeneration zone 218. The catalyst from separation zone 216 flows to the lower section of the stripper 232 that includes a catalyst stripping section into which a suitable stripping gas, such as steam, is introduced through streamline 234. The stripping section is typically provided with several baffles or structured packing (not shown) over which the downwardly flowing catalyst passes counter- currently to the flowing stripping gas. The upwardly flowing stripping gas, which is typically steam, is used to "strip" or remove any additional hydrocarbons that remain in the catalyst pores or between catalyst particles.

[71]   The stripped or spent catalyst is transported by lift forces from the combustion air stream 228 through a lift riser of the regeneration zone 218. This spent catalyst, which can also be contacted with additional combustion air, undergoes controlled combustion of any accumulated coke. Flue gases are removed from the regenerator via conduit 230. In the regenerator, the heat

produced from the combustion of the by-product coke is transferred to the catalyst raising the temperature required to provide heat for the endothermic cracking reaction in the reaction zone 214.

[72]   In one embodiment, a suitable FCC unit 200 that can be integrated into the systems of FIG. 1 that promotes formation of olefins and that minimizes olefin-consuming reactions includes a high severity FCC reactor, can be similar to those described in US Patent Number 6,656,346, and US Patent Publication Number 2002/0195373, both of which are incorporated herein by reference. Important properties of downflow reactors include introduction of feed at the top of the reactor with downward flow, shorter residence time as compared to riser reactors, and high catalyst to oil ratio, e.g., in the range of about 20:1 to about 30:1.

[73]   In certain embodiments, various fractions from the product separation zone can be separately introduced into one or more separate downer reactors of an FCC unit having multiple downers. For instance, the bottoms fraction can be introduced via a main downer, and a stream of naphtha and/or middle distillates can be introduced via a secondary downer. In this manner, olefin production can be maximized while minimizing the formation of methane and ethane, since different operating conditions can be employed in each downer.

[74]   In general, the operating conditions for the reactor of a suitable downflow FCC unit include:

reaction temperature of about 550°C to about 650°C, in certain embodiments about 580°C to about 630°C, and in further embodiments about 590°C to about 620°C;

reaction pressure of about 1 Kg/cm^2 to about 20 Kg/cm^2, in certain embodiments of about 1 Kg/cm^2 to about 10 Kg/cm^2, in further embodiments of about 1 Kg/cm^2 to about 3 Kg/cm^2;

contact time (in the reactor) of about 0.1 seconds to about 30 seconds, in certain embodiments about 0.1 seconds to about 10 seconds, and in further embodiments about 0.2 seconds to about 0.7 seconds; and

a catalyst to feed ratio of about 1:1 to about 40:1, in certain embodiments about 1:1 to about 30:1, and in further embodiments about 10:1 to about 30:1.

[75]   In certain embodiments, an FCC unit configured with a riser reactor is provided that operates under conditions that promote formation of olefins and that minimizes olefin-consuming reactions, such as hydrogen-transfer reactions. FIG. 5 is a generalized process flow diagram of an FCC unit 300 which includes a riser reactor and can be used in the hybrid system and process according to the present invention. FCC unit 300 includes a reactor/separator 310 having a riser portion 312, a reaction zone 314 and a separation zone 316. FCC unit 300 also includes a regeneration vessel 318 for regenerating spent catalyst.

[76]   All or a portion of one or more of streams 19, 38 and 71, serve as the charge to the FCC unit 200, alone or in combination with an additional feed (not shown). Hydrocarbon feedstock is conveyed via a conduit 320, and in certain embodiments also accompanied by steam or other suitable gas for atomization of the feed, for admixture and intimate contact with an effective quantity of heated fresh or regenerated solid cracking catalyst particles which are conveyed via a conduit 322 from regeneration vessel 318. The feed mixture and the cracking catalyst are contacted under conditions to form a suspension that is introduced into the riser 312.

[77]   In a continuous process, the mixture of cracking catalyst and hydrocarbon feedstock proceed upward through the riser 312 into reaction zone 314. In riser 312 and reaction zone 314, the hot cracking catalyst particles catalytically crack relatively large hydrocarbon molecules by carbon-carbon bond cleavage.

[78]   During the reaction, as is conventional in FCC operations, the cracking catalysts become coked and hence access to the active catalytic sites is limited or nonexistent. Reaction products are separated from the coked catalyst using any suitable configuration known in FCC units, generally referred to as the separation zone 316 in FCC unit 300, for instance, located at the top of the reactor 310 above the reaction zone 314. The separation zone can include any suitable apparatus known to those of ordinary skill in the art such as, for example, cyclones. The reaction product is withdrawn through conduit 324.

[79]   Catalyst particles containing coke deposits from fluid cracking of the hydrocarbon feedstock pass from the separation zone 314 through a conduit 326 to regeneration zone 318. In regeneration zone 318, the coked catalyst comes into contact with a stream of oxygen-containing gas, e.g., pure oxygen or air, which enters regeneration zone 318 via a conduit 328. The regeneration zone 318 is operated in a configuration and under conditions that are known in typical FCC operations. For instance, regeneration zone 318 can operate as a fluidized bed to produce regeneration off-gas comprising combustion products which is discharged through a conduit 330. The hot regenerated catalyst is transferred from regeneration zone 318 through conduit 322 to the bottom portion of the riser 312 for admixture with the hydrocarbon feedstock as noted above.

[80]   In one embodiment, a suitable FCC unit 300 that can be integrated into the system of FIG. 1 that promotes formation of olefins and that minimizes olefin-consuming reactions includes a high severity FCC reactor, can be similar to that described in US Patent Numbers 7,312,370, 6,538,169, and 5,326,465.

[81]   In certain embodiments, various fractions from the product separation zone can be separately introduced into one or more separate riser reactors of an FCC unit having multiple

risers. For instance, the bottoms fraction can be introduced via a main riser, and a stream of naphtha and/or middle distillates can be introduced via a secondary riser. In this manner, olefin production can be maximized while minimizing the formation of methane and ethane, since different operating conditions can be employed in each riser.

[82]   In general, the operating conditions for the reactor of a suitable riser FCC unit include:

reaction temperature of about 480 °C to about 650 °C, in certain embodiments about 500 °C to about 620 °C, and in further embodiments about 500 °C to about 600 °C;

reaction pressure of about 1 Kg/cm^2 to about 20 Kg/cm^2, in certain embodiments of about 1 Kg/cm^2 to about 10 Kg/cm^2, in further embodiments of about 1 Kg/cm^2 to about 3 Kg/cm^2;

contact time (in the reactor) of about 0.7 seconds to about 10 seconds, in certain embodiments of about 1 seconds to about 5 seconds, in further embodiments of about 1 seconds to about 2 seconds; and

a catalyst to feed ratio of about 1:1 to about 15:1, in certain embodiments of about 1:1 to about 10:1, in further embodiments of about 8:1 to about 20:1.

[83]   A catalyst that is suitable for the particular charge and the desired product is conveyed to the FCC reactor within the FCC reaction and separation zone. In certain embodiments, to promote formation of olefins and minimize olefin-consuming reactions, such as hydrogen-transfer reactions, an FCC catalyst mixture is used in the FCC reaction and separation zone, including an FCC base catalyst and an FCC catalyst additive.

[84]   In particular, a matrix of a base cracking catalyst can include one or more clays such as kaolin, montmorilonite, halloysite and bentonite, and/or one or more inorganic porous oxides such as alumina, silica, boria, chromia, magnesia, zirconia, titania and silica-alumina. The base

cracking catalyst preferably has a bulk density of 0.5 g/ml to 1.0 g/ml, an average particle diameter of 50 microns to 90 microns, a surface area of 50 m^2/g to 350 m^2/g and a pore volume of 0.05 ml/g to 0.5 ml/g.

[85]   A suitable catalyst mixture contains, in addition to a base cracking catalyst, an additive containing a shape-selective zeolite. The shape selective zeolite referred to herein means a zeolite whose pore diameter is smaller than that of Y-type zeolite, so that hydrocarbons with only limited shape can enter the zeolite through its pores. Suitable shape-selective zeolite components include ZSM-5 zeolite, zeolite omega, SAPO-5 zeolite, SAPO-11 zeolite, SAPO34 zeolite, and pentasil-type aluminosilicates. The content of the shape-selective zeolite in the additive is generally in the range of 20 to 70 wt%, and preferably in the range of 30 to 60 wt%.

[86]   The additive preferably has a bulk density of 0.5 g/ml to 1.0 g/ml, an average particle diameter of 50 microns to 90 microns, a surface area of 10 m^2/g to 200 m^2/g and a pore volume of 0.01 ml/g to 0.3 ml/g.

[87]   A percentage of the base cracking catalyst in the catalyst mixture can be in the range of 60 to 95 wt% and a percentage of the additive in the catalyst mixture is in a range of 5 to 40 wt%. If the percentage of the base cracking catalyst is lower than 60 wt% or the percentage of additive is higher than 40 wt%, high light-fraction olefin yield cannot be obtained, because of low conversions of the feed oil. If the percentage of the base cracking catalyst is higher than 95 wt%, or the percentage of the additive is lower than 5 wt%, high light-fraction olefin yield cannot be obtained, while high conversion of the feed oil can be achieved. For the purpose of this simplified schematic illustration and description, the numerous valves, temperature sensors, electronic controllers and the like that are customarily employed and well known to those of ordinary skill in the art of fluid catalyst cracking are not included. Accompanying components

that are in conventional hydrocracking units such as, for example, bleed streams, spent catalyst discharge sub-systems, and catalyst replacement sub-systems are also not shown. Further, accompanying components that are in conventional FCC systems such as, for example, air supplies, catalyst hoppers and flue gas handling are not shown.

[88] The method and system herein provides improvements over known steam pyrolysis cracking processes:

use of crude oil as a feedstock to produce petrochemicals such as olefins and aromatics;

the hydrogen content of the feed to the steam pyrolysis zone is enriched for high yield of olefins;

coke precursors are significantly removed from the initial whole crude oil which allows a decreased coke formation in the radiant coil of the steam pyrolysis unit;

additional impurities such as metals, sulfur and nitrogen compounds are also significantly removed from the starting feed which avoids post treatments of the final products.

[89] In addition, hydrogen produced from the steam cracking zone is recycled to the hydroprocessing zone to minimize the demand for fresh hydrogen. In certain embodiments the integrated systems described herein only require fresh hydrogen to initiate the operation. Once the reaction reaches the equilibrium, the hydrogen purification system can provide enough high purity hydrogen to maintain the operation of the entire system.

Example

[90] An Arab Light crude was hydrotreated at 370°C and 100-150 bar with a LHSV of 0.5 h^{-1}. The properties are shown in Table 1 below. The hydroprocessed feed is fractionated into two fractions at 350°C and both fractions are then sent to the two downer of an HS-FCC unit.

Table 1: Properties of Arab Light, upgraded Arab Light and its 350°C+ fraction

Sample	Sulfur (wt%)	Nitrogen (ppm)	Nickel (ppm)	Vanadium (ppm)	ConCarbon (wt%)	Density
Arab Light	1.94	961	<1	14		0.8584
Hydrotreated Arab Light	0.280	399.0	6	1	2.0	0.8581
350°C +	0.540	NA	6.8	6.3	4.80	0.937

[91]   The method and system of the present invention have been described above and in the attached drawings; however, modifications will be apparent to those of ordinary skill in the art and the scope of protection for the invention is to be defined by the claims that follow.

Claims:

1.   An integrated hydroprocessing, steam pyrolysis and catalytic cracking process for production of olefinic and aromatic petrochemicals from a crude oil feed, the process comprising:

a. charging the crude oil and hydrogen to a hydroprocessing zone operating under conditions effective to produce a hydroprocessed effluent having a reduced content of contaminants, an increased paraffinicity, reduced Bureau of Mines Correlation Index, and an increased American Petroleum Institute gravity;

b. thermally cracking hydroprocessed effluent in the presence of steam in a steam pyrolysis zone to produce a mixed product stream;

c. catalytically cracking heavy components derived from one or more of the hydroprocessed effluent, a heated stream within the steam pyrolysis zone, or the mixed product stream, to produce catalytically cracked products;

d. separating a combined product stream including thermally cracked products and catalytically cracked products;

e. purifying hydrogen recovered in step (d) and recycling it to step (a); and

f. recovering olefins and aromatics from the separated combined product stream.

2.   The integrated process of claim 1, further comprising recovering pyrolysis fuel oil from the separated combined product stream for use as at least a portion of the heavy components cracked in step (c).

3.   The integrated process of claim 1, further comprising separating the hydroprocessed

effluent from step (a) into a vapor phase and a liquid phase in a vapor-liquid separation zone,

wherein the vapor phase is the feed to step (b), and at least a portion of the liquid phase is

catalytically cracked in step (c).

4.   The integrated process of claim 3, wherein the vapor-liquid separation zone is a flash

separation apparatus.

5.   The integrated process of claim 3, wherein the vapor-liquid separation zone comprises a

flash vessel having at its inlet a vapor-liquid separation device including

          a pre-rotational element having an entry portion and a transition portion, the entry

portion having an inlet for receiving the hydroprocessed effluent and a curvilinear

conduit,

          a controlled cyclonic section having

                    an inlet adjoined to the pre-rotational element through convergence of the

curvilinear conduit and the cyclonic section, and

                    a riser section at an upper end of the cyclonic member through which

vapors pass,

          wherein a bottom portion of the flash vessel serves as a collection and settling zone for

the liquid phase prior to passage of all or a portion of said liquid phase to step (c).

6.   The integrated process of claim 1, wherein the hydroprocessed effluent is the feed to step

(b), and wherein step (b) further comprises

heating the hydroprocessed effluent in a convection section of the steam pyrolysis zone,

separating the heated hydroprocessed effluent into a vapor phase and a liquid phase,

passing the vapor phase to a pyrolysis section of the steam pyrolysis zone, and

discharging the liquid phase for use as at least a portion of the heavy components cracked

in step (c).

7.   The integrated process of claim 6 wherein separating the heated hydroprocessed effluent

into a vapor phase and a liquid phase is with a vapor-liquid separation device based on physical

and mechanical separation.

8.   The integrated process of claim 6 wherein separating the heated hydroprocessed effluent

into a vapor phase and a liquid phase is with a vapor-liquid separation device that includes

        a pre-rotational element having an entry portion and a transition portion, the entry

portion having an inlet for receiving the heated hydroprocessed effluent and a curvilinear

conduit,

        a controlled cyclonic section having

                an inlet adjoined to the pre-rotational element through convergence of the

curvilinear conduit and the cyclonic section,

                a riser section at an upper end of the cyclonic member through which

vapors pass;

        and

        a liquid collector/settling section through which liquid phase passes prior to

conveyance of all or a portion of said liquid phase to step (c).

9.   The integrated process of claim 1 wherein

step (d) comprises

compressing the thermally cracked mixed product stream with plural compression stages;

subjecting the compressed thermally cracked mixed product stream to caustic treatment to produce a thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide;

compressing the thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide;

dehydrating the compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide;

recovering hydrogen from the dehydrated compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide; and

obtaining olefins and aromatics from the remainder of the dehydrated compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide;

and

step (e) comprises purifying recovered hydrogen from the dehydrated compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide and carbon dioxide for recycle to the hydroprocessing zone.

10.   The integrated process of claim 9, wherein recovering hydrogen from the dehydrated compressed thermally cracked mixed product stream with a reduced content of hydrogen sulfide

and carbon dioxide further comprises separately recovering methane for use as fuel for burners and/or heaters in the thermal cracking step.

11.   The integrated process of claim 3, further comprising

separating hydroprocessed effluents in a high pressure separator to recover a gas portion that is cleaned and recycled to the hydroprocessing step as an additional source of hydrogen, and a liquid portion, and

separating the liquid portion derived from the high pressure separator into a gas portion and a liquid portion in a low pressure separator, wherein the liquid portion derived from the low pressure separator is the feed to the vapor-liquid separation zone and the gas portion derived from the low pressure separator is combined with the combined product stream after the steam pyrolysis zone and before separation in step (d).
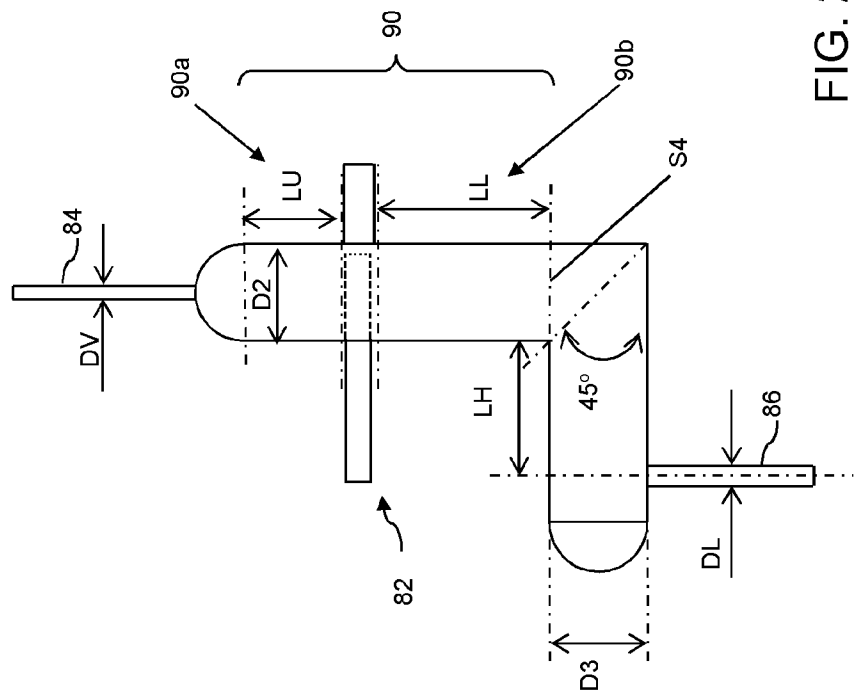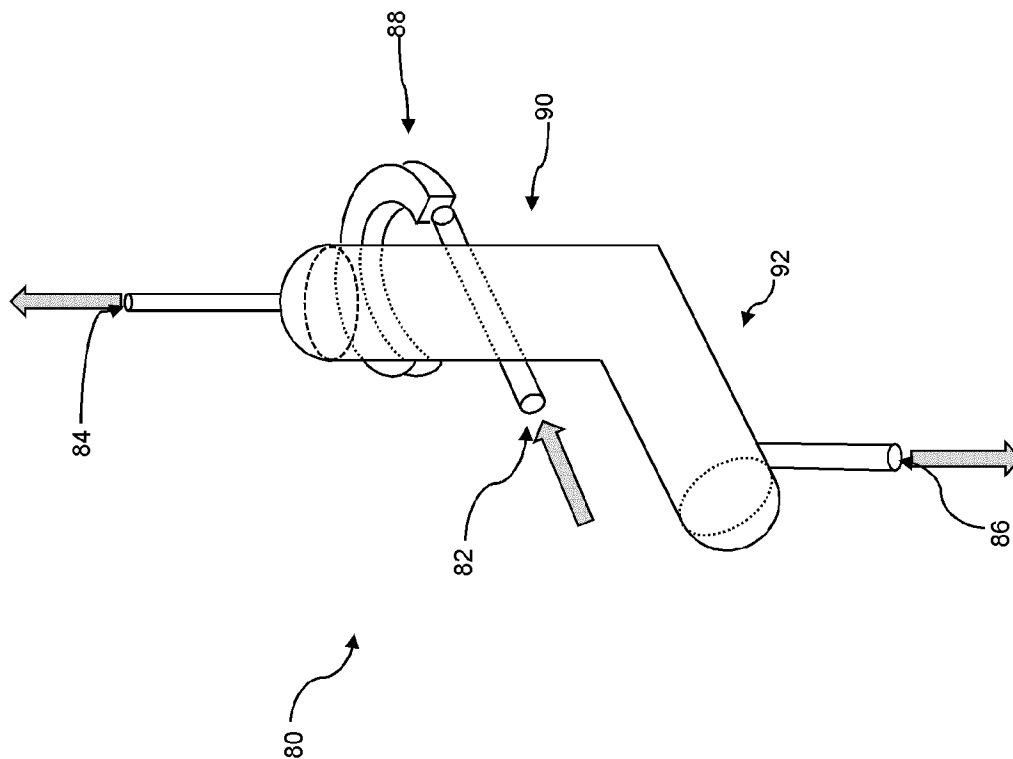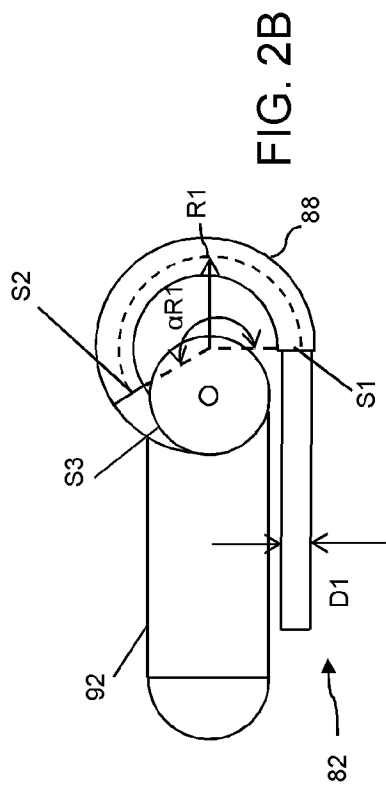
12.   The integrated process of claim 6, further comprising

separating hydroprocessed effluents in a high pressure separator to recover a gas portion that is cleaned and recycled to the hydroprocessing step as an additional source of hydrogen, and a liquid portion, and

separating the liquid portion derived from the high pressure separator into a gas portion and a liquid portion in a low pressure separator, wherein the liquid portion from the low pressure separator is the feed to the thermal cracking step and the gas portion from the low pressure separator is combined with the combined product stream after the steam pyrolysis zone and before separation in step (d).

FIG. 1

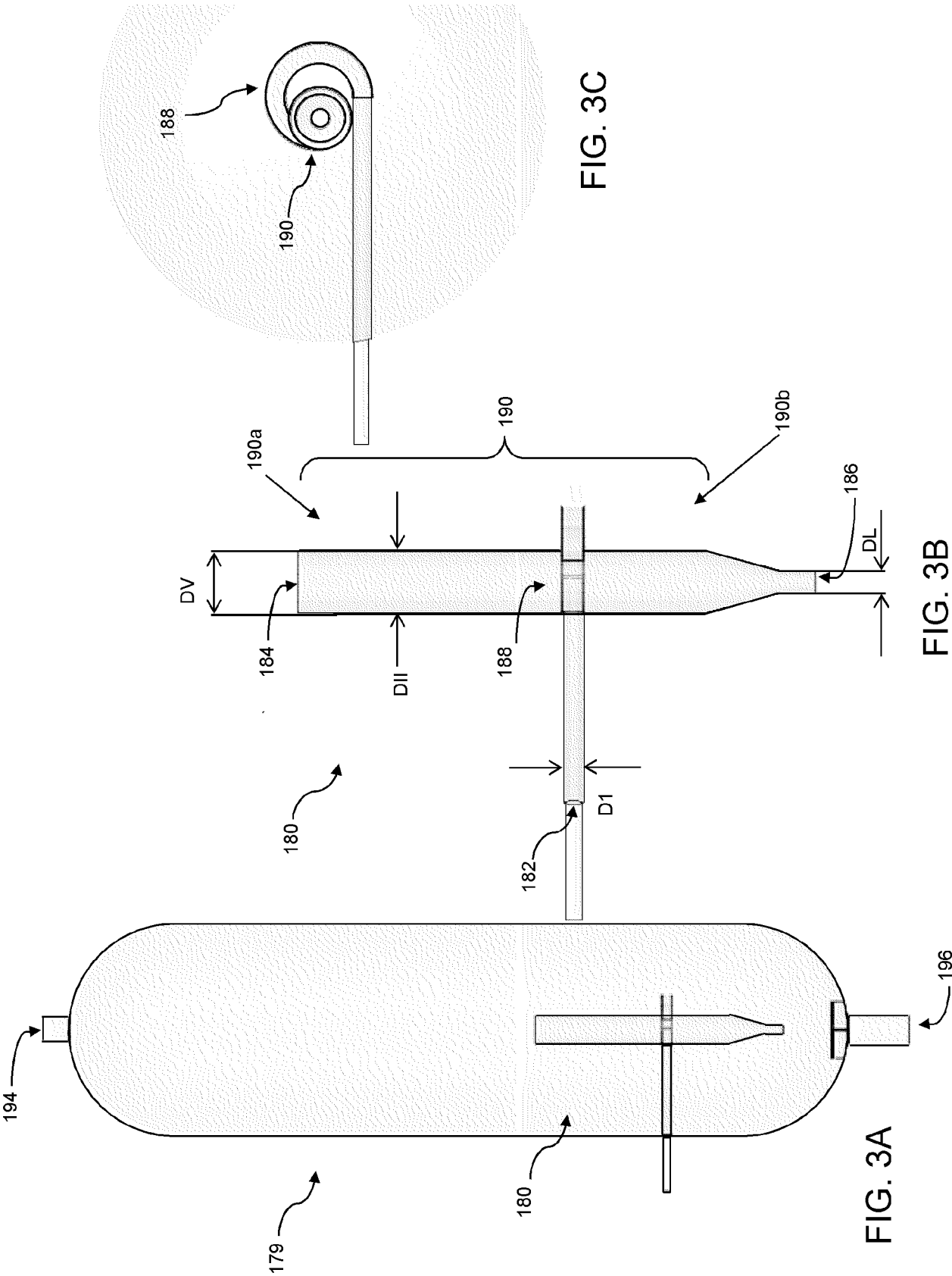FIG. 2B

FIG. 2C

FIG. 2A
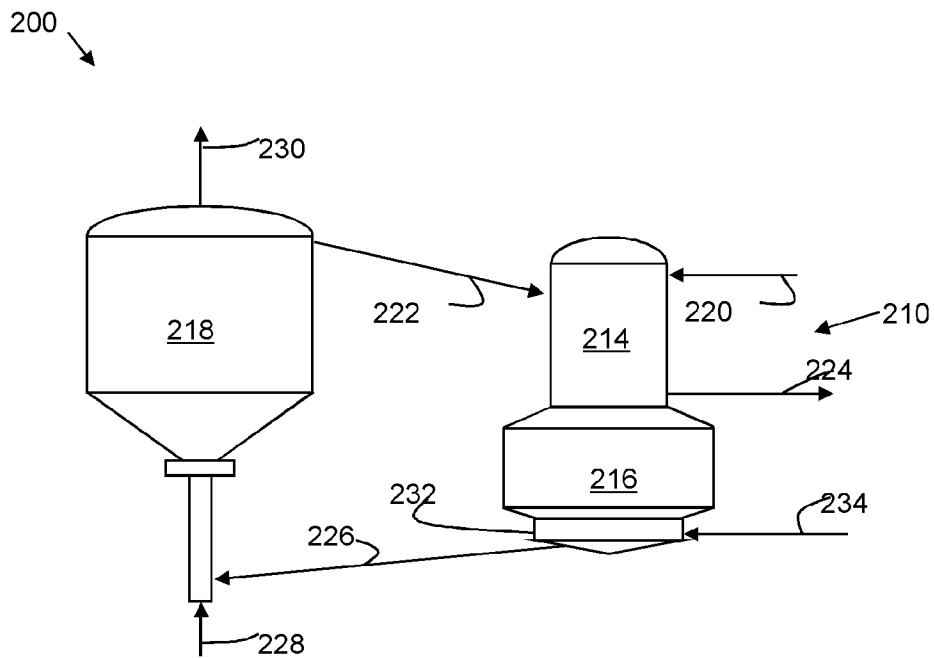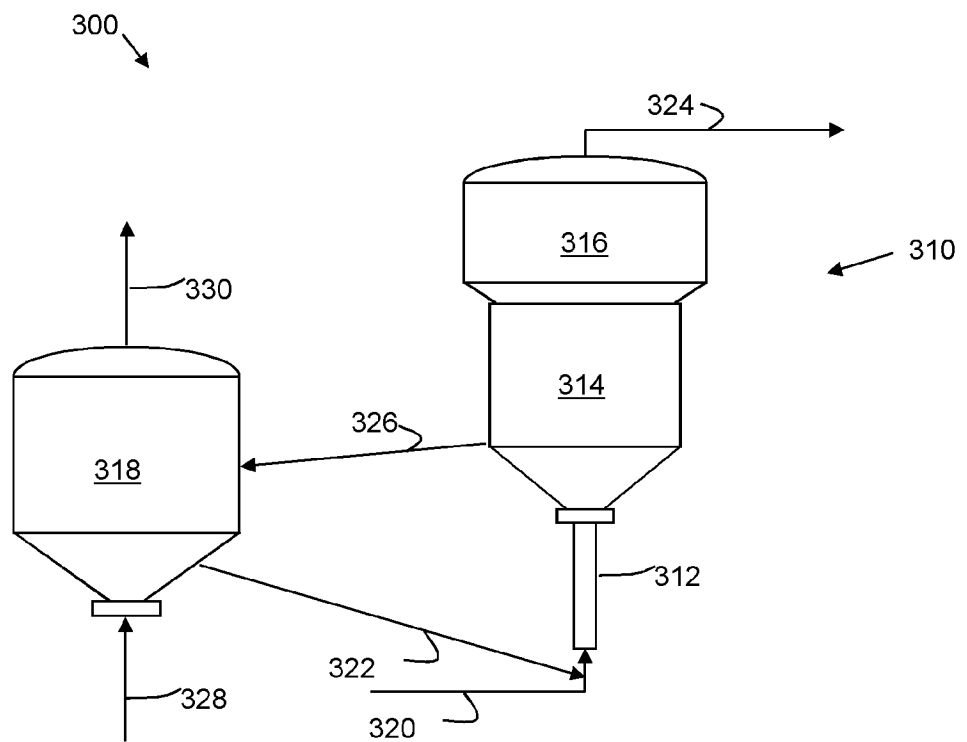
FIG. 3C

FIG. 3B

FIG. 3A
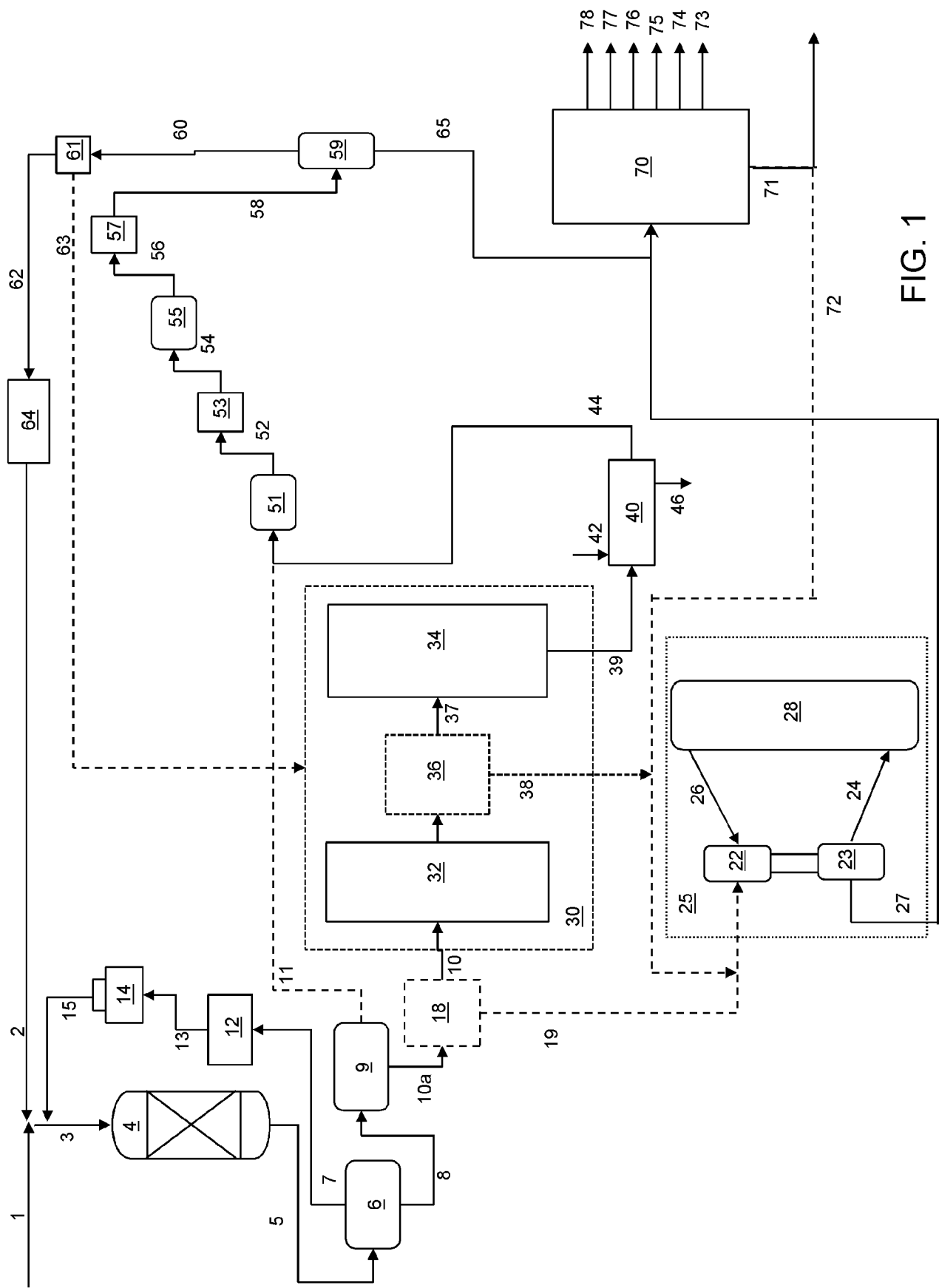
FIG. 4

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/033165

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G69/06   C10G69/04   C10G9/16   C10G55/04   C10G55/06
     C10G51/02   C10G51/06
ADD. B01D17/02   B01D19/00   B01D53/24   C10G47/00   C10G45/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D C10G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8 070 938 B2 (STEIN LOUIS EDWARD [US] ET AL) 6 December 2011 (2011-12-06)	1,2,6-8
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[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

Date of the actual completion of the international search	Date of mailing of the international search report
1 July 2013	10/07/2013

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