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(71) Applicant: **EXXONMOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventors: **HARANDI, Mohsen, N.**; 810 Sydni Court, New Hope, PA 18938 (US). **SMALLEY, Christopher, G.**; 11422 Donnington Court, Manassas, VA 20111 (US).

(74) Agents: **GUICE, Chad A.** et al.; ExxonMobil Research and Engineering Company, 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

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[Continued on next page]

(54) Title: SYSTEMS AND METHODS FOR UPGRADING OLEFIN-CONTAINING FEEDS

(57) Abstract: Systems and methods are provided for upgrading olefin-containing feeds. An olefin-containing feed can be exposed to an acidic conversion catalyst in a fluidized bed region of a reaction vessel to produce a reaction effluent that can include oligomerized olefins. The acidic conversion catalyst can be regenerated in a separate regeneration region within the reaction vessel. The effluent exiting the reaction vessel can include the reaction effluent from the fluidized bed region combined with an effluent from the regeneration region.

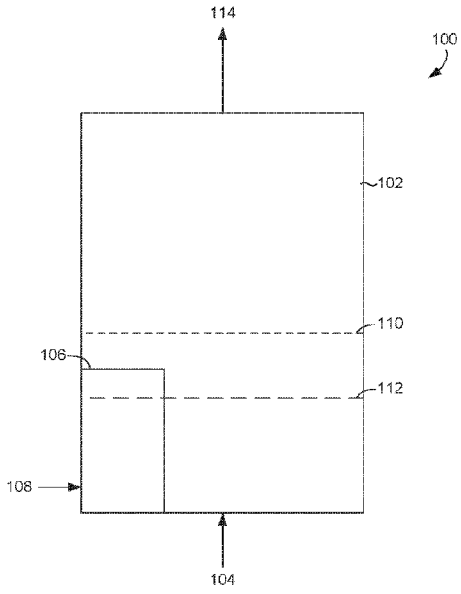


FIG. 1.

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SYSTEMS AND METHODS FOR UPGRADING OLEFIN-CONTAINING FEEDS

FIELD

[0001] Systems and methods are provided for the upgrading of olefin-containing feeds.

BACKGROUND

[0002] Certain processes for upgrading olefin-containing feeds, such as Mobil's Olefin to Gasoline (MOG) process, may be performed in a fluidized bed catalytic reactor. In such processes, it may be desirable to regenerate the catalyst after a period of time, e.g., by removing at least a portion of coke deposits on the catalyst. Regeneration of catalyst in a fluidized bed is typically performed continuously or semi-continuously by withdrawing catalyst from the bed, passing it into a regenerator, and then returning the regenerated catalyst to the bed. However, typical catalyst regeneration systems require separate reaction vessels and significant piping. Further, additional energy and resources are typically required to treat any flue gas generated during the regeneration process.

[0003] U.S. Patent No. 5,482,617 discloses a process for desulfurization of hydrocarbon streams having at least 50 ppmw organic sulfur compounds, and C_{5+} hydrocarbons including benzene. The hydrocarbon stream is exposed to a fluidized bed of an acidic catalyst in the absence of added hydrogen at a pressure of 0.0 psig to 400 psig and a temperature of 400°F to 900°F.

[0004] U.S. Patent No. 6,372,949 discloses a one-step process for converting an oxygenate-containing feed to liquid boiling range C_{5+} hydrocarbons. The feed is contacted with a catalyst having a unidimensional 10-ring zeolite at a temperature less than 350°C and a pressure above 40 psia.

SUMMARY

[0005] In an aspect a method for upgrading an olefin-containing feed is provided, comprising: exposing an olefin-containing feed having an olefin content of at least about 10 wt. % to a fluidized bed of an acidic conversion catalyst in a reaction vessel under effective conversion conditions to form a product effluent comprising C_{5+} oligomerized olefinic compounds and a coked catalyst stream; and exposing at least a portion of the coked catalyst stream to an oxygen-containing feed in a regeneration region in the reaction vessel to remove at least a portion of coke from the coked catalyst stream, wherein the product effluent exiting the reaction vessel comprises at least about 5 wt. % C_{5+} oligomerized olefinic compounds and at least about 0.1 wt. % of one or more of carbon monoxide and carbon dioxide formed in the regeneration region.

[0006] In another aspect, a conversion product from upgrading an olefin-containing feed is provided, comprising: at least about 10 wt. % C_{10+} compounds; at least about 5 wt. % C_{5+} olefinic compounds, wherein the at least about 10 wt. % C_{10+} compounds and at least about 5 wt. % C_{5+}

olefinic compounds are produced in a fluidized bed olefin oligomerization reactor using an olefin-containing feed; and at least about 0.1 wt. % more of one or more of carbon dioxide and carbon monoxide compared to a level of carbon monoxide and carbon dioxide in the olefin-containing feed.

[0007] In yet another aspect, a system for upgrading an olefin-containing feed is provided, comprising: a fluidized bed reaction vessel comprising a fluidized bed region and a regeneration region at least partly contained within the fluidized bed region; a fluidized bed reaction vessel outlet; a fluidized bed region outlet that is in fluid communication with the fluidized bed reaction vessel outlet; and a regeneration region outlet that is in fluid communication with the fluidized bed reaction vessel outlet.

BRIEF DESCRIPTION OF THE FIGURE

[0008] FIG. 1 schematically shows an example of a reaction system for upgrading an olefin-containing feed, according to an aspect of the invention.

DETAILED DESCRIPTION

Overview

[0009] In various aspects, systems and methods are provided for upgrading olefin-containing feeds using a fluidized bed reactor while reducing or minimizing the costs and/or equipment associated with catalyst regeneration. In one or more aspects, the olefin-containing feed can include light olefins, FCC naphtha, and/or olefinic naphtha. The olefin-containing feed may be exposed to conversion conditions in a reaction vessel, which can include exposure to an acidic catalyst. The conversion conditions can result in the oligomerization of at least a portion of olefins present in the olefin-containing feed. In the same or alternative aspects, at least a portion of the olefin-containing feed may undergo desulfurization.

[0010] In conventional olefin upgrading processes that utilize a fluidized bed reactor, regeneration of a coked conversion catalyst may be required to maintain catalytic activity. However, conventional catalyst regeneration processes are energy and resource intensive and require further treatment of any flue gas generated during the regeneration process.

[0011] In various aspects, the systems and processes described herein can address one or more of the above problems. For example, in certain aspects, the catalyst can be regenerated inside a separate regeneration region inside the reaction vessel, which may eliminate significant piping and valves. In such aspects, the reaction vessel can include a regeneration region for the regeneration of the coked catalyst and a fluidized bed region for the upgrading of the olefin-containing feed.

[0012] In various aspects, the olefin-containing feed may be exposed to the acidic catalyst by using a riser, moving bed, or fluid catalyst bed reactor. In a turbulent fluidized catalyst bed the

conversion reactions are conducted in a vertical reactor column by passing hot reactant vapor upwardly through at least a portion of the reaction zone at a velocity greater than dense bed transition velocity and less than transport velocity for the average catalyst particle. The catalyst may be regenerated, such as via continuous oxidative regeneration, which is discussed further below. Conventional fluid bed reactor systems are described in Avidan et al U.S. Pat. No. 4,547,616; Harandi & Owen U.S. Pat. No. 4,751,338; and in Tabak et al U.S. Pat. No. 4,579,999, and incorporated herein by reference.

[0013] In one or more aspects, the olefin upgrading process described herein may be performed in a fluidized bed reaction region within a reaction vessel, while coked catalyst may be regenerated in a regeneration region also positioned within the reaction vessel. The fluidized bed reaction region and the regeneration region may be separated from one another. In such aspects, the fluidized bed reaction region may define a first internal volume within the reaction vessel, and the regeneration region may define a second internal volume within the reaction vessel, with the first and second internal volumes being separate from one another while connected by piping. In one or more aspects, the regeneration region and/or the second internal volume defined by the regeneration region may be partially or entirely within the fluidized catalyst bed positioned inside the fluidized bed reaction region of the reaction vessel.

[0014] As used herein, a "reaction vessel" refers to any vessel capable of maintaining a moving or fluidized catalyst bed and that can accommodate separate internal volumes. It is appreciated that the exact construction of such a reaction vessel is not critical and that any convenient reactor design may be used.

[0015] The regeneration region and the fluidized bed reaction region may be separated by a physical barrier. As an example, the regeneration region may include a tube-like sealed structure (such as a standpipe) that defines a separated volume for catalyst regeneration, and that may be at least partly contained within the fluidized bed reaction region inside the reaction vessel. In such aspects, this sealed structure may include an inlet, e.g., near the bottom of the sealed structure, to allow for coked catalyst to enter from the fluidized bed reaction region. Further, in various aspects, one or more outlets may be positioned near the top of the sealed structure, which can be in fluid communication with the fluidized bed region to allow for flue gas to exit the regeneration region and enter the fluidized bed reaction region within the reaction vessel. Further, in such aspects, the fluidized bed region may be in fluid communication with an outlet of the reaction vessel, so that at least a portion of the products generated in the regeneration region and at least a portion of the products generated in the fluidized bed reaction region can mix prior to exiting the reaction vessel. The regenerated catalyst is then withdrawn and returned to the reaction zone, preferably in a riser

using a carrier gas, preferably at least a portion of the feed. The regeneration zone can be designed to operate in various fluidization regimes such as a bubbling regime or a turbulent regime. Preferably, it is run in a bubbling regime wherein in its top section the hot flue gas behaves as a stripping agent which can be supplemented with a stripping gas to minimize coke that is burned.

[0016] One way of viewing a reaction vessel having a separated fluidized bed region and regeneration region is that they provide a "reactor within a reactor" type configuration. For example, a first reactor can have a reactor volume. A pipe or other internal reactor structure can be used to isolate or segregate a portion of the reactor volume. This can result in the reactor volume including a first reaction volume outside of the pipe and a separated reaction volume inside of the pipe. The pipe or internal reactor structure can intersect the walls of the reactor at any convenient locations. One possibility can be to have a pipe that is aligned concentrically with the axis corresponding to the direction of flow in the reactor. Alternatively, one or more pipes can be offset from the central axis of a reactor. Another possibility can be to have an internal reactor structure that enters and/or exits the reactor via a sidewall. For example, existing manways in a reactor could be converted into inlet and/or outlet conduits for an internal structure in the reactor.

[0017] A pipe or conduit within the reactor can be constructed of any suitable materials for withstanding the conversion and/or regeneration conditions inside of the reactor. A pipe or conduit within the reactor volume can be exposed to conversion and/or regeneration conditions on both the inside and the outside of the conduit. Such a conduit can be constructed from a material that can withstand the reaction and/or regeneration conditions, or the conduit can have a coating or cladding layer on both the inside and the outside. Suitable materials for the conduit can be similar to materials used for constructing the reaction vessel. Cold wall or hot wall vessel and piping can be used.

[0018] In one or more aspects, physical separation of a fluidized bed region and a regeneration region inside a reaction vessel can allow for the separate processing of the olefin-containing feed and the coked catalyst. For example, in one or more aspects, the regeneration region may be a tube-shaped sealed structure having an internal volume that includes an inlet near the bottom to allow for coked catalyst to enter from the fluidized bed region for regeneration. In such aspects, this sealed structure can also include one or more outlets for regenerated catalyst and/or gas to escape and enter the fluidized bed region inside the reaction vessel. In this example, the fluidized bed region may be defined, at least partly, by one or more exterior walls of the sealed regeneration structure and one or more internal walls of the reaction vessel. In such a fluidized bed region, the olefin-containing feed can be upgraded. In one or more aspects, effluents from the fluidized bed region and the regeneration region may mix prior to exiting the reaction vessel.

[0019] In one or more aspects, the fluidized bed region and regeneration region within the reaction vessel may be different sizes. For example, in various aspects, the internal volume of the fluidized bed region is preferably larger than the internal volume of the regeneration region. In one or more aspects, the internal volume of the regeneration region may be less than about 70% of the internal volume of the fluidized bed region, or less than about 50%, or less than about 25%, or less than about 10%.

[0020] In various aspects, the coked catalyst that is passed into the regeneration region may undergo oxidative regeneration. In such aspects, an oxygen-containing feed can be provided to the regeneration region, which may strip off any hydrocarbon vapors or liquids present on the coked catalyst. In addition, hot flue gas can heat up the catalyst which can increase coke reaction rates to lighter molecules which are stripped away as well. Further, after stripping, coke on the catalyst surface may be burned off in the presence of the oxygen-containing feed. This exothermic process may generate a minimal amount of heat relative to the thermal mass of the catalyst bed in the fluidized bed reaction region, and thus, the heat generated during regeneration may dissipate into the fluidized bed reaction region without substantially changing the temperature of the fluidized bed. The fluidized reaction bed temperature may be controlled either by feed preheat and/or internal heat transfer coils. If the regeneration zone is not submerged in the fluid bed reaction zone, it is preferred to operate it under bubbling regime and allow a temperature gradient increasing from its top to the bottom. The olefin upgrading conditions disclosed herein may not result in a significant amount of coke on the catalyst, so the flue gas generated during regeneration, which can contain carbon monoxide and carbon dioxide, can be combined with product effluent from the fluidized bed reaction region and processed along with the light gas from the upgrading reaction, which can optionally but preferably be utilized as fuel gas.

[0021] In this discussion, unless otherwise specified, "diesel boiling range" refers to an initial or T5 boiling point of at least about 350°F (177°C), and/or a final or T95 boiling point of less than about 700°F (371°C). In this discussion, unless otherwise specified, "diesel boiling range compounds" refers to one or more compounds that exhibit the diesel boiling range specified above. In this discussion, unless otherwise specified, "naphtha boiling range" refers to an initial or T5 boiling point of at least about 50°F (10°C), and/or a final or T95 boiling point of less than about 450°F (232°C). In this discussion, unless otherwise specified, "naphtha boiling range compounds" refers to one or more compounds that exhibit the naphtha boiling range specified above. In this discussion, unless otherwise specified, "T5 boiling point" refers to a temperature at which 5 wt. % of the feed, effluent, product, stream, or composition of interest will boil. In this discussion, unless

otherwise specified, "T95 boiling point" refers to a temperature at which 95 wt. % of the feed, effluent, product, stream, or composition of interest will boil.

Olefin-Containing Feed

[0022] The olefin-containing feed can be any hydrocarbon feed that contains olefins. In various aspects, at least a portion of the olefin-containing feed can include one or more low value refinery streams, such as refinery fuel gas. Additionally or alternatively, at least a portion of the olefin-containing feed can include a higher boiling range fraction that contains olefins, such as a cracked naphtha fraction. Optionally, a partially distilled naphtha fraction could be used as a portion of a feed, such as a fraction formed by separating a naphtha at a cut point of about 300°F (149°C) or less, or about 250°F (121°C) or less, or about 225°F (107°C) or less. The fractionation of a naphtha feed is further discussed below.

[0023] In various aspects, as discussed above, the olefin-containing feed can include one or more low value refinery streams, such as refinery fuel gas. In such aspects, the one or more low value streams may be present in the olefin-containing feed in an amount of at least about 5 wt. %, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, at least about 50 wt. %, or at least about 60 wt. %. In the same or alternative aspects, the one or more low value streams may be present in the olefin-containing feed in an amount of about 100 wt. % or less, about 99 wt. % or less, about 95 wt. % or less, about 90 wt. % or less, about 80 wt. % or less, or about 70 wt. % or less. In various aspects, the one or more low value refinery streams may be a fuel gas form an FCC unit and/or an off-gas from a coker.

[0024] As discussed above, in one or more aspects, the olefin-containing feed can include one or more naphtha fractions, such as fluid catalytic cracking ("FCC") naphtha, coker naphtha, and/or olefinic naphtha. In such aspects, the one or more naphtha fractions may be present in the olefin-containing feed in an amount of at least about 10 wt. %, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, at least about 50 wt. %, or at least about 60 wt. %. In the same or alternative aspects, the one or more naphtha fractions may be present in the olefin-containing feed in an amount of about 100 wt. % or less, about 99 wt. % or less, about 95 wt. % or less, about 90 wt. % or less, about 80 wt. % or less, or about 70 wt. % or less. Non-limiting examples of naphtha fractions can include FCC naphtha (or cat naphtha), steam cracked naphtha, coker naphtha, or a combination thereof. This can include blends of olefinic naphthas (olefin content of at least about 5 wt. %) with non-olefinic naphthas (olefin content of about 5 wt. % or less). Olefinic naphtha refinery streams generally contain not only paraffins, naphthenes, and aromatics, but also unsaturates, such as open-chain and cyclic olefins, dienes, and cyclic hydrocarbons with olefinic

side chains. An olefinic naphtha feedstock can also have a diene concentration up to about 15 wt. %, but more typically less than about 5 wt. % based on the total weight of the feed.

[0025] In various aspects, the olefin-containing feed can include at least about 10 wt. % olefins, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, at least about 50 wt. %, or at least about 60 wt. %. In the same or alternative aspects, the olefin-containing feed can include less than about 100 wt. % olefins, less than about 90 wt. %, less than about 80 wt. %, or less than about 70 wt. %.

[0026] In various aspects, the olefin-containing feed can include at least about 5 wt. % C_1-C_3 (or C_1-C_4 or C_1-C_5) hydrocarbon compounds, with a portion being C_2-C_3 (or C_2-C_4 or C_2-C_5) olefins, such as the olefin amounts listed above, at least about 10 wt. %, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, at least about 50 wt. %, at least about 60 wt. %, or at least about 70 wt. %. In the same or alternative aspects, the olefin-containing feed can include less than about 100 wt. % C_1-C_3 (or C_1-C_4 or C_1-C_5) hydrocarbon compounds, with a portion being C_2-C_3 (or C_2-C_4 or C_2-C_5) olefins, such as the olefin amounts listed above, less than about 90 wt. %, less than about 80 wt. %, or less than about 70 wt. %. In certain aspects, the olefin-containing feed can include C_1-C_3 (or C_1-C_4 or C_1-C_5) hydrocarbon compounds, with a portion being C_2-C_3 (or C_2-C_4 or C_2-C_5) olefins, such that the C_1-C_3 (or C_1-C_4 or C_1-C_5) hydrocarbon compounds are at least about 10 wt. % greater than the amount (wt. %) of C_2-C_3 (or C_2-C_4 or C_2-C_5) olefins, at least about 20 wt. % greater, at least about 30 wt. % greater, at least about 40 wt. % greater, at least about 50 wt. % greater, or at least about 60 wt. % greater.

[0027] In various aspects, the olefin-containing feed can include C_{5+} compounds in an amount of about 50 wt. % or less, about 40 wt. % or less, about 30 wt. % or less, about 20 wt. % or less, about 10 wt. % or less, or about 5 wt. % or less. In the same or additional aspects, the olefin-containing feed can include C_{5+} compounds in an amount of at least about 0.5 wt. %, at least about 1 wt. %, or at least about 2.5 wt. %.

[0028] In various aspects, the olefin-containing feed can have a sulfur content of at least about 20 wppm, or at least about 500 wppm, or at least about 1000 wppm, or at least about 1500 wppm. In another aspect, the sulfur content can be about 7000 wppm or less, or about 6000 wppm or less, or about 5000 wppm or less, or about 3000 wppm or less. The sulfur may be present as organically bound sulfur.

[0029] In one or more aspects, nitrogen can also be present in the olefin-containing feed. In an aspect, the amount of nitrogen can be at least about 5 wppm, or at least about 10 wppm, or at least about 20 wppm, or at least about 40 wppm. In another aspect, the nitrogen content can be

about 250 wppm or less, or about 150 wppm or less, or about 100 wppm or less, or about 50 wppm or less.

[0030] It is appreciated that other olefin-containing feeds may be used in the processes disclosed herein and that the above-described feed properties are only exemplary.

Fractionation of Naphtha Boiling Range Compounds for the Olefin-Containing Feed

[0031] In certain aspects, a fraction of a naphtha boiling range feed may be utilized in the olefin-containing feed, in order to produce a product having a desirable combination of sulfur content, Reid Vapor Pressure (RVP), and octane rating. In such aspects, a naphtha boiling range feed can initially be fractionated to form a lower boiling fraction and a higher boiling fraction. In various aspects, small variations in the fractionation temperature and/or the quality of fractionation into a lower boiling and higher boiling portion can lead to substantial improvements in the properties of a resulting product after processing, such as the sulfur content. For example, controlling the fractionation can allow C_{2+} thiophenes (such as ethyl thiophenes) to be excluded from the lower boiling portion while retaining thiophene and methyl thiophenes. This can allow sulfur-containing compounds that are difficult to remove to be reduced or minimized in the lower boiling portion.

[0032] In this discussion, reference is made to a "lower boiling portion/fraction" and "a higher boiling portion/fraction". It is understood that a lower boiling portion can include multiple portions or fractions based on additional fractionation at temperatures (i.e., cut points) below the temperature for forming the lower boiling portion, and that similarly a higher boiling portion can include multiple portions or fractions based on additional fractionation at temperatures above the temperature for forming the higher boiling portion.

[0033] One consideration for performing a suitable fractionation or separation can be to perform a fractionation at a suitable temperature. In various aspects, the fractionation or separation temperature (sometimes referred to as a fractionation or separation cut point temperature) for forming a lower boiling naphtha fraction and a higher boiling naphtha fraction can be about 300°F (149°C) or less, or about 270°F (132°C) or less, or about 250°F (121°C) or less, or about 240°F (116°C) or less, or about 225°F (107°C) or less, or about 210°F (99°C) or less. Optionally, the fractionation temperature can be at least about 160°F (71°C), or at least about 170°F (77°C), or at least about 180°F (82°C).

[0034] Selecting a suitable fractionation temperature can assist with making a desired naphtha boiling range product based in part on the nature of the distribution of olefins and/or sulfur within the various compounds in a naphtha boiling range feed. In a naphtha boiling range feed, a substantial portion of the olefins present in the feed can correspond to olefinic compounds having

a boiling point of about 225°F (107°C) or less, or about 210°F (99°C) or less, or about 205°F (96°C) or less, or about 200°F (93°C) or less, or about 190°F (88°C) or less, or about 180°F (82°C) or less. The amount of olefinic compounds having such a boiling point can correspond to about 20% to 80% of the total weight of olefinic compounds in a naphtha boiling range feed. For example, a naphtha boiling range feed can be separated to form a lower boiling portion and higher boiling portion at a fractionation temperature of about 300°F (149°C) or less, 270°F (132°C) or less, or about 250°F (121°C) or less, or about 240°F (116°C) or less, or about 225°F (107°C) or less, or about 210°F (99°C) or less and/or at least about 160°F (71°C), or at least about 170°F (77°C), or at least about 180°F (82°C). After such a fractionation, the weight of olefins in the lower boiling portion can correspond to about 20% to about 80% of the weight of olefins present in the feed prior to fractionation, such as about 20% to about 40%, or about 20% to about 50%, or about 20% to about 60%, or about 20% to about 70%, or about 20% to about 80%, or about 30% to about 40%, or about 30% to about 50%, or about 30% to about 60%, or about 30% to about 70%, or about 30% to about 80%, or about 40% to about 50%, or about 40% to about 60%, or about 40% to about 70%, or about 40% to about 80%, or about 50% to about 60%, or about 50% to about 70%, or about 50% to about 80%, or about 60% to about 80%.

[0035] An alternative way of characterizing the amount of olefins in a lower boiling portion can be based on the weight percent of olefins in the lower boiling portion relative to the weight of the lower boiling portion. In such an alternative, the weight percentage of olefins in the lower boiling portion (based on the total weight of the lower boiling portion) can be about 20 wt. % to about 40 wt. %, or about 20 wt. % to about 50 wt. %, or about 20 wt. % to about 60 wt. %, or about 20 wt. % to about 70 wt. %, or about 20 wt. % to about 80 wt. %, or about 30 wt. % to about 40 wt. %, or about 30 wt. % to about 50 wt. %, or about 30 wt. % to about 60 wt. %, or about 30 wt. % to about 70 wt. %, or about 30 wt. % to about 80 wt. %, or about 40 wt. % to about 50 wt. %, or about 40 wt. % to about 60 wt. %, or about 40 wt. % to about 70 wt. %, or about 40 wt. % to about 80 wt. %, or about 50 wt. % to about 60 wt. %, or about 50 wt. % to about 70 wt. %, or about 50 wt. % to about 80 wt. %, or about 60 wt. % to about 80 wt. %.

[0036] Based on selecting a suitable fractionation temperature, a substantial portion of the olefins in naphtha boiling range feed can be separated into a lower boiling fraction that is not exposed to downstream hydrotreatment conditions. This can reduce, minimize, or eliminate the amount of olefin saturation that is performed on the lower boiling portion, which can provide a benefit in the octane rating of resulting naphtha boiling range product.

[0037] Another factor in selecting a fractionation temperature can be the distribution of sulfur-containing compounds in the feed. A substantial portion of the sulfur present in a naphtha boiling

range feed can be present in compounds with a boiling point of at least about 200°F (93°C), or at least about 205°F (96°C), or at least about 210°F (99°C), or at least about 225°F (107°C), or at least about 240°F (116°C). Additionally or alternately, the nature of the sulfur compounds in a higher boiling portion of a feed can tend to correspond to sulfur compounds that are more difficult to remove. A lower boiling portion of a naphtha boiling range feed can tend to contain sulfur containing compounds such as mercaptans or sulfides which are relatively easier to convert into H_2S for eventual separation and removal of the sulfur. Thiophenes, such as alkyl-substituted thiophenes, are examples of compounds with higher boiling points that contain sulfur that conventionally can be more difficult to convert. However, it has been discovered that thiophenes and C_1 thiophenes (i.e., methyl-thiophenes) can be substantially removed from a naphtha feed under sufficiently high pressures and/or in the presence of an additional olefin stream. Selecting an appropriate fractionation temperature can reduce or minimize the amount of sulfur compounds that are difficult to convert in the lower boiling portion of a naphtha feed. For example, the amount of alkyl-substituted thiophenes present in a lower boiling portion of a naphtha feed, and/or the amount of alkyl-substituted thiophenes having alkyl substitution containing two or more carbons (C_{2+} alkyl-substituted thiophenes), can be limited by performing an appropriate fractionation. Such compounds can instead be separated into the higher boiling portion, where the sulfur removal can be performed by exposing the compounds to a hydrotreating catalyst under effective hydrotreating conditions.

[0038] In various aspects, the sulfur content of a lower boiling portion that corresponds to sulfur contained in C_{2+} alkyl-substituted thiophenes in the lower boiling portion can be about 100 wppm or less, or about 75 wppm or less, or about 50 wppm or less, or about 30 wppm or less, or about 20 wppm or less. Additionally or alternately, the sulfur content of a lower boiling portion that corresponds to sulfur contained in C_{3+} alkyl-substituted thiophenes in the lower boiling portion can be about 50 wppm or less, or about 30 wppm or less, or about 20 wppm or less, or about 15 wppm or less, or about 10 wppm or less.

[0039] One option for controlling the amount of C_{2+} thiophenes (such as C_{2+} alkyl-substituted thiophenes) present in a lower boiling portion can be to control the sharpness of the separation or fractionation that is used for forming the lower boiling portion. In other words, in addition to selecting a suitable cut point temperature for performing a fractionation, another consideration in forming a lower boiling portion and a higher boiling portion can be performing the fractionation to reduce or minimize the amount of overlap in the boiling ranges for the lower boiling portion and the higher boiling portion. In a typical fractionation procedure, a "cut point" or target separation temperature can be selected to roughly determine the composition of a higher boiling and a lower

boiling portion. However, fractionation of a feed is rarely ideal, so there can typically be some overlap between the resulting boiling ranges for a lower boiling and a higher boiling fraction. For example, at a cut point of 200°F (93°C), a typical fractionation could lead to a lower boiling fraction that has a T95 boiling point greater than 200°F and/or a higher boiling fraction with a T5 boiling point of less than 200°F. As another example, a typical fractionation with a 200°F cut point could result in a lower boiling fraction with a final boiling point of at least about 210°F (99°C) and/or a higher boiling portion an initial boiling point of less than about 190°F (88°C).

[0040] One of the difficulties in performing an ideal separation can be related to the vapor pressure of various compounds in a mixture being separated. For example, the boiling point of 2-ethyl thiophene is roughly 132°C (270°F). This means that 2-ethyl thiophene can have a substantial vapor pressure at temperatures above 250°F (121°C). As a result, it can be difficult to completely exclude ethyl thiophenes and/or other C_{2+} thiophenes from a lower boiling fraction. However, the C_{2+} thiophene content of a lower boiling fraction can be reduced or minimized by controlling the nature of the separation. Because C_{2+} thiophenes (and other higher boiling sulfur compounds) can have a lower reactivity for certain sulfur removal processes, removing sulfur from such compounds can be difficult. As a result, achieving a desired target sulfur content in the lower boiling fraction can be assisted by controlling the separation that forms the lower boiling fraction to reduce or minimize the amount of C_{2+} alkyltyhiophenes, benzo-thiophenes, and/or other higher boiling sulfur compounds in the lower boiling fraction.

[0041] In various aspects, a fractionation of a naphtha boiling range feed can be performed using a separation device with sufficient separation power to provide a relatively narrow difference between a selected fractionation temperature and the actual final boiling point / initial boiling point of the respective fractions formed by the separation. An example of a fractionator for performing a separation with reduced or minimized overlap in the boiling ranges of the resulting fractions can be a distillation column having a separating efficiency equivalent to at least about 20 trays, or at least about 30 trays, or at least about 40 trays, or at least about 50 trays. In some aspects, a fractionation can be characterized based on the difference between the initial boiling point of the resulting higher boiling fraction and the final boiling point of the resulting lower boiling fraction. In such aspects, the difference between the initial boiling point of a higher boiling fraction and the final boiling point of a resulting lower boiling fraction can be about 40°F (21°C) or less, or about 30°F (17°C) or less, or about 25°F (14°C) or less, or about 20°F (11°C) or less, or about 15°F (8°C) or less, or about 10°F (6°C) or less. In other aspects, a fractionation can be characterized based on the difference between a T95 boiling point for the lower boiling fraction and the T5 boiling point for the higher boiling fraction. In such aspects, the difference between the T95 boiling point of the

lower boiling fraction and the T5 boiling point of the higher boiling fraction can be about 40°F (22°C) or less, or about 30°F (17°C) or less, or about 25°F (14°C) or less, or about 20°F (11°C) or less, or about 15°F (8°C) or less, or about 10°F (6°C) or less. Additionally or alternately, in such aspects, the T5 boiling point for the higher boiling fraction can be greater than the T95 boiling point for the lower boiling fraction, or at least 5°F (3°C) greater, or at least 10°F (6°C) greater. Such fractionation can be optimized based on the sulfur target in a gasoline pool, sulfur reduction severity, feed sulfur content and distribution, and/or processing costs such as capital equipment costs and energy costs.

Conditions for Upgrading an Olefin-Containing Feed

[0042] In various aspects, the olefin-containing feed can be exposed to an acidic catalyst (such as a zeolite) under effective conversion conditions for olefinic oligomerization and/or sulfur removal. Optionally, the zeolite or other acidic catalyst can also include a hydrogenation functionality, such as a Group VIII metal or other suitable metal that can activate hydrogenation / dehydrogenation reactions. The olefin-containing feed can be exposed to the acidic catalyst without providing substantial additional hydrogen to the reaction environment. Added hydrogen refers to hydrogen introduced as an input flow to the process, as opposed to any hydrogen that might be generated in-situ during processing. Exposing the feed to an acidic catalyst without providing substantial added hydrogen is defined herein as exposing the feed to the catalyst in the presence of a) less than about 100 SCF/bbl of added hydrogen, or less than about 50 SCF/bbl; b) a partial pressure of less than about 50 psig (350 kPag), or less than about 15 psig (100 kPag) of hydrogen; or c) a combination thereof.

[0043] The acidic catalyst used in the processes described herein can be a zeolite-based catalyst, that is, it can comprise an acidic zeolite in combination with a binder or matrix material such as alumina, silica, or silica-alumina, and optionally further in combination with a hydrogenation metal. More generally, the acidic catalyst can correspond to a molecular sieve (such as a zeolite) in combination with a binder, and optionally a hydrogenation metal. Molecular sieves for use in the catalysts can be medium pore size zeolites, such as those having the framework structure of ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, or MCM-22. Such molecular sieves can have a 10-member ring as the largest ring size in the framework structure. The medium pore size zeolites are a well-recognized class of zeolites and can be characterized as having a Constraint Index of 1 to 12. Constraint Index is determined as described in U.S. Pat. No. 4,016,218 incorporated herein by reference. Catalysts of this type are described in U.S. Pat. Nos. 4,827,069 and 4,992,067 which are incorporated herein by reference and to which reference is made for further details of such catalysts, zeolites and binder or matrix materials.

[0044] Additionally or alternately, catalysts based on large pore size framework structures (12-member rings) such as the synthetic faujasites, especially zeolite Y, such as in the form of zeolite USY. Zeolite beta may also be used as the zeolite component. Other materials of acidic functionality which may be used in the catalyst include the materials identified as MCM-36 and MCM-49. Still other materials can include other types of molecular sieves having suitable framework structures, such as silicoaluminophosphates (SAPOs), aluminosilicates having other heteroatoms in the framework structure, such as Ga, Sn, or Zn, or silicoaluminophosphates having other heteroatoms in the framework structure. Mordenite or other solid acid catalysts can also be used as the catalyst.

[0045] The exposure of the olefin-containing feed to the acidic catalyst can be performed in any convenient manner, such as exposing the olefin-containing feed to the acidic catalyst under fluidized bed conditions. In some aspects, the particle size of the catalyst can be selected in accordance with the fluidization regime which is used in the process. Particle size distribution can be important for maintaining turbulent fluid bed conditions as described in U.S. Pat. No. 4,827,069 and incorporated herein by reference. Suitable particle sizes and distributions for operation of dense fluid bed and transport bed reaction zones are described in U.S. Pat. Nos. 4,827,069 and 4,992,607 both incorporated herein by reference. Particle sizes in both cases will normally be in the range of 10 to 300 microns, typically from 20 to 100 microns.

[0046] Acidic zeolite catalysts suitable for use as described herein can be those exhibiting high hydrogen transfer activity and having a zeolite structure of ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, MCM-22, MCM-36, MCM-49, zeolite Y, and zeolite beta. Such catalysts can be capable of oligomerizing olefins from the olefin-containing feed. For example, such catalysts can convert C_2-C_4 olefins, such as those present in a refinery fuel gas, to C_{5+} olefins. Such catalysts can also be capable of converting organic sulfur compounds such as mercaptans to hydrogen sulfide without added hydrogen by utilizing hydrogen present in the hydrocarbon feed. Group VIII metals such as nickel may be used as desulfurization promoters. A fluid-bed reactor/regenerator can assist with maintaining catalyst activity in comparison with a fixed-bed system. Further, the hydrogen sulfide produced in accordance with the processes described herein can be removed using conventional amine based absorption processes.

[0047] ZSM-5 crystalline structure is readily recognized by its X-ray diffraction pattern, which is described in U.S. Pat. No. 3,702,866. ZSM-11 is disclosed in U.S. Pat. No. 3,709,979, ZSM-12 is disclosed in U.S. Pat. No. 3,832,449, ZSM-22 is disclosed in U.S. Pat. No. 4,810,357, ZSM-23 is disclosed in U.S. Pat. Nos. 4,076,842 and 4,104,151, ZSM-35 is disclosed in U.S. Pat. No.4,016,245, ZSM-48 is disclosed in U.S. Pat. No.4,375,573 and MCM-22 is disclosed in U.S.

Pat. No. 4,954,325. The U.S. Patents identified in this paragraph are incorporated herein by reference.

[0048] While suitable zeolites having a coordinated metal oxide to silica molar ratio of 20:1 to 200:1 or higher may be used, it can be advantageous to employ aluminosilicate ZSM-5 having a silica:alumina molar ratio of about 25:1 to 70:1, suitably modified. A typical zeolite catalyst component having Bronsted acid sites can comprises, consist essentially of, or consist of crystalline aluminosilicate having the structure of ZSM-5 zeolite with 5 to 95 wt. % silica, clay and/or alumina binder.

[0049] These siliceous zeolites can be employed in their acid forms, ion-exchanged or impregnated with one or more suitable metals, such as Ga, Pd, Zn, Ni, Co, Mo, P, and/or other metals of Periodic Groups III to VIII. The zeolite may include other components, generally one or more metals of group IB, IIB, IIIB, VA, VIA or VIIIA of the Periodic Table (IUPAC).

[0050] Useful hydrogenation components can include the noble metals of Group VIIIA, such as platinum, but other noble metals, such as palladium, gold, silver, rhenium or rhodium, may also be used. Base metal hydrogenation components may also be used, such as nickel, cobalt, molybdenum, tungsten, copper or zinc.

[0051] The catalyst materials may include two or more catalytic components which components may be present in admixture or combined in a unitary multifunctional solid particle.

[0052] In addition to the preferred aluminosilicates, the gallosilicate, ferrosilicate and "silicalite" materials may be employed. ZSM-5 zeolites can be useful in the process because of their regenerability, long life and stability under the extreme conditions of operation. Usually the zeolite crystals have a crystal size from about 0.01 to over 2 microns or more, such as 0.02-1 micron.

[0053] In various aspects, the fluidized bed catalyst particles can contain about 25 wt. % to about 40 wt. % H-ZSM-5 zeolite, based on total catalyst weight, contained within a silica-alumina matrix. Typical Alpha values for the equilibrium catalyst can be about 100 or less. Sulfur conversion to hydrogen sulfide can increase as the alpha value increases.

[0054] The Alpha Test is described in U.S. Pat. 3,354,078, and in the Journal of Catalysis, Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980), each incorporated herein by reference as to that description.

[0055] In one or more aspects, effective conversion conditions for exposing the olefin-containing feed to an acidic catalyst can include a temperature of about 300°F (149°C) to about 900°F (482°C), or about 350°F (177°C) to about 850°F (454°C); a pressure of about 50 psig (0.34 MPag) to about 1100psig (7.6MPag), or a pressure of about 100 psig (0.69 MPag) to about 1000

psig (6.9 MPag), or about 150 psig (1.0 MPag) to about 975 psig (6.7 MPag), or about 200 psig (1.4 MPag) to about 950 psig (6.6 MPag), or about 250 psig (1.7 MPag) to about 900 psig (6.2 MPag), or about 300 psig (4.1 MPag) to about 850 psig (5.9 MPag), or about 300 psig (4.1 MPag) to about 800 psig (5.5 MPag), or a pressure of at least about 50 psig (0.34 MPag), or a pressure of at least about 100 psig (0.69 MPag), or a pressure of at least about 150 psig (1.0 MPag), or a pressure of at least about 200 psig (1.4 MPag), or a pressure of at least about 250 psig (1.7 MPag), or a pressure of at least about 300 psig (4.1 MPag), or a pressure of at least about 350 psig (2.4 MPag); and a weight hourly space velocity of about 0.05 hr^{-1} to about 20 hr^{-1}, or about 0.05 to about 10 hr^{-1}, or about 0.1 to about 10 hr^{-1}, or about 0.1 to about 2 hr^{-1}, or about 0.1 hr^{-1} to about 1.0 hr^{-1}, or about 0.1 hr^{-1} to about 0.75 hr^{-1}, or about 0.1 hr^{-1} to about 0.6 hr^{-1}.

[0056] It is noted that in some aspects, temperatures of about 550°F (260°C) to about 700°F (371°C) can provide a beneficial combination of reactivity and run length. Temperatures below 550°F can result in high rates of coking on catalyst, which can lead to reduced reactivity for catalyzing an oligomerization reaction. Temperatures above about 700°F (371°C) can lead to increased formation of aromatics, which are less desirable as part of a diesel boiling range fuel.

[0057] In various aspects, exposing an olefin-containing feed to the conversion conditions discussed above can produce a fluidized bed reaction region (product) effluent that includes oligomerized olefins. In such aspects, this fluidized bed region effluent can include compounds with 5 or more carbon atoms (C_{5+} compounds) in an amount of at least about 5 wt.%, at least about 10 wt. %, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, or at least about 50 wt. %. In certain aspects, at least about 10 wt. % of the olefins from the olefin-containing feed can be incorporated into the oligomerized olefins in the fluidized bed region effluent, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, or at least about 50 wt. %. In certain aspects, such as when the olefin-containing feed includes naphtha boiling range compounds, the fluidized bed region effluent can include diesel boiling range compounds with 10 or more carbon atoms (C_{10+} compounds). The C_{10+} compounds can be present in the fluidized bed reaction region effluent in an amount of at least about 5 wt. %, at least about 10 wt. %, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, or at least about 50 wt. %. In one or more aspects, the C_{5+} compounds and/or the C_{10+} compounds can have a reduced sulfur content compared to the olefin-containing feed. In such aspects, the sulfur content of the C_{5+} compounds and/or the C_{10+} compounds in the fluidized bed region effluent can be about 100 wppm or less, or about 75 wppm or less, or about 50 wppm or less, or about 30 wppm or less, or about 20 wppm or less, or about 10 wppm or less. Further, in such aspects, at least about 40 wt. % of C_{5+} mercaptans (compounds with 5 or more carbon atoms having organically bound sulfur) present in the olefin-containing feed

are converted to H_2S, or at least about 50 wt. %, or at least about 60 wt. %, or at least about 70 wt. %, or at least about 80 wt. %, or at least about 90 wt. %.

Catalyst Regeneration in a Regeneration Region of the Reaction Vessel

[0058] In various aspects, continuous oxidative regeneration of the catalyst can occur by withdrawing a portion of coked catalyst from the fluidized bed reaction region and transporting it to the regeneration region, oxidatively regenerating the withdrawn catalyst, e.g., by exposure to an oxygen-containing feed, and returning regenerated catalyst to the fluidized bed region from the regeneration region at a rate to control catalyst activity and reaction severity to effect feedstock conversion. It is appreciated that in the processes described herein any conventional systems, such as piping and/or valves, may be used to control the movement of the coked catalyst and/or regenerated catalyst between the fluidized bed reaction region and the regeneration region.

[0059] In various aspects, inside the regeneration region, the coked catalyst can be exposed to effective regeneration conditions to burn off at least a portion of the carbonaceous deposits (e.g., coke) deposited on the catalyst. In such aspects, the coked catalyst can be exposed to an oxygen-containing feed to facilitate removal of the coke deposits.

[0060] In certain aspects, the oxygen-containing feed can be plant air, instrument air, air, oxygen, or a combination thereof. In one or more aspects, the oxygen-containing feed may include a low level of oxygen or no excess oxygen, in order to favor formation of carbon monoxide as opposed to carbon dioxide during the oxidative regeneration process. In such aspects, a regeneration region flue gas with decreased levels of carbon dioxide and increased levels of carbon monoxide may be more suitable for eventual use as a refinery fuel gas while minimizing regeneration exotherm and oxygen requirements.

[0061] In one or more aspects, the oxygen-containing feed may enter the bottom region of the regeneration region where it can contact the coked catalyst that has been withdrawn from the fluidized bed reaction region. In such aspects, this initial exposure of the withdrawn coked catalyst to the oxygen-containing feed may strip off at least a portion of any hydrocarbon liquid and/or vapor remaining on the withdrawn coked catalyst.

[0062] In various aspects, when the oxygen-containing feed enters the bottom region of the regeneration region, where the withdrawn coked catalyst also enters the regeneration region, a temperature gradient within the regeneration region may be formed. For example, the bottom portion of the regeneration region, where the initial coke burning occurs, would be hotter than the top portions of the regeneration region, where the exothermic flue gas is heating the cooler catalyst from the fluidized bed reaction region. In one or more aspects, such a temperature gradient can increase the stripping efficiency and coke cracking in the upper regions of the regeneration region,

which can minimize the coke to be burned off during regeneration. Further, in such aspects, minimizing the coke to be burned off during regeneration may decrease the oxygen requirement for regeneration.

[0063] In various aspects, the heat generated in this exothermic regeneration process may be small compared to the relative thermal mass of the catalyst bed in the fluidized bed reaction region, and thus, such heat may be dissipated into the heat of the catalyst bed in the fluidized bed reaction region which is tightly controlled by feed preheat or other heat control mechanisms without any adverse effects on the upgrading process.

[0064] In various aspects, once the catalyst has been regenerated, it can be returned to the fluidized bed reaction region. In such aspects, the regenerated catalyst may be returned to the reaction zone by any conventional methods. For example, in one or more aspects, the regenerated catalyst may be lifted by at least a portion of olefin-containing feed or another gas into the fluid bed of the fluidized bed reaction region.

[0065] In various aspects, the olefin conversion reaction described above may not result in a significant level of coke on the catalyst, and the resulting level of carbon monoxide, carbon dioxide, water, and/or nitrogen in the flue gas generated in the regeneration process would not substantially affect the rate and/or yield of the olefin conversion reaction. In such aspects, therefore, the flue gas from the regeneration process does not need to be segregated from the fluidized bed region or from the reaction product stream.

[0066] In various aspects, exposing the coked catalyst to an oxygen-containing feed in the regeneration region can result in a regeneration region effluent that includes at least about 1 wt. % carbon dioxide, or at least about 2.5 wt. %, or at least about 5 wt. %. In the same or alternative aspects, the regeneration region effluent can include less than about 10 wt. % carbon dioxide, or less than about 5 wt. %, or less than about 2.5 wt. %, or less than about 1 wt. %. In one or more aspects the regeneration region effluent can include at least about 1 wt. % carbon monoxide, or at least about 2.5 wt. %, or at least about 5 wt. %. In certain aspects, the regeneration region effluent can include less than about 10 wt. % carbon monoxide, or less than about 5 wt. %, or less than about 2.5 wt. %, or less than about 1 wt. %.

Reaction Vessel Effluent

[0067] In one or more aspects, as discussed above, the regeneration process can produce a regeneration region effluent that mixes with the fluidized bed reaction region effluent of the conversion process to form a reaction vessel effluent. In various aspects, the reaction vessel effluent can include oligomerized olefins. In such aspects, this reaction vessel effluent can include compounds with 5 or more carbon atoms (C_{5+} compounds) in an amount of at least about 5 wt.%,

at least about 10 wt. %, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, or at least about 50 wt. %. In certain aspects, at least about 10 wt. % of the olefins from the olefin-containing feed can be incorporated into the oligomerized olefins in the reaction vessel effluent, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, or at least about 50 wt. %. In certain aspects, such as when the olefin-containing feed includes naphtha boiling range compounds, the reaction vessel effluent can include diesel boiling range compounds with 10 or more carbon atoms (C_{10+} compounds). The C_{10+} compounds can be present in the reaction vessel effluent in an amount of at least about 5 wt. %, at least about 10 wt. %, at least about 20 wt. %, at least about 30 wt. %, at least about 40 wt. %, or at least about 50 wt. %. In one or more aspects, the C_{5+} compounds and/or the C_{10+} compounds can have a reduced sulfur content compared to the olefin-containing feed. In such aspects, the sulfur content of the C_{5+} compounds and/or the C_{10+} compounds in the reaction vessel effluent can be about 100 wppm or less, or about 75 wppm or less, or about 50 wppm or less, or about 30 wppm or less, or about 20 wppm or less, or about 10 wppm or less. In one or more aspects, the reaction vessel effluent can include at least about 0.1 wt. % carbon dioxide, or at least about 1 wt. %, or at least about 2.5 wt. %, or at least about 5 wt. %. In the same or alternative aspects, the reaction vessel effluent can include less than about 10 wt. % carbon dioxide, or less than about 5 wt. %, or less than about 2.5 wt. %, or less than about 1 wt. %. In one or more aspects the reaction vessel effluent can include at least about 0.1 wt. % carbon monoxide, or at least about 1 wt. %, or at least about 2.5 wt. %, or at least about 5 wt. %. In certain aspects, the reaction vessel effluent can include less than about 10 wt. % carbon monoxide, or less than about 5 wt. %, or less than about 2.5 wt. %, or less than about 1 wt. %. In various aspects, the reaction vessel effluent can include at least about 0.1 wt. % more carbon dioxide and/or carbon monoxide compared to the level of carbon monoxide and carbon dioxide in the olefin-containing feed, or at least about 1 wt. % more, or at least about 2.5 wt. % more, or at least about 5 wt. % more.

Example of Reaction Vessel Configuration

[0068] FIG. 1 depicts one example of a reaction vessel 100 for upgrading an olefin-containing feed. Initially, an olefin-containing feed 104 can be exposed to conversion conditions in the fluidized bed region reaction 102 of the reaction vessel 100. As discussed above, in various aspects, the olefin-containing feed can include light olefins and/or naphtha boiling range compounds. In the fluidized bed reaction region 102, the olefin-containing feed can be exposed to a conversion catalyst, such as one or more of the acidic conversion catalysts discussed above. In one or more aspects, the reaction vessel 100 can also include a regeneration region 106 for the regeneration of at least a portion of the coked catalyst. In certain aspects, as discussed above, the

regeneration region 106 can be physically separated from the fluidized bed reaction region 102. In such aspects, the regeneration region 106 may be partially contained within the fluidized catalyst bed inside the reaction vessel 100, as illustrated by the fluidized catalyst bed level 112 in FIG. 1 that only partially covers the regeneration region 106. In alternative aspects, the regeneration region 106 may be entirely contained within the fluidized catalyst bed inside the reaction vessel 100, as illustrated by the fluidized catalyst bed level 110 in FIG. 1 that entirely covers the regeneration region 106. Alternatively, the regeneration zone can be outside the fluidized reaction zone and connected to the reaction zone by piping. In an aspect, the regeneration zone is a standpipe to the fluidized bed reaction zone. In various aspects, appropriate piping and control valves are used for catalyst transfer to and/or from the regeneration zone.

[0069] In various aspects, at least a portion of coked catalyst from the reaction zone 102 can be withdrawn to the regeneration zone 106, e.g., via a valve. The coked catalyst present in the regeneration zone 106 can be exposed to an oxygen-containing feed 108, such as the oxygen-containing feed discussed above. In various aspects, the exposure to the oxygen-containing feed may strip at least a portion of hydrocarbon liquid or vapors on the coked catalyst and burn off at least a portion of the coke deposits on the catalyst. The regenerated catalyst can be returned to the fluidized bed reaction region 102. The reaction vessel effluent 114 exiting the reaction vessel 100 can include both a fluidized bed reaction region effluent, which can include oligomerized olefins and/or a reduced sulfur content olefin-containing feed, and a regeneration region effluent, which can include carbon monoxide and/or carbon dioxide.

Additional Embodiments

[0070] Embodiment 1. A method for upgrading an olefin-containing feed, comprising: exposing an olefin-containing feed having an olefin content of at least about 10 wt. % to a fluidized bed of an acidic conversion catalyst in a reaction vessel under effective conversion conditions to form a product effluent comprising C_{5+} oligomerized olefinic compounds and a coked catalyst stream; and exposing at least a portion of the coked catalyst stream to an oxygen-containing feed in a regeneration region in the reaction vessel to remove at least a portion of coke from the coked catalyst stream, wherein the product effluent exiting the reaction vessel comprises at least about 5 wt. % C_{5+} oligomerized olefinic compounds and at least about 0.1 wt. % of one or more of carbon monoxide and carbon dioxide formed in the regeneration region.

[0071] Embodiment 2. The method of embodiment 1, wherein at least a portion of the regeneration region is positioned within the fluidized bed of acidic conversion catalyst.

[0072] Embodiment 3. The method of any of the above embodiments, wherein the fluidized bed region defines a first internal volume of the reaction vessel and the regeneration region defines

a second internal volume of the reaction vessel, wherein the second internal volume is separated from the first internal volume, wherein the exposing an olefin-containing feed having an olefin content of at least about 10 wt. % to an acidic conversion catalyst under effective conversion conditions occurs within the first internal volume, and wherein the exposing at least a portion of the coked catalyst stream to an oxygen-containing feed occurs within the second internal volume.

[0073] Embodiment 4. The method of embodiment 4, wherein the second internal volume is less than about 70% of the first internal volume.

[0074] Embodiment 5. The method of any of the above embodiments, wherein the product effluent has a sulfur content of about 100 wppm or less.

[0075] Embodiment 6. The method of any of the above embodiments, wherein the olefin-containing feed comprises naphtha boiling range compounds.

[0076] Embodiment 7. The method of any of the above embodiments, wherein the product effluent further comprises diesel boiling range compounds.

[0077] Embodiment 8. The method of any of the above embodiments, wherein the oxygen-containing feed comprises air, plant air, instrument air, or a combination thereof.

[0078] Embodiment 9. The method of any of the above embodiments, wherein the acidic conversion catalyst comprises an acidic zeolite catalyst.

[0079] Embodiment 10. The method of any of the above embodiments, wherein the product effluent further comprises at least about 1 wt. % carbon dioxide.

[0080] Embodiment 11. The method of any of the above embodiments, wherein the effective conversion conditions comprise a pressure of at least about 100 psig and a temperature of from about 300°F to about 900°F.

[0081] Embodiment 12. The method of any of the above embodiments, wherein the olefin-containing feed comprises one or more of fuel gas from an FCC unit and coker off-gas.

[0082] Embodiment 13. The method of any of the above embodiments, wherein the olefin-containing feed further comprises naphtha boiling range compounds that are derived from one or more of an FCC naphtha fraction and a coker naphtha fraction.

[0083] Embodiment 14. The method of any of the above embodiments, wherein at least about 60 wt. % of C_{5+} mercaptans present in the olefin-containing feed are converted to H_2S.

[0084] Embodiment 15. A conversion product from upgrading an olefin-containing feed, comprising: at least about 10 wt. % C_{10+} compounds; at least about 5 wt. % C_{5+} olefinic compounds, wherein the at least about 10 wt. % C_{10+} compounds and at least about 5 wt. % C_{5+} olefinic compounds are produced in a fluidized bed olefin oligomerization reactor using an olefin-containing feed; and at least about 0.1 wt. % more of one or more of carbon dioxide and carbon

monoxide compared to a level of carbon monoxide and carbon dioxide in the olefin-containing feed.

[0085] Embodiment 16. The conversion product of embodiment 15, wherein the at least about 1 wt. % carbon monoxide and the at least about 1 wt. % carbon dioxide are an effluent from a catalyst regeneration process.

[0086] Embodiment 17. A system for upgrading an olefin-containing feed, comprising: a fluidized bed reaction vessel comprising a fluidized bed region and a regeneration region at least partly contained within the fluidized bed region; a fluidized bed reaction vessel outlet; a fluidized bed region outlet that is in fluid communication with the fluidized bed reaction vessel outlet; and a regeneration region outlet that is in fluid communication with the fluidized bed reaction vessel outlet.

[0087] Embodiment 18. The system of embodiment 17, wherein the regeneration region is entirely contained within the fluidized bed region.

[0088] Embodiment 19. The system of embodiment 17 or embodiment 18, wherein the regeneration region comprises a standpipe to the fluidized bed region.

[0089] Although the present invention has been described in terms of specific embodiments, it is not so limited. Suitable alterations/modifications for operation under specific conditions should be apparent to those skilled in the art. It is therefore intended that the following claims be interpreted as covering all such alterations/modifications as fall within the true spirit/scope of the invention.

CLAIMS:

1. A method for upgrading an olefin-containing feed, comprising:

exposing an olefin-containing feed having an olefin content of at least about 10 wt. % to a fluidized bed of an acidic conversion catalyst in a reaction vessel under effective conversion conditions to form a product effluent comprising C_{5+} oligomerized olefinic compounds and a coked catalyst stream; and

exposing at least a portion of the coked catalyst stream to an oxygen-containing feed in a regeneration region in the reaction vessel to remove at least a portion of coke from the coked catalyst stream, wherein the product effluent exiting the reaction vessel comprises at least about 5 wt. % C_{5+} oligomerized olefinic compounds and at least about 0.1 wt. % of carbon monoxide and/or carbon dioxide formed in the regeneration region.

2. The method of claim 1, wherein at least a portion of the regeneration region is positioned within the fluidized bed of acidic conversion catalyst.

3. The method of claim 1, wherein the fluidized bed region defines a first internal volume of the reaction vessel and the regeneration region defines a second internal volume of the reaction vessel, wherein the second internal volume is separated from the first internal volume, wherein the exposing an olefin-containing feed having an olefin content of at least about 10 wt. % to an acidic conversion catalyst under effective conversion conditions occurs within the first internal volume, and wherein the exposing at least a portion of the coked catalyst stream to an oxygen-containing feed occurs within the second internal volume.

4. The method of claim 3, wherein the second internal volume is less than about 70% of the first internal volume.

5. The method of claim 1, wherein the product effluent has a sulfur content of about 100 wppm or less.

6. The method of claim 1, wherein the olefin-containing feed comprises naphtha boiling range compounds.

7. The method of claim 6, wherein the product effluent further comprises diesel boiling range compounds.

8. The method of claim 1, wherein the oxygen-containing feed comprises air, plant air, instrument air, or a combination thereof.

9. The method of claim 1, wherein the acidic conversion catalyst comprises an acidic zeolite catalyst.

10. The method of claim 1, wherein the product effluent further comprises at least about 1 wt. % carbon dioxide.

11. The method of claim 1, wherein the effective conversion conditions comprise a pressure of at least about 100 psig and a temperature of from about 300°F to about 900°F.

12. The method of claim 1, wherein the olefin-containing feed comprises one or more of fuel gas from an FCC unit and coker off-gas.

13. The method of claim 12, wherein the olefin-containing feed further comprises naphtha boiling range compounds that are derived from one or more of an FCC naphtha fraction and a coker naphtha fraction.

14. The method of claim 1, wherein at least about 60 wt. % of C_{5+} mercaptans present in the olefin-containing feed are converted to H_2S.

15. A conversion product from upgrading an olefin-containing feed, comprising:

at least about 10 wt. % C_{10+} compounds;

at least about 5 wt. % C_{5+} olefinic compounds, wherein the at least about 10 wt. % C_{10+} compounds and at least about 5 wt. % C_{5+} olefinic compounds are produced in a fluidized bed olefin oligomerization reactor using an olefin-containing feed; and

at least about 0.1 wt. % more of one or more of carbon dioxide and carbon monoxide compared to a level of carbon monoxide and carbon dioxide in the olefin-containing feed.

16. The conversion product of claim 15, wherein the at least about 1 wt. % carbon monoxide and the at least about 1 wt. % carbon dioxide are an effluent from a catalyst regeneration process.

17. A system for upgrading an olefin-containing feed, comprising:

a fluidized bed reaction vessel comprising a fluidized bed region and a regeneration region at least partly contained within the fluidized bed region;

a fluidized bed reaction vessel outlet;

a fluidized bed region outlet that is in fluid communication with the fluidized bed reaction vessel outlet; and

a regeneration region outlet that is in fluid communication with the fluidized bed reaction vessel outlet.

18. The system of claim 17, wherein the regeneration region is entirely contained within the fluidized bed region.

19. The system of claim 17, wherein the regeneration region comprises a standpipe to the fluidized bed region.

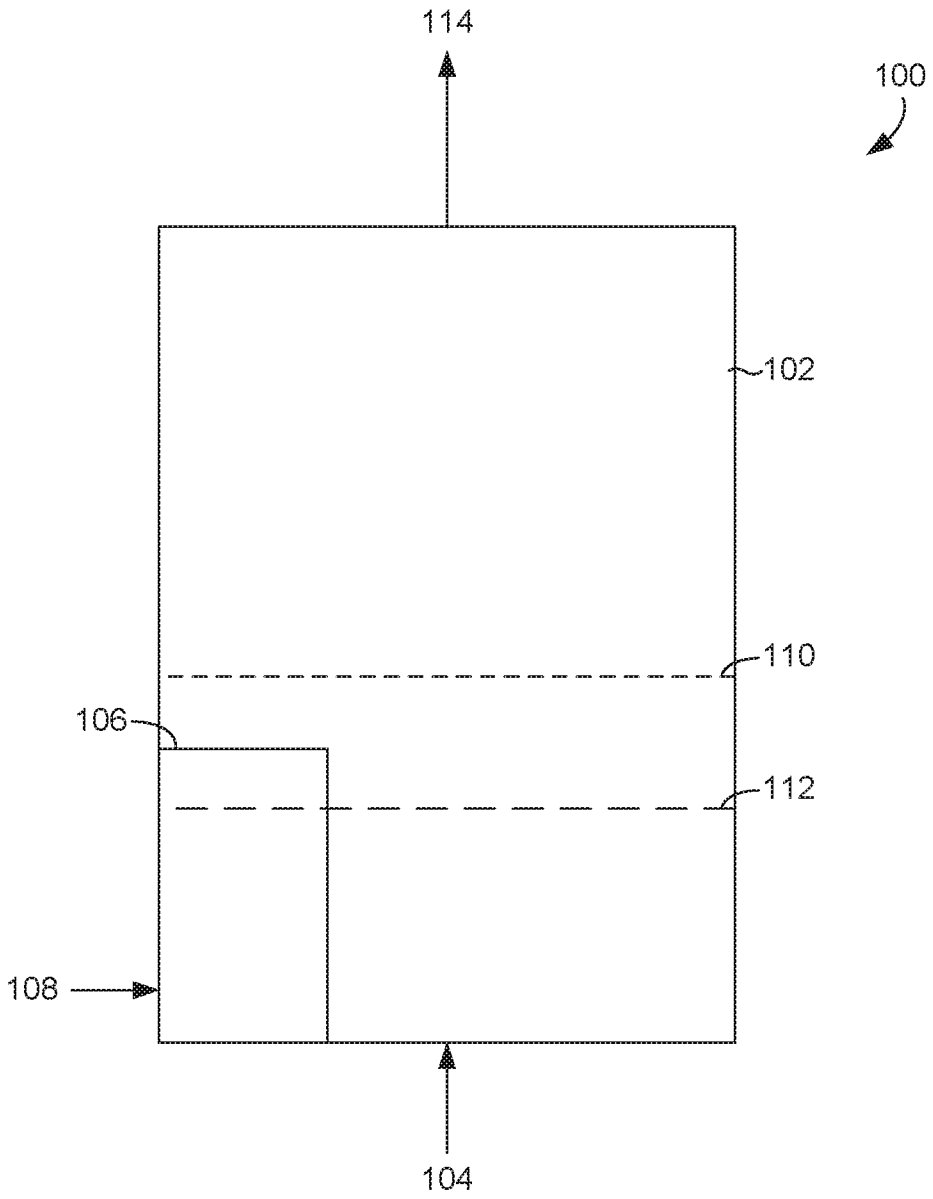


FIG. 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/064524

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 15, 16
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/064524

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G50/00 B01J8/26
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G B01J

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.
Y	US 4 822 477 A (AVIDAN AMOS A [US] ET AL) 18 April 1989 (1989-04-18) column 5, line 14 - column 6, line 4 figure 1	1-14
X	GB 1 508 777 A (EXXON RESEARCH ENGINEERING CO) 26 April 1978 (1978-04-26)	17-19
Y	page 2, lines 35-62 figures 3-6	1-14
X	US 2 514 288 A (NICHOLSON EDWARD W S) 4 July 1950 (1950-07-04)	17-19
Y	claim 3 column 1, lines 16-26 column 1, line 49 - column 2, line 2 figure 1	1-14

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

[X] See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2017	21/02/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Pardo Torre, J

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/064524

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/172650 A1 (LIU SHETIAN [US] ET AL) 4 July 2013 (2013-07-04) claims 1-10	1-14, 17-19

A	US 4 456 779 A (OWEN HARTLEY [US] ET AL) 26 June 1984 (1984-06-26) column 3, line 13 - column 4, line 2 column 14, line 37 - column 15, line 28	1-14, 17-19

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/064524

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4822477 A	18-04-1989	NONE	
GB 1508777 A	26-04-1978	NONE	
US 2514288 A	04-07-1950	NONE	
US 2013172650 A1	04-07-2013	US 2013172650 A1	04-07-2013
		WO 2013103515 A1	11-07-2013
US 4456779 A	26-06-1984	AR 247191 A1	30-11-1994
		AU 568636 B2	07-01-1988
		BR 8401942 A	04-12-1984
		CA 1215078 A	09-12-1986
		DE 3464894 D1	27-08-1987
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		JP S59206484 A	22-11-1984
		NZ 207608 A	20-02-1987
		US 4456779 A	26-06-1984
		ZA 8402746 B	27-11-1985

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 15, 16

1 A meaningful search is not possible on the basis of claims 15 and 16.

1.1 Claim 15 defines a conversion product comprising "at least about 0.1 wt.% more of one or more of carbon dioxide and carbon monoxide compared to a level of carbon monoxide and carbon dioxide in the olefin-containing feed."

1.2 The attention of the applicant is drawn to the fact that "the patentability of a product defined by a product-by-process claim does not depend on its method of production. A product is not rendered novel merely by the fact that it is produced by means of a new process" (PCT Guidelines 5.26-27 and A5.26[1]).

1.3 Therefore, that the product results from a process for upgrading an olefin-containing feed does not limit the scope of the claim.

1.4 More importantly, the feature above results in a definition that is neither clear nor concise, since the product claimed depends on the feed to the process mentioned in the preamble of the claim. The process itself is also undefined.

1.5 Therefore the skilled person has no means to assess the novelty and inventive step of the above-mentioned feature nor of the claim as a whole.

1.6 Claim 16 is also unclear since it depends on claim 15. In addition, claim 16 is unclear in that it refers to a carbon monoxide/dioxide content which is different from that of claim 15.

1.7 Claims 15 and 16 thus fail to comply with the requirements of Article 6 PCT to such extent that no meaningful search can be performed.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.