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(54) UPGRADING OLEFIN-CONTAINING FEEDS TO DIESEL BOILING RANGE COMPOUNDS

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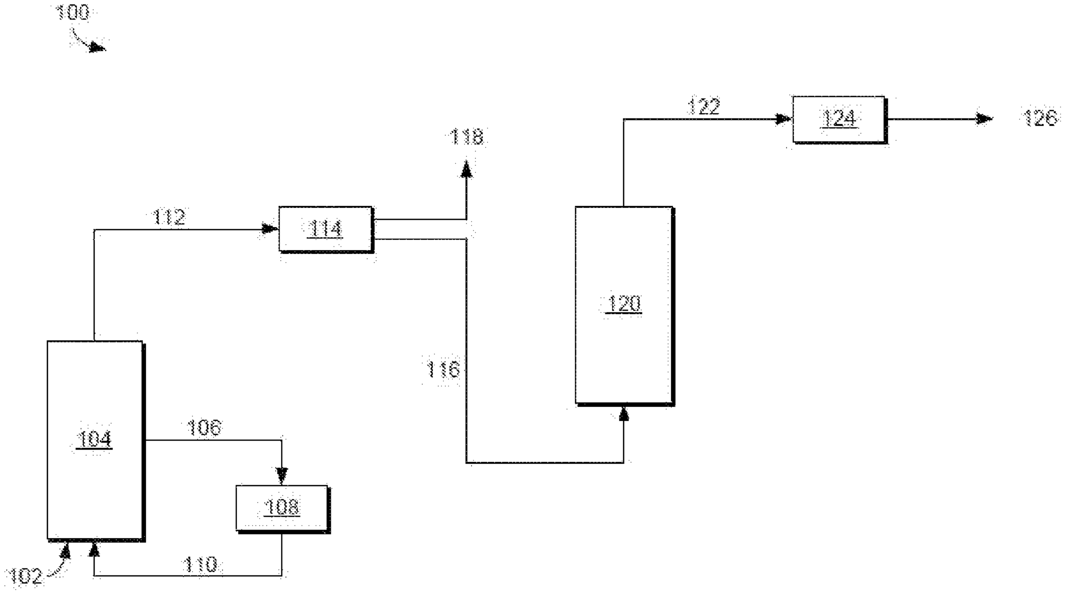
(57) ABSTRACT

Systems and methods are provided for producing diesel boiling range compounds from an olefin-containing feed. The olefin-containing feed can include a refinery fuel gas and/or a naphtha feed. The olefin-containing feed can be exposed to a first set of conversion conditions that can include a low pressure to produce an oligomerized olefin effluent. The oligomerized olefin effluent can be exposed to a second set of conversion conditions that include a higher pressure than the first set of conversion conditions to produce a product effluent that includes diesel boiling range compounds.



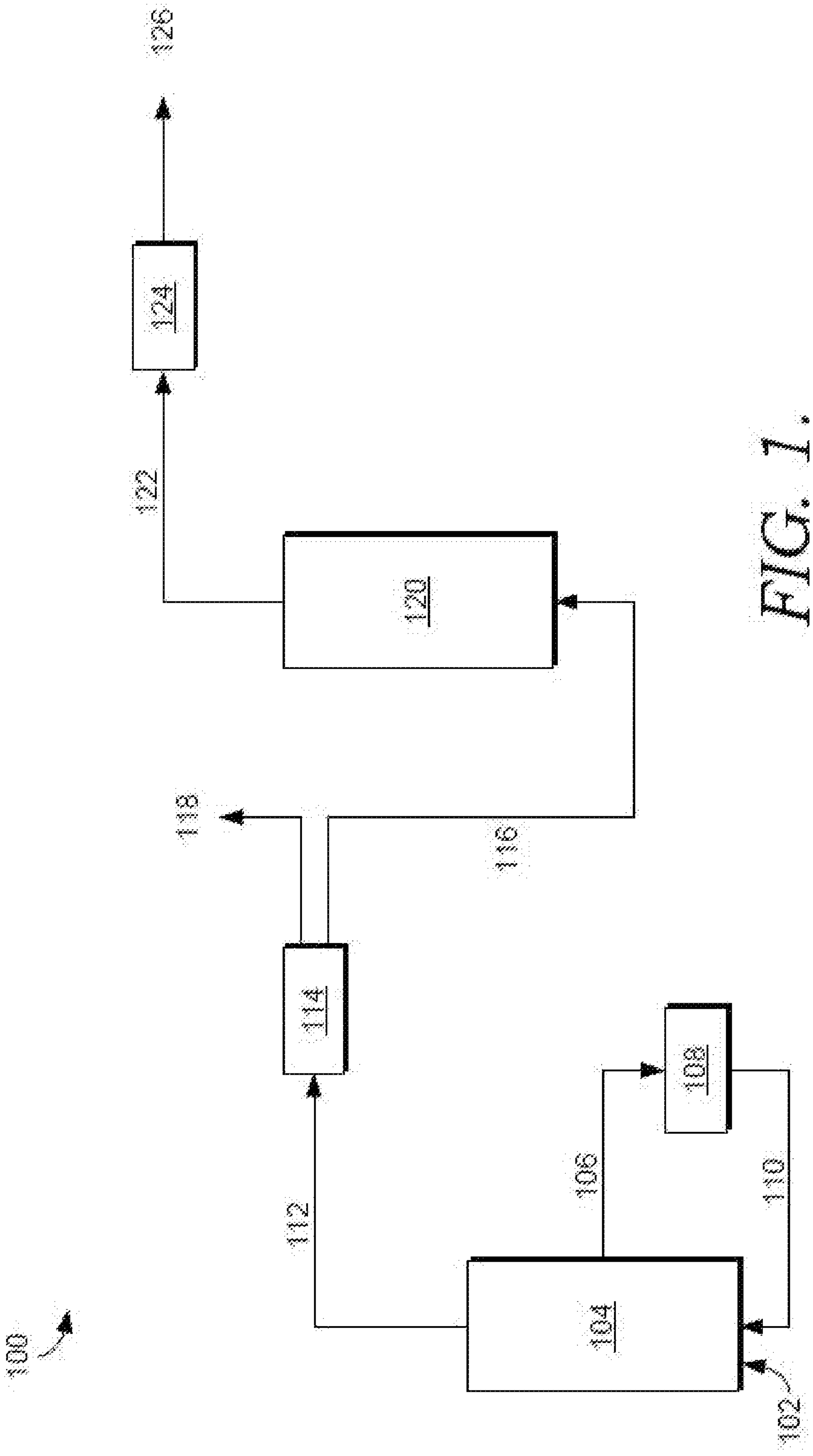


FIG. 1.

UPGRADING OLEFIN-CONTAINING FEEDS TO DIESEL BOILING RANGE COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application Ser. No. 62/247,289 filed Oct. 28, 2015, which is herein incorporated by reference in its entirety.

FIELD

[0002] Systems and methods are provided for the manufacture of diesel boiling range compounds from olefin-containing feeds.

BACKGROUND

[0003] Converting olefin-containing feeds to diesel fuel is a potentially industrially valuable process; however, many barriers remain for such a process to he commercially valuable. For example, it was conventionally thought that forming diesel fuel from olefin-containing feeds would require high pressure and a fixed bed reactor. However, such processes can be highly exothermic and require multiple beds to allow for intermediate cooling. Additionally, processes that utilize specific low weight olefin feeds, such as olefin feeds from crackers, can lead to poor cycle length and/or incomplete conversion due to the presence of sulfur, nitrogen, di-olefins, and/or paraffins in the feed. Further, typical low weight feeds containing ethylene can be difficult to compress due to the presence of methane in the feed.

[0004] U.S. Pat. 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.

[0005] U.S. Pat. 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

[0006] In an aspect, a method for converting an olefin-containing feed to diesel boiling range compounds is provided, comprising: exposing an olefin-containing feed having an olefin content of at least about 10 wt % to a conversion catalyst under first effective conversion conditions to form an oligomerized olefin effluent comprising C_5+ olefinic compounds, wherein the first effective conversion conditions comprise a pressure of less than about 300 psig (2.1 MPa) and a temperature of from about 550° F. (288° C.) to about 800° F. (427° C.); and exposing at least a portion of the C_5+ olefinic compounds to effective fixed bed conversion conditions to form a product effluent comprising diesel boiling range compounds, wherein the effective fixed bed conversion conditions comprise a pressure of at least about 300 psig and a temperature of from about 400° F. (204° C.) to about 700° F. (371° C.), wherein the first effective conversion conditions comprise a pressure that is at least about 50 psi (0.3 MPa) lower than the effective fixed bed conversion conditions.

[0007] In another aspect, a method for converting an olefin-containing feed to diesel boiling range compounds is provided, comprising: exposing an olefin-containing feed having an olefin content of at least about 10 wt % to first effective conversion conditions comprising fluidized bed conditions to form an oligomerized olefin effluent comprising C_5+ olefinic compounds, wherein the effective conversion conditions in the first reaction vessel include a pressure of from about 50 psig to about 250 psig and a temperature of from about 550° F. (288° C.) to about 800° F. (427° C.); separating at least a portion of the oligomerized olefin effluent to form a first fraction comprising at least a portion of the C_5+ olefinic compounds and a second fraction comprising compounds having three carbon atoms or less; and exposing the at least a portion of the C_5+ olefinic compounds to effective conversion conditions in a second reaction vessel to form a product effluent comprising diesel boiling range compounds, wherein the effective conversion conditions in the second reaction vessel include a pressure of from about 300 psig (2.1 MPa) to about 1500 psig (10.3 MPa) and a temperature of from about 550° F. (288° C.) to about 700° F. (371° C.).

[0008] In still another aspect, a diesel boiling range effluent is provided, the diesel boiling range effluent comprising at least a first wt % of C_{10+} oligomerized compounds and/or at least a second wt % of C_{10+} olefins, the C_{10+} oligomerized compounds and/or C_{10+} olefins optionally being formed by oligomerization of C_{2-5} olefins.

BRIEF DESCRIPTION OF THE FIGURES

[0009] FIG. **1** schematically shows an example of a reaction system for converting an olefin-containing feed to a product effluent comprising diesel boiling range compounds, according to an aspect of the invention.

DETAILED DESCRIPTION

Overview

[0010] In various aspects, systems and methods are provided for producing diesel boiling range compounds from an olefin-containing feed. In one or more aspects, the olefin-containing feed can include fuel gas, FCC naphtha, and/or olefinic naphtha. The olefin-containing feed is exposed to a first set of conversion conditions in a first reaction vessel, which can include exposure to an acidic catalyst at a low pressure. At least a portion of the effluent from this first set of conversion conditions can include oligomerized olefins (such as C_5+ olefins) and/or the effluent can exhibit a reduced sulfur content. The effluent from this first set of conversion conditions can then be exposed to a second set of conversion conditions that can include exposure to an acidic catalyst at a higher pressure than the pressure in the first set of conversion conditions. The product effluent from the second set of conditions, which can include diesel boiling range compounds, can be optionally hydrotreated to enhance one or more of its properties. Depending on the feed, this can provide a variety of advantages. For example, converting the olefins in fuel gas to a product effluent having diesel boiling range compounds can enhance refinery economics, as fuel gas is typically utilized for low value purposes. Converting FCC naphtha to a product having diesel boiling range compounds in the methods disclosed herein can allow for sulfur reduction of the FCC naphtha without any external hydrogen supply. In one or more aspects, an existing reaction vessel, e.g., an idle hydrotreating or reformer reactor, can be re-rated for use as the second reaction vessel, further enhancing refinery economics.

[0011] One of the difficulties with conventional oligomerization methods is that the oligomerization catalysts are susceptible to coking and/or poisoning, such as by ammonia or other basic compounds. As coke and/or poison(s) form on the catalyst, the catalyst can become deactivated, leading to a reduced activity. The oligomerization process can also tend to be exothermic, which can pose problems for temperature control. In various aspects, one or more of the above difficulties can be reduced or minimized by performing the processes described herein in a fluidized bed reactor or riser reactor. Alternatively, moving bed and fixed bed reactor systems can also be used.

[0012] Another difficulty with conventional oligomerization processes is that it is difficult to handle low molecular weight gases in the feed. Compressing low molecular weight gases, such as methane or ethylene, can require a substantial equipment investment due to the difficulties in compressing such gases. Additionally, low molecular weight olefins are often accompanied by other low molecular weight alkanes that are unreactive, which also require compression without providing any reaction value. Many conventional processes avoid the use of feeds with low molecular weight components in order to mitigate the expense of compression.

[0013] In some aspects, the systems and processes described herein can address one or more of the above problems. A first fluidized bed oligomerization reactor can be operated at low pressure and under fluidized bed conditions. The low pressure can facilitate using a feed with low molecular weight components, thus allowing C_2 and/or C_3 olefins to be used with high conversion per pass (such as 90+%) for formation of larger olefins. The fluidized bed conditions can also allow for control of temperature within the reactor and/or allow for regeneration of catalyst to remove coke and/or temporary poisons. After the initial oligomerization, a separation can be performed to remove low molecular weight components. The remaining portion of the oligomerized effluent can then be passed to a second oligomerization stage for formation of diesel boiling range compounds. Optionally, the second oligomerization stage can be a fixed bed stage. Because the feed into the second oligomerization stage is already partially reacted, the second stage can be operated at higher pressure while still having a reduced or minimized amount of coke and/or temporary poisons formation on the catalyst. The combination of the first lower pressure oligomerization stage and the second higher pressure oligomerization stage can allow a variety of low value refinery streams to be effectively converted to diesel boiling range compounds, such as fuel gas, flue gas from a cracking or coking process, or another olefin-containing stream. Additionally or alternately, at least a portion of the feed can correspond to 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. or less, or about 250° F. or less, or about 225° F. or less. The lower boiling portion from such a separation can be used as a feed while the higher boiling portion could be used for any convenient purpose, such as in a naphtha boiling range fuel.

[0014] 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, "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

[0015] 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 or flue gas from a cracking or coking process. 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.

[0016] In various aspects, the olefin-containing feed can include 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 % olefins. In the same or alternative aspects, the olefin-containing feed can include less than about 100 wt %, less than about 90 wt %, less than about 80 wt %, or less than about 70 wt % olefins.

[0017] In various aspects, the olefin-containing feed can include 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 %, at least about 50 wt %, at least about 60 wt %, or at least about 70 wt % C_1-C_3 hydrocarbon compounds, with a portion being C_2-C_3 olefins, such as the olefin amounts listed above. In the same or alternative aspects, the olefin-containing feed can include less than about 100 wt %, less than about 90 wt %, less than about 80 wt %, or less than about 70 wt % C_1-C_3 hydrocarbon compounds, with a portion being C_2-C_3 olefins, such as the olefin amounts listed above. In certain aspects, the olefin-containing feed can include C_1-C_3 hydrocarbon compounds, with a portion being C_2-C_3 olefins, such that the C_1-C_3 hydrocarbon compounds are at least about 10 wt % greater, 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 than the amount (wt %) of C_2-C_3 olefins.

[0018] In one or more aspects, the olefin-containing feed can include 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 %, at least about 50 wt %, at least about 60 wt %, or at least about 70 wt % C_1-C_4 hydrocarbon compounds, with a portion being C_2-C_4 olefins, such as the olefin amounts listed above. In the same or alternative aspects, the olefin-containing feed can include less than about 100 wt %, less than about 90 wt %, less than about 80 wt %, or less than about 70 wt % C_1-C_4 hydrocarbon compounds, with a portion being C_2-C_4 olefins, such as the olefin amounts listed above. In certain aspects, the olefin-containing feed can include C_1-C_4 hydrocarbon compounds, with a portion being C_2-C_4 olefins, such that the C_1-C_4 hydrocarbon compounds are at least about 10 wt % greater, 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 than the amount (wt %) of C_2-C_4 olefins.

[0019] In one or more aspects, the olefin-containing feed can include 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 %, at least about 50 wt %, at least about 60 wt %, or at least about 70 wt % C_1-C_5 hydrocarbon compounds, with a portion being C_2-C_5 olefins, such as the olefin amounts listed above. In the same or alternative aspects, the olefin-containing feed can include less than about 100 wt %, less than about 90 wt %, less than about 80 wt %, or less than about 70 wt % C_1-C_5 hydrocarbon compounds, with a portion being C_2-C_5 olefins, such as the olefin amounts listed above. In certain aspects, the olefin-containing feed can include C_1-C_5 hydrocarbon compounds, with a portion being C_2-C_5 olefins, such that the C_1-C_5 hydrocarbon compounds are at least about 10 wt % greater, 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 than the amount (wt %) of C_2-C_5 olefins.

[0020] In one or more aspects, the olefin-containing feed can include 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 %, at least about 50 wt %, at least about 60 wt %, or at least about 70 wt % C_1-C_9 hydrocarbon compounds, with a portion being C_2-C_9 olefins, such as the olefin amounts listed above. In the same or alternative aspects, the olefin-containing feed can include less than about 100 wt %, less than about 90 wt %, less than about 80 wt %, or less than about 70 wt % C_1-C_9 hydrocarbon compounds, with a portion being C_2-C_9 olefins, such as the olefin amounts listed above. In certain aspects, the olefin-containing feed can include C_1-C_9 hydrocarbon compounds, with a portion being C_2-C_9 olefins, such that the C_1-C_9 hydrocarbon compounds are at least about 10 wt % greater, 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 than the amount (wt %) of C_2-C_9 olefins.

[0021] 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 %.

[0022] As discussed above, in various aspects, the olefin-containing feed can include one or more low value refinery streams, such as refinery fuel gas or flue gas from a cracking or coking process. 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 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 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.

[0023] 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 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.

[0024] In certain aspects, the olefin-containing feed can include a hydrocarbon feed having a boiling point less than the boiling point of diesel boiling range compounds. In such aspects, the olefin-containing feed can exhibit a final or T95 boiling point of less than about 350° F. (177° C.), less than about 325° F. (163° C.), less than about 300° F. (149° C.), less than about 275° F. (135° C.), or less than about 250° F. (121° C.).

[0025] In various aspects, the olefin-containing feed can have a sulfur content of at least about 100 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.

[0026] 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.

[0027] 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.

Conditions for Oligomerizing Olefins in an Olefin-Containing Feed

[0028] 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 (about 17 m^3/m^3) of added hydrogen, or less than about 50 SCF/bbl (about 10 m^3/m^3); b) a partial pressure of less than about 50 psia (350 kPa) of hydrogen, or less than about 15 psia (100 kPa); or c) a combination thereof.

[0029] The acidic catalyst used in the processes described herein can be any alumina-containing catalyst, such as a zeolite-based catalyst. For example, the acidic catalyst 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.

[0030] 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.

[0031] 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.

[0032] 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, 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.

[0033] 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.

[0034] 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 Brønsted 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.

[0035] 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).

[0036] 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.

[0037] 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.

[0038] 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.

[0039] 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 catalyst can be about 100 or less. Sulfur conversion to hydrogen sulfide can increase as the alpha value increases.

[0040] The Alpha Test is described in U.S. Pat. No. 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.

[0041] In various aspects, the olefin-containing feed may be exposed to the acidic catalyst by using a moving or fluid catalyst bed reactor. In such aspects, the catalyst may be regenerated, such via continuous oxidative regeneration. The extent of coke loading on the catalyst can then be continuously controlled by varying the severity and/or the frequency of regeneration. In a turbulent fluidized catalyst bed the conversion reactions are conducted in a vertical reactor column by passing hot reactant vapor upwardly through the reaction zone and/or reaction vessel at a velocity greater than dense bed transition velocity and less than transport velocity for the average catalyst particle. A continuous process is operated by withdrawing a portion of coked catalyst from the reaction zone and/or reaction vessel, oxidatively regenerating the withdrawn catalyst and returning regenerated catalyst to the reaction zone at a rate to control catalyst activity and reaction severity to effect feedstock conversion. Preferred 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 Gould et al. U.S. Pat. No. 4,579,999, incorporated herein by reference. In other aspects, other types of reactors can be used, such as fixed bed reactors, riser reactors, fluid bed reactors, and/or moving bed reactors.

[0042] In one or more aspects, the effective conversion conditions for exposing the olefin-containing feed to an acidic catalyst can include a temperature of about 500° F. (177° C.) to about 900° F. (482° C.), or about 550° F. (260° C.) to about 800° F. (427° C.), or about 650° F. (343° C.) to about 750° F. (399° C.); a pressure of about 50 psig (0.34 MPag) to about 350 psig (2.4 MPag), or about 100 psig (0.69 MPag) to about 300 psig (4.1 MPag), or about 100 psig (0.69 MPag) to about 200 psig (1.4 MPag), or a pressure of about 350 psig (2.4 MPag) or less, or a pressure of about 300 psig (4.1 MPag) or less; 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}.

[0043] 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 selectivity, reactivity, and run length. Temperatures below 550° F. can result in unacceptably low reaction rates due to reduced reactivity for catalyzing the oligomerization reaction. Temperatures above about 700° F. (371° C.) can lead to increased formation of saturates, which are not as desirable for subsequently producing diesel boiling range fuel.

[0044] In various aspects, exposing an olefin-containing feed to the conversion conditions discussed above can produce an effluent that includes oligomerized olefins. In such aspects, this oligomerized olefin effluent can include an increased C_5+ content compared to the olefin-containing feed. In certain aspects, 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % of the olefins from the olefin-containing feed can be incorporated into the oligomerized olefins in the oligomerized olefin effluent. In one or more aspects, the oligomerized olefin effluent can have a reduced sulfur content compared to the olefin-containing feed. In such aspects, the sulfur content of the oligomerized olefin 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, or about 5 wppm or less. Additionally or alternately, exposing an olefin-containing feed to the conversion conditions discussed above can achieve at least about 50% desulfurization of the olefin-containing feed, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%.

Fractionation of the Oligomerized Olefin Effluent

[0045] In one or more aspects, prior to converting the oligomerized olefin effluent to a product having diesel boiling range compounds, the oligomerized olefin effluent can be fractionated or separated, e.g., to remove a lighter portion. For example, in such aspects, at least a portion of the C_4 (or C_3 or C_2) or lower carbon-containing species can be separated from the oligomerized olefin effluent. It is appreciated that any type of general separating process can be utilized to separate out a portion of the oligomerized olefin effluent, such as by adjusting the temperature and/or pressure, or exposing the oligomerized olefin effluent to a simple liquid-vapor separator and/or a distillation column having one or more trays. In one aspect, the diesel fraction present in the first reactor effluent can be fractionated to prevent further reaction in the second stage. This can improve or maximize diesel yield and in particular can improve or maximize formation of a lighter distillate fraction which can reduce or minimize viscosity and pour point of diesel fuel.

[0046] In various aspects, a fractionation or separation process can remove compounds having four carbon atoms (C_4) or less, compounds having three carbon atoms (C_3) or less, or compounds having two carbon atoms (C_2) or less from the oligomerized olefin effluent.

[0047] By removing the lighter carbon species from the oligomerized olefin effluent, the subsequent conversion of the oligomerized olefin effluent to a product that includes diesel boiling range compounds may be more economically favorable. For example, cutting the lighter compounds from the oligomerized olefin effluent allows for the subsequent conversion step to have a higher olefin concentration in the feed to improve or maximize diesel production while still having a reduced or minimal amount of coking of the catalyst.

Conversion of an Oligomerized Olefin Effluent to Diesel Boiling Range Compounds

[0048] In various aspects, the oligomerized olefin effluent can be exposed to effective conversion conditions to form a product effluent with at least a portion being in the diesel boiling range. The oligomerized olefin effluent can be exposed to an acidic catalyst, such as the acidic catalysts discussed above. In one or more aspects, the oligomerized Olefin effluent can be exposed to one or more catalyst beds of the acidic catalysts discussed above or other catalyst, in one or more fixed bed reactors. Effective conversion conditions for exposing the olefin-containing feed to an acidic catalyst can include a temperature of about 350° F. (177° C.)

to about 750° F. (399° C.), or about 400° F. (204° C.) to about 700° F. (371° C.), or about 500° F. (260° C.) to about 650° F. (343° C.), or about 450° F. (232° C.) to about 650° F. (316° C.); a pressure of about 200 psig (1.4 MPag) to about 1000 psig (6.9 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 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}. The reactor is optionally but preferably a fixed bed reactor system. Considering the feed was previously partially oligomerized and its coke precursors and poisons at least substantially removed, the heat of reaction can be managed in a fixed bed reaction section.

[0049] The product effluent can include diesel boiling range compounds. In various aspects, the product effluent can include compounds with 10 or more carbon atoms (C_{10}+ compounds). In such aspects, the C_{10}+ compounds can be 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 %, at least about 70 wt %, at least about 80 wt %, at least about 90 wt %, at least about 95 wt % or at least about 99 wt % of the total weight of the product effluent. The product effluent can exhibit an initial (or T5) boiling point of at least about 250° F. (121° C.), at least about 300° F. (149° C.), or at least about 350° F. (177° C.), and/or exhibit a final (or T95) boiling point of about 800° F. (427° C.) or less, about 750° F. (399° C.) or less, or about 700° F. (371° C.) or less. The product effluent can have a boiling range (initial or T5 to T95 or final) of from about 250° F. (121° C.) to about 800° F. (427° C.), or from about 300° F. (149° C.) to about 750° F. (399° C.), or from about 350° F. (177° C.) to about 700° F. (371° C.). The product effluent can have an aromatic content of less than about 20 wt %, less than about 15 wt %, less than about 10 wt %, less than about 5 wt %, or less than about 1 wt %. Due to the nature of how the C_{10+} compounds are formed by oligomerization, a substantial percentage of the C_{10+} compounds can correspond to olefins, In various aspects, 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % of the C_{10+} compounds in the product effluent can be olefins.

[0050] In various aspects, the oligomerized C_{10+} compounds in the product effluent can correspond to 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % of the weight of olefins in the olefin-containing feed. In other words, 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % of the olefins present in the olefin-containing feed can be incorporated into the oligomerized C_{10+} compounds in the product effluent. Additionally or alternatively, the oligomerized C_{10+} compounds in the product effluent can correspond to 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 %, at least about 70 wt %, or at least about 80 wt % of the weight of oligomerized olefins in the oligomerized olefin effluent. In other words, 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 %, at least about 70 wt %, or at least about 80 wt % of the oligomerized olefins from the oligomerized olefin effluent can be incorporated into the oligomerized C_{10+} compounds in the product effluent.

Optional Hydrotreatments of the Product Effluent

[0051] Optionally, the product effluent can be treated in one or more hydroprocessing stages to improve properties of the product effluent. In various aspects, the product effluent can be subjected to hydroprocessing for one or more of sulfur reduction, olefin saturation, and/or dewaxing, such as iso-dewaxing (i.e., by catalytic dewaxing in the presence of a catalyst that dewaxes primarily by isomerization).

[0052] The reaction conditions for sulfur reduction hydroprocessing can include an LHSV of 0.3 to 5.0 hr^{-1}, a total pressure from about 200 psig (1.4 MPag) to about 3000 psig (20.7 MPa), a treat gas containing at least about 80% hydrogen (remainder inert gas), and a temperature of from about 500° F. (260° C.) to about 800° F. (427° C.). Preferably, the reaction conditions include an LHSV of from about 0.5 to about 1.5 hr^{-1}, a total pressure from about 700 psig (4.8 MPa) to about 2000 psig (13.8 MPa), and a temperature of from about 600° F. (316° C.) to about 700° F. (399° C.). The treat gas rate can be from about 500 SCF/B (84 Nm^3/m^3) to about 10000 SCF/B (1685 Nm^3/m^3) of hydrogen, depending on various factors including the nature of the feed being hydrotreated. Note that the above treat gas rates refer to the rate of hydrogen flow. If hydrogen is delivered as part of a gas stream having less than 100% hydrogen, the treat gas rate for the overall gas stream can be proportionally higher.

[0053] In some aspects, the hydroprocessing can reduce the sulfur content of the product effluent to a suitable level. For example, the sulfur content can be reduced sufficiently so that the product effluent can have about 500 wppm sulfur or less, or about 250 wppm or less, or about 100 wppm or less, or about 50 wppm or less, or about 20 wppm or less, or about 10 wppm or less, or about 5 wppm or less. Additionally or alternately, the sulfur content of the product effluent can be at least about 1 wppm sulfur, or at least about 5 wppm, or at least about 10 wppm.

[0054] The catalyst in a hydroprocessing treatment for reducing sulfur content can be a conventional hydrotreating catalyst, such as a catalyst composed of a Group VIB metal (Group 6 of IUPAC periodic table) and/or a Group VIII metal (Groups 8-10 of IUPAC periodic table) on a support. Suitable metals include cobalt, nickel, molybdenum, tungsten, or combinations thereof. Preferred combinations of metals include nickel and molybdenum or nickel, cobalt, and molybdenum. Suitable supports include silica, silica-alumina, alumina, and titania.

[0055] After hydroprocessing for reducing sulfur content, the hydrotreated effluent can optionally but preferably be separated, such as by separating the gas phase effluent from a liquid phase effluent, in order to remove gas phase contaminants generated during hydroprocessing. Alternatively, in some aspects the entire hydrotreated effluent can be cascaded into another hydroprocessing stage, such as a stage for iso-dewaxing.

[0056] In olefin saturation (hydrofinishing) treatment, a feed, e.g., the product effluent, can be exposed to a hydrofinishing catalyst. Hydrofinishing catalysts can include catalysts containing Group VI metals, Group VIII metals, and mixtures thereof. In an aspect, preferred metals include at least one metal sulfide having a strong hydrogenation function. In another aspect, the hydrofinishing catalyst can include a Group VIII noble metal, such as Pt, Pd, or a combination thereof. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is about 30 wt % or greater based on catalyst. Suitable metal oxide supports include low acidic oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. The preferred hydrofinishing catalysts will comprise at least one metal having relatively strong hydrogenation function on a porous support. Typical support materials include amorphous or crystalline oxide materials such as alumina, silica, and silica-alumina. The support materials may also be modified, such as by halogenation, or in particular fluorination. The metal content of the catalyst is often as high as about 20 wt % for non-noble metals. In an aspect, a preferred hydrofinishing catalyst can include a crystalline material belonging to the M41S class or family of catalysts. The M41S family of catalysts are mesoporous materials having high silica content. Examples include MCM-41, MCM-48 and MCM-50. A preferred member of this class is MCM-41.

[0057] Hydrofinishing conditions can include temperatures from about 125° C. (257° F.) to about 425° C. (797° F.), or about 180° C. (356° F.) to about 280° C. (536° F.); a total pressure from about 200 psig (1.4 MPa) to about 800 psig (5.5 MPa), or about 400 psig (2.8 MPa) to about 700 psig (4.8 MPa); and a liquid hourly space velocity from about 0.1 hr^{-1} to about 5 hr^{-1} LEW, preferably about 0.5 hr^{-1} to about 1.5 hr^{-1}. The treat gas rate can be selected to be similar to a catalytic dewaxing stage discussed below, similar to a hydroprocessing for sulfur reduction discussed above, or any other convenient selection.

[0058] In various aspects, the product effluent (or an effluent of one or more of the hydroprocesses discussed above) can undergo a dewaxing hydrotreatment, e.g., to improve one or more cold flow properties of a diesel fuel such as pour point or cloud point. In such aspects, the product effluent can be exposed to a dewaxing catalyst under effective dewaxing conditions to produce a dewaxed effluent.

[0059] Suitable dewaxing catalysts can include molecular sieves such as crystalline aluminosilicates (zeolites). In some aspects, any conventional dewaxing catalyst can be used. In other aspects, the molecular sieve can comprise, consist essentially of, or be ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, zeolite Beta, or a combination thereof, for example ZSM-23 and/or ZSM-48, or ZSM-48 and/or zeolite Beta. Optionally, molecular sieves that are selective for dewaxing by isomerization as opposed to cracking can be used, such as ZSM-48, zeolite Beta, ZSM-23, or a combination thereof. Additionally or alternately, the molecular sieve can comprise, consist essentially of or be a 10-member ring 1-D molecular sieve. Examples include EU-1, ZSM-35 (or ferrierite), ZSM-11, ZSM-57, NU-87, SAPO-11, ZSM-48, ZSM-23, and ZSM-22. In certain aspects, the molecular sieve includes EU-2, EU-11, ZBM-30, ZSM-48, or ZSM-23. Note that a zeolite having the ZSM-23 structure with a silica to alumina ratio of from about 20:1 to about 40:1 can sometimes be referred to as SSZ-32. Other molecular sieves that are isostructural with the above materials include Theta-1, NU-10, EU-13, KZ-1, and NU-23. Optionally, the dewaxing catalyst can include a binder for the molecular sieve, such as alumina, titania, silica, silica-alumina, zirconia, or a combination thereof, for example alumina and/or titania or silica and/or zirconia and/or titania.

[0060] In various aspects, the dewaxing catalysts can he catalysts with a low ratio of silica to alumina. For example, for ZSM-48, the ratio of silica to alumina in the zeolite can be less than about 200:1, such as less than about 110:1, or less than about 100:1, or less than about 90:1, or less than about 75:1. In various embodiments, the ratio of silica to alumina can be from 50:1 to 200:1, such as 60:1 to 160:1, or 70:1 to 100:1.

[0061] In one or more aspects, the catalysts can further include a metal hydrogenation component. The metal hydrogenation component is typically a Group VI and/or a Group VIII metal. In certain aspects, the metal hydrogenation component can be a Group VIII noble metal. In one or more aspects, the metal hydrogenation component can be Pt, Pd, or a mixture thereof. In an alternative aspect, the metal hydrogenation component can be a combination of a non-noble Group VIII metal with a Group VI metal. Suitable combinations can include Ni, Co, or Fe with Mo or W, preferably Ni with Mo or W.

[0062] The metal hydrogenation component may be added to the catalyst in any convenient manner, One technique for adding the metal hydrogenation component is by incipient wetness. For example, after combining a zeolite and a binder, the combined zeolite and binder can be extruded into catalyst particles. These catalyst particles can then be exposed to a solution containing a suitable metal precursor. Alternatively, metal can he added to the catalyst by ion exchange, where a metal precursor is added to a mixture of zeolite (or zeolite and binder) prior to extrusion.

[0063] The amount of metal in the catalyst can be at least 0.1 wt. % based on catalyst, or at least 0.15 wt %, or at least 0.2 wt %, or at least 0.25 wt %, or at least 0.3 wt %, or at least 0.5 wt % based on catalyst. The amount of metal in the catalyst can be 20 wt % or less based on catalyst, or 10 wt % or less, or 5 wt % or less, or 2.5 wt % or less, or 1 wt % or less. For aspects where the metal is Pt, Pd, another Group VIII noble metal, or a combination thereof, the amount of metal can be from 0.1 to 5 wt %, preferably from 0.1 to 2 wt %, or 0.25 to 1.8 wt %, or 0.4 to 1.5 wt %. For aspects where the metal is a combination of a non-noble Group VIII metal with a Group VI metal, the combined amount of metal can be from 0.5 wt % to 20 wt %, or 1 wt % to 15 wt %, or 2.5 wt % to 10 wt %.

[0064] Process conditions in a catalytic dewaxing zone can include a temperature of from 200 to 450° C., preferably 270 to 400° C., an LHSV from about 0.2 h^{-1} to about 10 h^{1}, such as from about 0.5 h^{-1} to about 5 h^{-1}, and a treat gas rate of from 35.6 m^3/m^3 (200 SCF/B) to 1781 m^3/m^3 (10,000 SCF/B), preferably 178 m^3/m^3 (1000 SCF/B) to 890.6 m^3/m^3 (5000 SCF/B). With regard to pressure, the dewaxing can be performed at a pressure of about 300 psig (2.1 MPag) to about 700 psig (4.8 MPag), or about 300 psig (2.1 MPag) to about 600 psig (4.2 MPag), or about 300 psig (2.1 MPag) to about 500 psig (3.5 MPag), or about 400 psig (2.8 MPag) to about 700 psig (4.8 MPag), or about 400 psig (2.8 MPag) to about 600 psig (4.2 MPag), or about 400 psig (2.8 MPag) to about 500 psig (3.5 MPag), or about 500 psig (3.5 MPag) to about 700 psig (4.8 MPag).

[0065] Catalytic dewaxing can be performed by exposing a feedstock to a dewaxing catalyst under effective (catalytic) dewaxing conditions. Effective dewaxing conditions can include a temperature of at least about 500° F. (260° C.), or at least about 550° F. (288° C.), or at least about 600° F. (316° C.), or at least about 650° F. (343° C.). Alternatively, the temperature can be about 750° F. (399° C.) or less, or about 700° F. (371° C.) or less, or about 650° F. (343° C.) or less. The pressure can be at least about 200 psig (1.4 MPa), or at least about 500 psig (3.4 MPa), or at least about 750 psig (5.2 MPa), or at least about 1000 psig (6.9 MPa). Alternatively, the pressure can be about 1500 psig (10.3 MPa) or less, or about 1200 psig (8.2 MPa) or less, or about 1000 psig (6.9 MPa) or less, or about 800 psig (5.5 MPa) or less. The Liquid Hourly Space Velocity (LHSV) can be at least about 0.5 hr^{-1}, or at least about 1.0 hr^{-1}, or at least about 1.5 hr^{-1}. Alternatively, the LHSV can be about 5.0 hr^{-1} or less, or about 3.0 hr^{-1} or less, or about 2.0 hr^{-1} or less. The treat gas rate can be at least about 500 SCF/bbl (84 m^3/m^3), at least about 750 SCF/bbl (126 m^3/m^3), or at least about 1000 SCF/bbl (169 m^3/m^3). Alternatively, the treat gas rate can be about 4000 SCF/bbl (674 m^3/m^3) or less, or about 2000 SCF/bbl (337 m^3/m^3) or less, or about 1500 SCF/bbl (253 m^3/m^3) or less, or about 1250 SCF/bbl (211 m^3/m^3) or less.

[0066] Based on dewaxing under effective catalytic dewaxing conditions, the cloud point of a dewaxed effluent can be reduced relative to the dewaxing feedstock (e.g., the product effluent (or an effluent of one or more of the hydroprocesses discussed above)) by at least about 10° F. (5° C.), such as at least about 20° F. (11° C.), or at least about 30° F. (17° C.). The amount of cloud point reduction can depend on a variety of factors, including the sulfur content of the feedstock, the nitrogen content of the feedstock, and the selected effective dewaxing conditions.

Example of Reaction Configuration

[0067] FIG. **1** depicts one example of a reaction system **100** for upgrading an olefin-containing feed to diesel boiling range compounds. Initially, an olefin-containing feed **102** can be exposed to conversion conditions in a first reaction vessel **104**. Although not shown in FIG. **1**, the olefin-containing feed **102** may be heated prior to entering the first reaction vessel **104**. In various aspects, as discussed above, the olefin-containing teed **102** can include one or more of a refinery fuel gas, FCC naphtha, or olefinic naphtha. In the first reaction vessel **104**, the olefin-containing feed **102** can be exposed to a conversion catalyst, such as one or more of the acidic catalysts discussed above. The first reaction vessel **104** can be a fluidized bed reactor. In one or more aspects, a portion **106** of the conversion catalyst in the first reaction vessel **104** can be sent to a regenerator **108** for regeneration. The regenerated catalyst **110** can be returned to the first reaction vessel **104**.

[0068] The effective conversion conditions in the first reaction vessel **104** may result in olefin oligomerization and/or reduction in the sulfur content of the olefin-containing feed. The oligomerized olefin effluent **112** can be exposed to a separator **114** to separate out the lighter compounds, such as compounds **118** having **2** carbon atoms or less, prior to subjecting the remainder **116** of the oligomerized olefin effluent to reaction conditions in a second reaction vessel **120**. The second reaction vessel **120** may be a fixed bed reactor having one or more beds of a conversion catalyst, such as one or more of the acidic catalysts discussed above. The conversion conditions in the second reaction vessel **120** can include a pressure that is greater than the pressure of that in the first reaction vessel **104**. The product effluent **122** can include diesel boiling range compounds. Optionally, at least a portion of the product effluent **122** can be exposed to one or more hydroprocessor(s) **124**. The hydroprocessor(s) **124** can he utilized to reduce the sulfur content of the product effluent, for olefinic saturation, and/or for dewaxing, as discussed above.

Additional Embodiments

Embodiment 1

[0069] A method for converting an olefin-containing feed to diesel boiling range compounds, comprising: exposing an olefin-containing feed having an olefin content of at least about 10 wt % to a conversion catalyst under first effective conversion conditions to form an oligomerized olefin effluent comprising C_5+ olefinic compounds, wherein the first effective conversion conditions comprise a pressure of less than about 300 psig (2.1 MPa) and a temperature of about 550° F. (288° C.) to about 800° F. (427° C.); and exposing at least a portion of the C_5+ olefinic compounds to effective fixed bed conversion conditions to form a product effluent comprising diesel boiling range compounds, wherein the effective fixed bed conversion conditions comprise a pressure of at least about 300 psig (2.1 MPa) and a temperature of about 400° F. (204° C.) to about 700° F. (371° C.), wherein the first effective conversion conditions comprise a pressure that is at least about 50 psi (0.3 MPa) lower than the effective fixed bed conversion conditions.

Embodiment 2

[0070] The method of Embodiment 1, further comprising separating the oligomerized olefin effluent to form at least a first fraction comprising the at least a portion of the C_5+ olefinic compounds and a second fraction comprising compounds having three carbon atoms or less.

Embodiment 3

[0071] A method for converting an olefin-containing feed to diesel boiling range compounds, comprising: exposing an olefin-containing feed having an olefin content of at least about 10 wt % to first effective conversion conditions comprising fluidized bed conditions to form an oligomerized olefin effluent comprising C_5+ olefinic compounds, wherein the effective conversion conditions in the first reaction vessel include a pressure of from about 50 psig to about 250 psig and a temperature of from about 550° F. (288° C.) to about 800° F. (427° C.); separating at least a portion of the oligomerized olefin effluent to form a first fraction comprising at least a portion of the C_5+ olefinic compounds and a second fraction comprising compounds having three carbon atoms or less; and exposing the at least a portion of the C_5+ olefinic compounds to effective conversion conditions in a second reaction vessel to form a product effluent comprising diesel boiling range compounds, wherein the effective conversion conditions in the second reaction vessel include a pressure of about 300 psig (2.1 MPa) to about 1500 psig (10.3 MPa) and a temperature of about 550° F. (288° C.) to about 700° F. (371° C.).

Embodiment 4

[0072] The method of any of the above embodiments, wherein the first effective conversion conditions comprise fluidized bed conditions.

Embodiment 5

[0073] The method of any of the above embodiments, wherein the effective fixed bed conversion conditions comprise a pressure of about 300 psig (2.1 MPa) to about 800 psig (5.5 MPa), a temperature of about 450° F. (232° C.) to about 600° F. (316° C.), or a combination thereof.

Embodiment 6

[0074] The method of any of the above embodiments, wherein the olefin-containing feed comprises refinery fuel gas.

Embodiment 7

[0075] The method of any of the above embodiments, wherein the olefin-containing feed comprises FCC naphtha, olefinic naphtha, or mixtures thereof.

Embodiment 8

[0076] The method of Embodiment 7, wherein the second fraction comprises compounds having four carbon atoms or less.

Embodiment 9

[0077] The method of any of the above embodiments, wherein at least about 60 wt % of the olefins present in the olefin-containing feed are converted to compounds present in the product effluent comprising diesel boiling range compounds, or at least about 70 wt %, or at least about 80 wt %, or at least about 90 wt %.

Embodiment 10

[0078] The method of any of the above embodiments, wherein the aromatic content of the product effluent comprising diesel boiling range compounds is about 20 wt. % or less, or 15 wt % or less, or 10 wt % or less.

Embodiment 11

[0079] The method of any of the above embodiments, further comprising hydrotreating at least a portion of the product effluent comprising diesel boiling range compounds.

Embodiment 12

[0080] The method of any of the above embodiments, wherein the exposing the olefin-containing feed to first effective conversion conditions and/or effective fixed bed conversion conditions comprises exposing the olefin-containing feed to an acidic zeolite catalyst.

Embodiment 13

[0081] The method of any of the above embodiments, wherein the olefin-containing feed comprises about 50 wt % or less of C_{5+} compounds, or about 40 wt % or less, or about 30 wt % or less, or about 20 wt % or less, or about 10 wt % or less, or about 5 wt % or less, wherein the olefin-containing feed comprises about 50 wt % or less of C_5+ olefinic compounds, or about 40 wt % or less, or about 30 wt % or less, or about 20 wt % or less, or about 10 wt % or less, or about 5 wt % or less, or a combination thereof.

Embodiment 14

[0082] The method of any of the above embodiments, wherein the olefin-containing feed comprises C_1-C_4 hydrocarbon compounds, at least a portion of the C_1-C_4 hydrocarbon compounds comprising C_2-C_4 olefins, a weight percentage of the C_2-C_4 olefins relative to the weight of the olefin-containing feed being at least about 10 wt % lower than a weight percentage of the C_1-C_4 hydrocarbon compounds, or at least about 20 wt % lower, or at least about 30 wt % lower, or at least about 40 wt % lower, or at least about 50 wt % lower, or at least about 60 wt % lower.

Embodiment 15

[0083] A system for converting an olefin-containing feed to diesel boiling range compounds, comprising: a fluidized bed reactor comprising a fluidized bed of an acidic molecular sieve, the fluidized bed being fluidized with an olefin-containing feed comprising C_1-C_4 hydrocarbon compounds, the olefin-containing feed having an olefin content of at least about 10 wt %, the bed being fluidized at a pressure of about 50 psig (0.3 MPa) to about 250 psig (1.7 MPa) and a temperature of about 550° F. (288° C.) to about 800° F. (427°C.); a separator in fluid communication with the fluidized bed reactor for performing a separation on an effluent from the fluidized bed reactor; and a fixed bed reactor in fluid communication with the separator to receive a separated fraction comprising C_5+ olefinic compounds, the fixed bed reactor comprising a fixed bed of a second acidic molecular sieve, the fixed bed reactor having a pressure of about 300 psig (2.1 MPa) to about 1500 psig (10.3 MPa) and a temperature of from about 550° F. (288° C.) to about 700° F. (371° C.).

Embodiment 16

[0084] The system of Embodiment **15**, wherein the fixed bed of a second acidic molecular sieve comprises the same molecular sieve as the fluidized bed of an acidic molecular sieve.

Embodiment 17

[0085] The system of Embodiment 15 or 16, wherein at least one of the fluidized bed of an acidic molecular sieve and the fixed bed of a second acidic molecular sieve comprises a zeolite.

Embodiment 18

[0086] The system of any of Embodiments 15 to 17, wherein the molecular sieve or the zeolite comprises a 10-member ring molecular sieve or zeolite.

Embodiment 19

[0087] A diesel boiling range effluent comprising 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % C_{10+} oligomerized compounds, the C_{10+} oligomerized compounds being formed by oligomerization of C_{2-5} olefins.

Embodiment 20

[0088] The diesel boiling range effluent of Embodiment 19, wherein the diesel boiling range effluent comprises 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % C_{10+} olefins.

Embodiment 21

[0089] The diesel boiling range effluent of Embodiment 20, wherein the 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % C_{10+} olefins comprise oligomerized olefins formed by oligomerization of C_{2-5} olefins.

Embodiment 22

[0090] The diesel boiling range effluent of any of Embodiments 19-21, wherein the 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % C_{10+} oligomerized compounds incorporate 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 %, at least about 70 wt %, at least about 80 wt %, or at least about 90 wt % of C_{2-5} olefins present in a feed for the oligomerization of the C_{2-5} olefins.

[0091] 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.

1. A method for converting an olefin-containing feed to diesel boiling range compounds, comprising:

exposing an olefin-containing feed having an olefin content of at least about 10 wt % to a conversion catalyst under first effective conversion conditions to form an oligomerized olefin effluent comprising C_5+ olefinic compounds, wherein the first effective conversion conditions comprise a pressure of less than about 300 psig (2.1 MPa) and a temperature of from about 550° F. (288° C.) to about 800° F. (427° C.) and

exposing at least a portion of the C_5+ olefinic compounds to effective fixed bed conversion conditions to form a product effluent comprising diesel boiling range compounds, wherein the effective fixed bed conversion conditions comprise a pressure of at least about 300 psig and a temperature of from about 400° F. (204° C.) to about 700° F. (371° C.), wherein the first effective conversion conditions comprise a pressure that is at least about 50 psi (0.3 MPa) lower than the effective fixed bed conversion conditions.

2. The method of claim **1**, wherein the first effective conversion conditions comprise fluidized bed conditions.

3. The method of claim **1**, wherein the effective fixed bed conversion conditions comprise a pressure of about 300 psig (2.1 MPa) to about 800 psig (5.5 MPa), a temperature of about 450° F. (232° C.) to about 600° F. (316° C.), or a combination thereof.

4. The method of claim **1**, wherein the olefin-containing feed comprises refinery fuel gas.

5. The method of claim **1**, wherein the olefin-containing feed comprises FCC naphtha, olefinic naphtha, or mixtures thereof.

6. The method of claim **1**, further comprising separating the oligomerized olefin effluent to form at least a first fraction comprising the at least a portion of the C_5+ olefinic compounds and a second fraction comprising compounds having three carbon atoms or less.

7. The method of claim **6**, wherein the second fraction comprises compounds having four carbon atoms or less.

8. The method of claim **1**, wherein the aromatic content of the product effluent comprising diesel boiling range compounds is about 20 wt % or less.

9. The method of claim **1**, further comprising hydrotreating at least a portion of the product effluent comprising diesel boiling range compounds.

10. The method of claim **1**, wherein the exposing the olefin-containing feed to first effective conversion conditions and/or effective fixed bed conversion conditions comprises exposing the olefin-containing feed to an acidic zeolite catalyst.

11. The method of claim **1**, wherein the olefin-containing feed comprises about 30 wt % or less of C_5+ compounds, wherein the olefin-containing feed comprises about 20 wt % or less of C_5+ olefinic compounds, or a combination thereof.

12. The method of claim **1**, wherein the olefin-containing feed comprises C_1-C_4 hydrocarbon compounds, at least a portion of the C_1-C_4 hydrocarbon compounds comprising C_2-C_4 olefins, a weight percentage of the C_2-C_4 olefins relative to the weight of the olefin-containing feed being at least about 10 wt % lower than a weight percentage of the C_1-C_4 hydrocarbon compounds.

13. The method of claim **1**, wherein at least about 70 wt % of the olefins present in the olefin-containing feed are incorporated into C_{10+} compounds present in the product effluent.

14. A diesel boiling range effluent comprising at least about 50 wt % C_{10+} oligomerized compounds, the C_{10+} oligomerized compounds being formed by oligomerization of C_{2-5} olefins.

15. The diesel boiling range effluent of claim **14**, wherein the diesel boiling range effluent comprises at least about 50 wt % C_{10+} olefins.

16. The diesel boiling range effluent of claim **15**, wherein the at least about 50 wt % C_{10+} olefins comprise oligomerized olefins formed by oligomerization of C_{2-5} olefins.

17. The diesel boiling range effluent of claim **14**, wherein the at least about 50 wt % C_{10+} oligomerized compounds incorporate at least about 50 wt % of C_{2-5} olefins present in a feed for the oligomerization of the C_{2-5} olefins.

18. A system for converting an olefin-containing feed to diesel boiling range compounds, comprising:

a fluidized bed reactor comprising a fluidized bed of an acidic molecular sieve, the fluidized bed being fluidized with an olefin-containing feed comprising C_1-C_4 hydrocarbon compounds, the olefin-containing feed having an olefin content of at least about 10 wt %, the bed being fluidized at a pressure of about 50 psig (0.3 MPa) to about 250 psig (1.7 MPa) and a temperature of about 550° F. (288° C.) to about 800° F. (427° C.);

a separator in fluid communication with the fluidized bed reactor for performing a separation on an effluent from the fluidized bed reactor; and

a fixed bed reactor in fluid communication with the separator to receive a separated fraction comprising C_5+ olefinic compounds, the fixed bed reactor comprising a fixed bed of a second acidic molecular sieve, the fixed bed reactor having a pressure of about 300 psig (2.1 MPa) to about 1500 psig (10.3 MPa) and a temperature of from about 550° F. (288° C.) to about 700° F. (371° C.).

19. The system of claim **18**, wherein the fixed bed of a second acidic molecular sieve comprises the same molecular sieve as the fluidized bed of an acidic molecular sieve.

20. The system of claim **18**, wherein at least one of the fluidized bed of an acidic molecular sieve and the fixed bed of a second acidic molecular sieve comprises a zeolite, the zeolite optionally comprising a 10-member ring zeolite.

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