(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 August 2006 (10.08.2006)

PCT

(10) International Publication Number
WO 2006/084286 A2

(51) International Patent Classification:
C10L 1/08 (2006.01) *C10G 50/02* (2006.01)

(21) International Application Number:
PCT/US2006/004876

(22) International Filing Date: 27 January 2006 (27.01.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/648,947	31 January 2005 (31.01.2005)	US
60/648,938	31 January 2005 (31.01.2005)	US
60/685,577	27 May 2005 (27.05.2005)	US

(71) Applicant *(for all designated States except US)*: **EXXONMOBIL CHEMICAL PATENTS INC.** [US/US]; A Corporation of the State of Delaware, 5200 Bayway Drive, Baytown, Texas 77520-5200 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **BROWN, Stephen, H.** [US/US]; 45 Mullens Lane, Bernardsville, New Jersey 07924 (US). **KUECHLER, Keith, H.** [US/US]; 912 Applewood Drive, Friendswood, Texas 77546 (US). **VERBERCKMOES, An** [BE/BE]; Damstraat 3, B-9260 Serskamp (BE). **PUTTEMANS, Marc** [BE/BE]; Kraanstraat 41, B-1703 Dilbbek (BE). **SILVERBERG, Steven, E.** [US/US]; 1615 Fairoaks, Seabrook, Texas 77586 (US). **LUO, Shifang** [US/US]; 4 Delancy Court, Bridgewater, New Jersey 08807 (US). **CHENG, Jane, C.** [US/US]; 1303 Pinhorn Drive, Bridgewater, NJ 08807 (US). **JAENSCH, Helge** [DE/DE]; Avenue Herge 13, B-1050 Ixelles - Bruxelles (BE). **MATHYS, Georges, M.** [BE/BE]; Eikenboomlaan 66, B-3360 Bierbeek (BE).

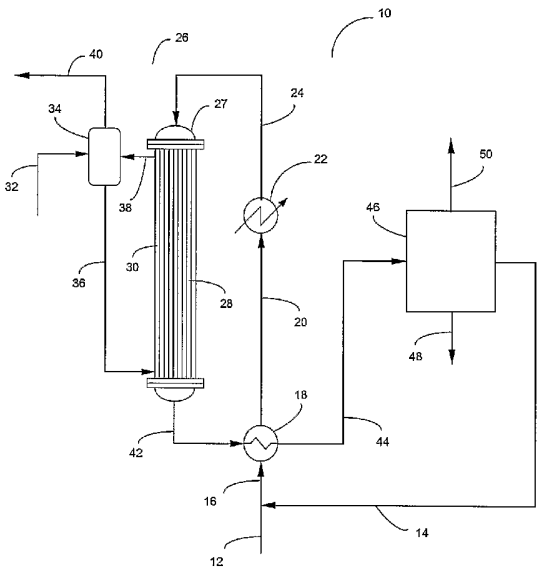
(74) Agents: **REID, Frank, E.** et al.; Exxonmobil Chemical Company, Law Technology, P.O. Box 2149, Baytown, Texas 77522-2149 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH,

[Continued on next page]

(54) Title: HYDROCARBON COMPOSITIONS USEFUL FOR PRODUCING FUELS AND METHODS OF PRODUCING THE SAME



(57) Abstract: A hydrocarbon composition comprises at least 90 wt.% of C_9 to C_{20} non- normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition, at least 2 wt.% and not greater than 25 wt.% of C_9 hydrocarbons based on the weight of the hydrocarbon composition, and less than 15 wt.% of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition, wherein said hydrocarbon composition has a specific gravity at 15°C of at least 0.730 and less than 0.775. The composition is produced by oligomerization of at least one C_3 to C_8 olefin and an olefinic recycle stream rich in C_9-hydrocarbons. The composition is useful in producing fuel blends, such as jet fuel and diesel fuel.

WO 2006/084286 A2

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

HYDROCARBON COMPOSITIONS USEFUL FOR PRODUCING FUELS AND METHODS OF PRODUCING THE SAME

FIELD

[0001] This invention relates to hydrocarbon compositions useful for producing fuels, such as jet fuel and diesel fuel, and to methods of producing such compositions.

BACKGROUND

[0002] Improved hydrocarbon compositions are needed to help meet the growing demand for middle distillate products, such as aviation turbine fuels, for example, JP-8, and diesel fuel. Diesel fuel generally provides a higher energy efficiency in compression ignition engines than automotive gasoline provides in spark combustion engines, and has a higher rate of demand growth than automotive gasoline, especially outside the U.S. Further, improved fuel compositions are needed to meet the stringent quality specifications for aviation fuel and the ever tightening quality specifications for diesel fuel as established by industry requirements and governmental regulations.

[0003] One known route for producing hydrocarbon compositions useful as fuels is the oligomerization of olefins over various molecular sieve catalysts. Exemplary patents relating to olefin oligomerization include U.S. Patent Nos. 4,444,988; 4,456,781; 4,504,693; 4,547,612 and 4,879,428. In these disclosures, feedstock olefins are mixed with an olefinic recycle material and contacted with a zeolite, particularly in a series of fixed bed reactors. The oligomerized reaction product is then separated to provide a distillate stream, and typically a gasoline stream, and any number of olefinic recycle streams.

[0004] However, in these known oligomerization processes, the focus is on producing relatively heavy distillate products, and even lube base stocks. To enable the production of relatively heavy materials, the processes employ, either directly or indirectly, a relatively large amount of olefinic recycle (typically >2:1 w/w relative to feed), containing significant quantities of C_{10}+ material. The

relatively large recycle rate provides control over the exotherm of the oligomerization reaction in the preferred fixed bed, adiabatic reactor system, while the relatively heavy recycle composition (in conjunction with high conversion of light olefin feed, in part enabled by a relatively low WHSV) enables the growth of heavier oligomers and thus higher molecular weight and denser distillate product. However, the high rate of recycle requires much larger equipment to handle the increased volumetric flow rate, and uses more separation/fractionation energy, and hence more and larger associated energy conservation elements. Further, the high molecular weight of the oligomer product requires very high temperatures for the fractionation tower bottoms streams that may eliminate the use of simple steam reboilers and require more expensive and complicated fired heaters.

[0005] The recycle streams in conventional olefin oligomerization processes are produced in a variety of fashions, typically including some sort of single stage flash drum providing a very crude separation of reactor product as a means of providing the relatively heavy components, followed by various fractionation schemes which may or may not provide sharper separations, and again often provide heavy components as recycle. The dense distillate product is generally characterized by a relatively high specific gravity (in excess of 0.775) and a high viscosity, in part due to the composition comprising relatively high levels of aromatics and naphthenes.

[0006] Very few references discuss both the merits and methods of producing lighter distillate products, typified by such as jet fuel, kerosene and No. 1 Diesel, via the oligomerization of C_3 to C_8 olefins. Jet/kero is generally overlooked as a particularly useful middle distillate product, inasmuch as the volume consumed in the marketplace is considerably smaller than its heavier cousins, No. 2 Diesel and No. 4 Diesel (fuel oil). However, jet/kero is a high volume commercial product in its own right, and is also typically suitable as a particular light grade of diesel, called No. 1 Diesel, that is especially useful in colder climates given its tendency to remain liquid and sustain volatility at much lower temperatures. In addition, jet/kero type streams are often blended in with other stocks to produce No. 2 Diesel, both to modify the diesel fuel characteristics, and to allow introduction of otherwise less valuable blendstocks into the final higher value product.

[0007] U.S. Patent No. 4,720,600 discloses an oligomerization process for converting lower olefins to distillate hydrocarbons, especially useful as high quality jet or diesel fuels, wherein an olefinic feedstock is reacted over a shape selective acid zeolite, such as ZSM-5, to oligomerize feedstock olefins and further convert recycled hydrocarbons. The reactor effluent is fractionated to recover a light-middle distillate range product stream and to obtain light and heavy hydrocarbon streams for recycle. The middle distillate product has a boiling range of about 165°C to 290°C and contains substantially linear C_9 to C_{16} mono-olefinic hydrocarbons, whereas the major portion of the C_6 to C_8 hydrocarbon components are contained in the lower boiling recycle stream, and the major portion (e.g. 50 wt.% to more than 90 wt.%) of the C_{16}^+ hydrocarbon components are contained in the heavy recycle fraction.

[0008] U.S. Patent No. 4,788,366 discloses a multi-stage process for upgrading an ethene-rich feed into heavier hydrocarbon products boiling in the lubricant, distillate and gasoline ranges. The process involves initially contacting the ethene-rich feed in a primary reaction stage with a fluidized bed of a zeolite catalyst, such as ZSM-5, and then separating the resultant effluent into at least a liquid stream containing a major amount of aromatics-rich C_5+ hydrocarbons and a gas stream rich in propene and butene. The gas stream is then fed to a secondary reaction stage comprising a series of fixed bed reactors containing a medium pore zeolite oligomerization catalyst, such as ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23 or ZSM-35, preferably having a silica/alumina molar ratio of 20 to 200 and a crystal size of 0.2 to 1 micron. In the secondary reaction stage, at least part of the aromatics-rich, liquid primary stage effluent is mixed with a hot inter-stage stream containing partially upgraded olefins to quench said inter-stage stream and the resultant mixed stream is passed to at least one downstream oligomerization reactor. The conditions in the secondary reaction stage can be varied to control the product slate, but generally include a temperature of 235°C to 315°C, a pressure of 2800 to 10,000 kPa and a weight hourly space velocity of 0.1 to 1.5. The product necessarily contains a significant quantity of aromatic hydrocarbons.

[0009] A similar process is described in U.S. Patent No. 4,855,524, in which an olefin-containing light gas or light naphtha is oligomerized to a C_{10}+ aliphatic

hydrocarbon product in multistage reaction zones. In particular, lower alkenes in the feed are oligomerized to intermediate range olefins, mainly in the C_5 to C_9 range, in a low severity primary reaction zone containing zeolite catalyst particles, preferably in the form of a fluidized bed. The primary reaction zone effluent is then separated into a C_4- light gas stream and a predominantly olefinic C_5+ intermediate stream substantially free of C_4- components. The intermediate stream is then contacted with a medium pore, shape selective, acid oligomerization catalyst in a secondary reaction zone under oligomerization conditions to produce a predominantly C_{10}+ product. To maximize the yield of distillate product, the '524 patent teaches that C_{10}+ hydrocarbons should be removed from said intermediate stream before passage through said secondary reaction zone and that said secondary reaction zone should be operated with catalyst having an average activity alpha greater than 10, at weight hourly space velocity (WHSV) in the range from about 0.1 to about 10 hr^{-1}, at an inlet pressure in excess of about 3200 kPa, an inlet temperature in the range from about 149°C to about 232°C and an outlet temperature in the range from about 232°C to about 343°C. The overall yield and/or quality of the distillate may be further increased by recycling an insufficiently oligomerized portion of the product stream to the secondary reaction zone.

[0010] In accordance with the known olefin conversion and oligomerization processes, catalysts are specified that have certain characteristics conducive to their desired products, typically aromatics and heavier distillate products, even lube base stocks. Such characteristics of these known catalysts are not necessarily conducive to the production of lighter distillate products, for example, relatively large crystal size to constrain the larger molecules to enable oligomerization, and relatively high activity to increase the rate of reaction of the less reactive larger molecules. Further, such catalyst attributes in conjunction with the known process conditions favor the production of byproduct cyclics, e.g., aromatics, which are known to be detrimental to distillate and aviation fuel properties.

[0011] According to the present invention, it has now been found that by controlling the conditions of the oligomerization process and, in particular, the amount and composition of the recycle, C_3 to C_8 olefins can be converted into a

novel hydrocarbon composition similar in make-up to that of conventional diesel and jet fuel, but with an unusually low specific gravity making it an excellent blending stock to produce fuel products, such as Jet Fuel A and No.1 and No. 2 Diesel. In addition, the hydrocarbon composition of the invention is very low in sulfur, naphthenes and aromatics, has a high cetane number and, in view of its low n-paraffin content, has a very low freezing point.

SUMMARY

[0012] In one aspect, the present invention resides in a hydrocarbon composition comprising at least 90 wt.% of C_9 to C_{20} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition, at least 2 wt.% and not greater than 25 wt.% of C_9 hydrocarbons based on the weight of the hydrocarbon composition, and less than 15 wt.% of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition, wherein said hydrocarbon composition has a specific gravity at 15°C of at least 0.730 and less than 0.775.

[0013] Conveniently, the hydrocarbon composition comprises at least 92 wt%, such as at least 95 wt.%, of C_9 to C_{20} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition. In one embodiment, the hydrocarbon composition comprises at least 60 wt.% and no greater than 90 wt.% of C_{11} to C_{18} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition. In another embodiment, the hydrocarbon composition comprises at least 50 wt.% and no greater than 75 wt.% of C_{12} to C_{16} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition.

[0014] Conveniently, the hydrocarbon composition comprises at least 3 wt.% and no greater than 20 wt.%, such as at least 4 wt.% and no greater than 15 wt.% of C_9 hydrocarbons based on the weight of the hydrocarbon composition.

[0015] Conveniently, the hydrocarbon composition comprises less than 10 wt.%, for example less than 5 wt.% of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition. Typically, the hydrocarbon composition comprises

at least 1 wt.%, for example at least 3 wt.%, of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition.

[0016] Conveniently, the hydrocarbon composition comprises no greater than 12 wt.%, for example no greater than 7 wt.%, of C_{17} to C_{20} hydrocarbons based on the weight of the hydrocarbon composition. In one embodiment, the hydrocarbon composition comprises no greater than 8 wt.%, such as no greater than 5 wt.%, of C_{19} to C_{20} hydrocarbons based on the weight of the hydrocarbon composition.

[0017] Conveniently, the hydrocarbon composition comprises no greater than 3 wt.%, such as no greater than 1 wt.%, of C_{21}+ hydrocarbons based on the weight of the hydrocarbon composition.

[0018] In one embodiment, the hydrocarbon composition comprises no greater than 5 wt.%, such as no greater than 3 wt.%, for example no greater than 1 wt.%, of C_8- hydrocarbons based on the weight of the hydrocarbon composition.

[0019] Conveniently, the hydrocarbon composition comprises less than 5000 ppm wt., such as less than 500 ppm wt., and even less than 15 ppm wt., of sulfur.

[0020] Conveniently, the hydrocarbon composition has a specific gravity at 15°C of at least 0.740 and no greater than 0.770, such as at least 0.750 and no greater than 0.765.

[0021] In one embodiment, the hydrocarbon composition has a flash point of at least 38°C, such as at least 40°C, for example at least 45°C.

[0022] In a further aspect, the invention resides in a process for producing a hydrocarbon composition, the process comprising:

(a) contacting a feed comprising at least one C_3 to C_8 olefin and an olefinic recycle stream with a molecular sieve catalyst in at least one reaction zone under olefin oligomerization conditions such that the recycle to feed weight ratio is about 0.5 to about 2.0, the WHSV is at least 1.5 based on the olefin in the feed, and the difference between the highest and lowest temperatures within the or each reaction zone is 40°F (22°C) or less, said contacting producing a oligomerization effluent stream; and

(b) separating said oligomerization effluent stream into at least a hydrocarbon product stream and said olefinic recycle stream,

wherein the olefinic recycle stream contains no more than 10 wt.% of C_{10}+ non-normal olefins, and the hydrocarbon product stream contains at least 1 wt.% and no more than 30 wt.% of C_9 non-normal olefins.

[0023] Conveniently, the recycle to feed weight ratio in said contacting (a) is about 0.7 to about 1.3.

[0024] Conveniently, the contacting (a) is conducted at a WHSV of about 1.8 to about 9 based on the olefin in the feed and/or a WHSV of about 2.3 to about 14 based on the olefin in the combined feed and olefinic recycle stream.

[0025] In yet a further aspect, the invention resides in a process for producing a hydrocarbon product, the process comprising:

(a) contacting a feed comprising at least one C_3 to C_8 olefin and an olefinic recycle stream rich in C_9- hydrocarbons with a crystalline molecular sieve catalyst having an average crystal size no greater than 0.15 micron and an alpha value between about 100 and about 600 in at least one reaction zone under olefin oligomerization conditions including an inlet temperature between about 180°C and about 350°C, a pressure of at least 2,860 kPa and a recycle to feed weight ratio of about 0.1 to about 3.0, said contacting producing a oligomerization effluent stream; and

(b) separating said oligomerization effluent stream into at least a hydrocarbon product stream rich in C_9+ hydrocarbons and said olefinic recycle stream.

[0026] Conveniently, the crystalline molecular sieve catalyst has an average crystal size no greater than 0.12, 0.10, 0.07, or 0.05 micron. Further, the crystalline molecular sieve catalyst can have an alpha value between about 200 and about 400, or between about 250 and about 350.

[0027] Conveniently, the crystalline molecular sieve catalyst comprises an aluminosilicate having a silica to alumina molar ratio from about 20 to about 300, particularly from about 20 to about 150, preferably about 45 to about 90.

[0028] Conveniently, said feed comprises a mixture of C_3 to C_5 olefins comprising at least 5 wt.% of C_4 olefin, preferably at least 40 wt.% of C_4 olefin

and at least 10 wt.% of C_5 olefin. Where the feed contains C_4 olefin, the contacting (a) is conveniently conducted so as to convert about 80 wt.% to about 99 wt.% of the C_4 olefin in the feed.

[0029] Conveniently, the contacting (a) is conducted in a plurality of reaction zones connected in series and the difference between the highest and lowest temperatures within each reaction zone is 40°F (22°C) or less.

[0030] In one embodiment, the highest and lowest temperatures within the or each reaction zone are between about 150°C and about 350 °C.

[0031] Conveniently, said catalyst comprises a molecular sieve having a Constraint Index of about 1 to about 12, preferably ZSM-5, ZSM-12, and/or MCM-22.

[0032] Conveniently, said olefinic recycle stream contains no more than 7 wt.% of C_{10}+ non-normal olefins. Typically, said olefinic recycle stream contains no more than 30 wt.% of C_9+ non-normal olefins. In one embodiment, said olefinic recycle stream has a final boiling point of no greater than 340°F (170°C).

[0033] In still yet a further aspect, the invention resides in a blend useful as a fuel and comprising (a) a first hydrocarbon composition comprising at least 90 wt.% of C_9 to C_{20} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition, at least 2 wt.% and not greater than 25 wt.% of C_9 hydrocarbons based on the weight of the hydrocarbon composition, and less than 15 wt.% C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition, wherein said hydrocarbon composition has a specific gravity at 15°C of at least 0.730 and less than 0.775 and (b) a second hydrocarbon composition different from the first hydrocarbon composition and having at least one of the following properties (i) a specific gravity at 15°C greater than 0.775, (ii) a freezing point of greater than -47°C and (iii) a kinematic viscosity at 40°C greater than 1.3 mm^2/s.

[0034] Conveniently, the second hydrocarbon composition has a specific gravity at 15°C less than 0.890.

[0035] Conveniently, the second hydrocarbon composition has a freezing point of greater than -40°C.

[0036] Conveniently, the second hydrocarbon composition has a kinematic viscosity at 40°C greater than 1.9 mm^2/s.

[0037] Conveniently, the first hydrocarbon composition has a final boiling point of at least 270°C, such as at least 290°C. Conveniently, the second hydrocarbon composition has a final boiling point of at least 220°C, such as at least 240°C and no greater than 320°C, such as no greater than 300°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0038] Figure 1 is a flow diagram of a process for producing a hydrocarbon composition according to one example of the invention.

[0039] Figure 2 is a graph of percentage conversion against time on stream for the ZSM-5 catalysts A to D of Example 1.

[0040] Figure 3 is a graph of percentage carbon number interconversion (sum of C5 +C6 + C7 + C9 + C10 + C11 + C13 + C14 + C15) against percentage conversion for the ZSM-5 catalysts A to D of Example 1.

[0041] Figure 4 is a graph of selectivity to C_8, C_{12} and C_{16}+ hydrocarbons against percentage conversion for the ZSM-5 catalysts A to D of Example 1.

[0042] Figure 5 is a graph of selectivity to n-butane against percentage conversion for the ZSM-5 catalysts A to D of Example 1.

[0043] Figure 6 is a graph of percentage conversion against time on stream for the ZSM-5 catalysts A and D of Example 1 and the ZSM-12 catalyst of Example 2.

[0044] Figure 7 is a graph of selectivity to C_8, C_{12} and C_{16}+ hydrocarbons against percentage conversion for the ZSM-5 catalysts A and D of Example 1 and the ZSM-12 catalyst of Example 2.

[0045] Figure 8 is a graph of lights (C_5 to C_7) make against percentage conversion for the ZSM-5 catalysts A and D of Example 1 and the ZSM-12 catalyst of Example 2.

[0046] Figure 9 is a graph of percentage carbon number interconversion (sum of C5 +C6 + C7 + C9 + C10 + C11 + C13 + C14 + C15) against percentage conversion for the ZSM-5 catalysts A and D of Example 1 and the ZSM-12 catalyst of Example 2.

[0047] Figure 10 is a graph of percentage conversion against time on stream for the ZSM-5 catalysts A and D of Example 1 and the MCM-22 catalyst of Example 3.

[0048] Figure 11 is a graph of selectivity to C_8, C_{12} and C_{16}+ hydrocarbons against percentage conversion for the ZSM-5 catalysts A and D of Example 1 and the MCM-22 catalyst of Example 3.

[0049] Figure 12 is a graph of ratio the amount of C_5 to C_7 hydrocarbons to the amount of C_9 to C_{11} and C_{13} hydrocarbons against percentage conversion for the ZSM-5 catalysts A and D of Example 1 and the MCM-22 catalyst of Example 3.

[0050] Figure 13 is a graph of percentage carbon number interconversion (sum of C5 +C6 + C7 + C9 + C10 + C11 + C13 + C14 + C15) against percentage conversion for the ZSM-5 catalysts A and D of Example 1 and the MCM-22 catalyst of Example 3.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0051] As used herein, the term "C_x hydrocarbon" indicates hydrocarbon molecules having the number of carbon atoms represented by the subscript "x". The term "C_x+ hydrocarbons" indicates those molecules noted above having the number of carbon atoms represented by the subscript "x" or greater. For example, "C_{17}+ hydrocarbons" would include C_{17}, C_{18} and higher carbon number hydrocarbons. Similarly "C_x- hydrocarbons" indicates those molecules noted above having the number of carbon atoms represented by the subscript "x" or fewer.

[0052] Distillation temperature values cited herein, including end point (or final boiling point), 90 vol% recovered temperature (T90) and 10 vol% recovered temperature (T10) refer to measurements made in accordance with ASTM Test Method D86, the entire contents of which test are incorporated herein by reference.

[0053] References herein to flash point temperatures refer to measurements made in accordance with ASTM Test Method D56, the entire contents of which test are incorporated herein by reference.

[0054] References herein to freezing point temperatures refer to measurements made in accordance with ASTM Test Method D2386, the entire contents of which test are incorporated herein by reference.

[0055] References herein to Jet Fuel Thermal Oxidation Test (JFTOT) breakthrough results refer to measurements made in accordance with ASTM Test Method D4231, the entire contents of which test are incorporated herein by reference.

[0056] Kinematic viscosity values cited herein refer to measurements made in accordance with ASTM Test Method D445, the entire contents of which test are incorporated herein by reference.

[0057] References herein to the aromatics content of hydrocarbon compositions refer to measurements made in accordance with ASTM Test Method D1319, the entire contents of which test are incorporated herein by reference.

[0058] References herein to the sulfur content of hydrocarbon compositions refer to measurements made in accordance with ASTM Test Method D129, the entire contents of which test are incorporated herein by reference.

[0059] As used herein, the term "specific gravity" is to be understood as including the reference density of water at 4°C; the temperature attached to the term herein is for that of the density of the material being described. For example, as used herein the phrase "hydrocarbon having a specific gravity at 15°C" is to be understood as the ratio of the density of the hydrocarbon at 15°C to the density of water at 4°C.

[0060] The present invention provides a novel hydrocarbon composition, methods of producing the hydrocarbon composition by olefin oligomerization, optionally together with hydrogenation, and fuel blends containing the hydrocarbon composition.

Hydrocarbon Composition

[0061] The novel hydrocarbon composition of the invention has at least the following properties:

(a) at least 90 wt.% of the hydrocarbon composition is composed of C_9 to C_{20} non-normal olefins, non-normal saturates or combinations thereof;

(b) at least 2 wt.% and not greater than 25 wt.% of the hydrocarbon composition is composed of C_9 hydrocarbons;

(c) less than 15 wt.% of the hydrocarbon composition is composed of C_{17}+ hydrocarbons; and

(d) said hydrocarbon composition has a specific gravity at 15°C of at least 0.730 and less than 0.775.

[0062] With regard to property (a), the hydrocarbon composition typically, comprises at least 92 wt%, such as at least 95 wt%, or even at least 97 wt% C_9 to C_{20} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition. In one embodiment, the hydrocarbon composition comprises between about 60 wt.% and about 90 wt.% of C_{11} to C_{18} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition. In another embodiment, the hydrocarbon composition comprises between about 50 wt.% and about 75 wt.% C_{12} to C_{16} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition. This is particularly advantageous for the flexible use of the composition as an aviation or diesel fuel.

[0063] With regard to property (b), some or all of said C_9 hydrocarbons may be non-normal olefins, non-normal saturates or combinations thereof. Typically, the hydrocarbon composition comprises at least 3 wt.%, such as at least 4 wt.%, for example at least 5 wt.%, or even at least 10 wt.% of C_9 hydrocarbons based on the weight of the hydrocarbon composition, but generally comprises no greater than 20 wt.%, such as no greater than 15 wt.% of C_9 hydrocarbons based on the weight of the hydrocarbon composition.

[0064] With regard to property (c), some or all of the C_{17}+ hydrocarbons may be non-normal olefins, non-normal saturates or combinations thereof. Typically,

the hydrocarbon composition comprises less than 12 wt.%, such as less than 10 wt.%, for example less than 8 wt.%, even less than 5 wt.% of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition. Although there is no lower limit on the amount of C_{17}+ hydrocarbons, in general the hydrocarbon composition comprises at least 1 wt.%, such as at least 2 wt.%, for example at least 3 wt.%, even as high as 5 wt.% or 10 wt.% of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition.

[0065] Of the C_{17}+ hydrocarbons in the hydrocarbon composition of the invention, there should generally be no greater than 12 wt.%, for example no greater than 10 wt.%, such as no greater than 7 wt.%, even not greater than 2 wt.% of C_{17} to C_{20} hydrocarbons based on the weight of the hydrocarbon composition. In addition, there should generally be no greater than 8 wt.%, such as no greater than 5 wt.%, for example no greater than 3 wt.% of C_{19} to C_{20} hydrocarbons based on the weight of the hydrocarbon composition. Moreover, there should generally be no greater than 3.0 wt.%, for example no greater than 1.0 wt.%, such as no greater than 0.5 wt%, even no greater than 0.2 wt.% of C_{21}+ hydrocarbons based on the weight of the hydrocarbon composition.

[0066] With regard to property (d), the hydrocarbon composition of the invention generally has a specific gravity at 15°C of at least 0.740, such as at least 0.750, and no greater than 0.770, such as no greater than 0.765.

[0067] In addition to the C_9+ components discussed above, the hydrocarbon composition of the invention can contain at least 0.1 wt%, such as at least 0.2 wt.% of C_8- hydrocarbons based on the weight of the hydrocarbon composition. However, the composition should generally contain no greater than 5 wt%, such as no greater than 3 wt.%, for example no greater than 1 wt.% of C_8- hydrocarbons based on the weight of the hydrocarbon composition. Typically, the hydrocarbon composition contains less than 5 wt.%, such as less than 2 wt.%, for example less than 1 wt.%, such as less than 0.5 wt.%, for example less than 0.1 wt.%, such as less than 0.05 wt.%, for example less than 0.01 wt.%, even less than 0.005 wt.% aromatics.

[0068] The initial boiling point of the hydrocarbon composition of the invention is typically at least 127°C (260°F) , such as at least 140°C (284°F),

conveniently at least 150°C (302°F), including at least 160°C (320°F), or even at least 170°C (338°F). The final boiling point of the hydrocarbon composition of the invention is typically no greater than 350°C, such as no greater than 330°C, for example no greater than 310°C or even no greater than 300°C.

[0069] Typically, the hydrocarbon composition of the invention has a flash point of at least 38°C, such as at least 40°C, for example at least 45°C, or at least 50°C or even at least 55°C. It is, however, to be appreciated that it may be necessary to reduce the content of C_9 non-normal hydrocarbons in the composition to achieve these higher flash points. For, example, to achieve a flash point of at least 55°C, it may be necessary to reduce the content of C_9 non-normal hydrocarbons in the composition to no greater than about 10 wt.%.

[0070] Conveniently, the hydrocarbon composition of the invention has a Jet Fuel Thermal Oxidation Test (JFTOT) breakpoint result of at least 260°C, more typically at least 270°C, such as at least 280°C, for example at least 290°, such as at least 300°C, even at least 310°C.

[0071] Typically, the hydrocarbon composition of the invention meets all the specifications for a No. 1-D S5000 diesel fuel, and generally for a No.1-D S500 diesel fuel, or even a No.1-D S15 diesel fuel as set out in Table 1 of ASTM D975-04a, the entire contents of which standard are incorporated herein by reference. In the generic designation "SXXX" in ASTM D975-04a, XXX is the wppm of sulfur in the fuel. Thus, the present composition is exceedingly low in sulfur.

[0072] Typically, the hydrocarbon composition of the invention has a low electrical conductivity, such as no greater than 150 pS/m, such as no greater than 100 pS/m, for example no greater than 50 pS/m or even as low as 10 pS/m, according to ASTM Test Method D2624, the entire contents of which test are incorporated herein by reference. Whereas this is not necessarily an attractive attribute for a fuel, especially an aviation fuel, additives to increase electrical conductivity, for example, Stadis 450 (marketed by Octel America, 200 Executive Drive, Newark, NJ 19702), can be combined with the present composition such that composition including the additive has an electrical conductivity of at least 50 pS/m, such as at least 100 pS/m, for example at least 150 pS/m, or at least 200

pS/m or even at least 250 pS/m, but no greater than 450 pS/m, again according to ASTM Test Method D2624.

[0073] The hydrocarbon composition of the invention may further include other additives, the types and proportions of which may be found in Table 2 of ASTM D1655-04, the entire contents of which standard are incorporated herein by reference.

Process of Producing the Hydrocarbon Composition

[0074] The hydrocarbon composition of the invention can be produced by oligomerizing a feed containing at least one C_3 to C_8 olefin together with an olefinic recycle stream rich in C_9- hydrocarbons over a molecular sieve catalyst. The resultant oligomerization product is then separated into a hydrocarbon stream according to the invention and at least one light olefinic stream. At least part of the light olefinic stream(s) is then recycled to the oligomerization process.

[0075] The fresh feed to the oligomerization process can include any single C_3 to C_8 olefin or any mixture thereof in any proportion. Particularly suitable feeds include mixtures of propylene and butylenes having at least 5 wt.%, such as at least 10 wt.%, for example at least 20 wt.%, such as at least 30 wt.% or at least 40 wt.% C_4 olefin. Also useful are mixtures of C_3 to C_5 olefins having at least 40 wt.% C_4 olefin and at least 10 wt.% C_5 olefin.

[0076] Conveniently, the feed should contain no more than about 1.0 wt.%, or even no more than 0.1 wt.% of C_2- hydrocarbons, since ethylene is less reactive in the present process than other light olefins, and thus requires substantially more processing to obtain a good ultimate conversion. Further, ethylene and light saturates, such as ethane and methane, are highly volatile, and it will require much more work to recover them in the separation system, likely necessitating the use of expensive and complicated refrigeration systems. It is also of benefit to limit the amount of C_{10}+ hydrocarbons, of any kind, in the feed, to say no more than about 10 wt%, or no more than 5 wt.% or even no more than 1 wt.%, since C_9 hydrocarbons are useful components of the hydrocarbon product stream and so it is counter-productive to subject them to the oligomerization process of the invention.

[0077] It is also desirable to limit the amount of saturates in the feed, since saturates are not converted in the oligomerization step and tend to accumulate in the recycle stream, thereby reducing the light olefin content of the recycle stream. The amount of non-olefins, especially saturates, in the feed should be less than 45 wt.%, such as less than 35 wt.%, for example less than 25 wt.%, typically less than 15 wt.%, or less than 10 wt.% or even less than 5 wt.%.

[0078] In one embodiment, the olefinic feed is obtained by the conversion of an oxygenate, such as methanol, to olefins over a either silicoaluminophosphate (SAPO) catalyst, according to the method of, for example, U.S. Patent Nos. 4,677,243 and 6,673,978, or an aluminosilicate catalyst, according to the method of, for example, WO04/18089, WO04/16572, EP 0 882 692 and Patent No. U.S. 4,025,575. Alternatively, the olefinic feed can be obtained by the catalytic cracking of relatively heavy petroleum fractions, or by the pyrolysis of various hydrocarbon streams, ranging from ethane to naphtha to heavy fuel oils, in admixture with steam, in a well understood process known as "steam cracking".

[0079] As stated above, the feed to the oligomerization process also contains an olefinic recycle stream rich in C_9- hydrocarbons and typically containing no more than 10 wt.% C_{10}+ non-normal olefins. Generally, the olefinic recycle stream should contain no greater than 7.0 wt.%, for example no greater than 5.0 wt.%, such as no greater than 2.0 wt.%, or no greater than 1.0 wt.% or even 0.1 wt.% C_{10}+ olefin. Alternatively, the final boiling point temperature of the olefinic recycle stream should be no greater than 340°F (170°C), such as no greater than 320°F (160°C), for example no greater than 310°F (155°C), or even 305°F (150°C). In one embodiment, the olefinic recycle stream contains no greater than 30.0 wt.%, such as no greater than 25.0 wt.%, for example no greater than 20.0 wt.%, or no greater than 15.0 wt.%, or no greater than 10.0 wt.% C_9+ olefin. Alternatively, the final boiling point temperature of the olefinic recycle stream should be no greater than 290°F (140°C), such as no greater than 275°F (135°C), for example no greater than 260°F (130°C).

[0080] In one embodiment, the olefinic recycle stream contains no greater than 30 wt.%, or no greater than 25 wt.%, or no greater than 20 wt.%, or no greater than 10 wt.%, or no greater than 5 wt.% C_4 hydrocarbons (of any species). This

can be achieved, for example, by employing an additional separation of all or a portion of the light olefinic stream into a first stream comprising C_4- with only a small amount of C_5+ hydrocarbons, and a second, debutanized stream as all or a portion of the olefinic recycle stream provided to the oligomerization reactor.

[0081] The amount of olefinic recycle stream fed to the oligomerization process is such that the recycle to fresh feed weight ratio is from about 0.5 to about 2.0. More particularly, the mass ratio of olefinic recycle stream to fresh olefinic feedstock can be at least 0.7 or at least 0.9, but generally is no greater than 1.8, or no greater than 1.5 or no greater than 1.3.

[0082] The catalyst used in the oligomerization process can include any crystalline molecular sieve which is active in olefin oligomerization reactions. In one embodiment, the catalyst includes a medium pore size molecular sieve having a Constraint Index of about 1 to about 12. Constraint Index and a method of its determination are described in U.S Patent No. 4,016,218, which is incorporated herein by reference. Examples of suitable medium pore size molecular sieves are those having 10-membered ring pore openings and include those of the TON framework type (for example, ZSM-22, ISI-1, Theta-1, Nu-10, and KZ-2), those of the MTT framework type (for example, ZSM-23 and KZ-1), of the MFI structure type (for example, ZSM-5), of the MFS framework type (for example, ZSM-57), of the MEL framework type (for example, ZSM-11), of the MTW framework type (for example, ZSM-12), of the EUO framework type (for example, EU-1) and members of the ferrierite family (for example, ZSM-35).

[0083] Other examples of suitable molecular sieves include those having 12-membered pore openings, such as ZSM-18, zeolite beta, faujasites, zeolite L, mordenites, as well as members of MCM-22 family of molecular sieves (including, for example, MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, ITQ-2, MCM-36, MCM-49 and MCM-56).

[0084] In one embodiment, the crystalline aluminosilicate molecular sieve has an average (d_{50}) crystal size no greater than 0.15 micron, such as no greater than 0.12, 0.10, 0.07 or 0.05 micron, or such as about 0.01 to about 0.10 micron, about 0.02 to about 0.08 micron, or about 0.02 to about 0.05 micron. In addition, the molecular sieve is preferably selected so as to have an alpha value between about

100 and about 600, conveniently between about 200 and about 400, or between about 250 and about 350. The alpha value of a molecular sieve is an approximate indication of its catalytic cracking activity compared with a standard silica-alumina catalyst test (with an alpha value of 1). The alpha test is described in U.S. Patent No. 3,354,078; 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. The experimental conditions of the test used herein include a constant temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, Vol. 61, p. 395.

[0085] Conveniently the crystalline aluminosilicate molecular sieve having a silica to alumina molar ratio of about 20 to about 300, such as about 20 to about 150, for example about 45 to about 90.

[0086] In one preferred embodiment, the molecular sieve catalyst comprises ZSM-5. Suitable methods to produce ZSM-5 useful in the present invention are exemplified in U.S. Patent Nos. 3,926,782, 5,369,071 and 6,180,550, specifically directed to producing crystals with a crystal size less than 0.15 micron, and significantly less than 0.15 as desired. Methods are also known to control ZSM-5 crystal morphology, e.g., geometry and size homogeneity, such as disclosed in European Patent Application 0 093 519 and U.S. Patent Nos. 4,526,879 and 5,063,187. These references also provide information on the control of silica to alumina ratio and alpha properties.

[0087] The molecular sieve used in the catalyst may be supported or unsupported, for example in powder form, or used as an extrudate with an appropriate binder. Where a binder is employed, the binder is conveniently a metal oxide, such as alumina, and is present in an amount such that the oligomerization catalyst contains between about 2 and about 80 wt.% of the molecular sieve.

[0088] The oligomerization reaction should be conducted at sufficiently high WHSV of fresh feed to the reactor to ensure the desired low level of C_{17}+ oligomers in the reaction product. In general, the reaction should occur at a WHSV of no less than 1.5, or no less than 2, or no less than 2.2, or no less than 2.5, or no less than 2.8, or no less than 3.1, or no less than 3.8, or no less than 4.6,

or no less than 5.4, or no less than 6.2 based on olefin in the fresh feed to the reactor and the amount of molecular sieve in the oligomerization catalyst. With regard to the combined fresh olefin feed and recycle to the reactor, the WHSV should be no less than 2.3, or no less than 2.8, or no less than 3.4, or no less than 3.8, or no less than 4.6 or no less than 5.5 again based on the amount of molecular sieve in the oligomerization catalyst. The upper level of WHSV is not narrowly defined but is generally not more than 9 or 8 based on olefin in the fresh feed to the reactor and the amount of molecular sieve in the oligomerization catalyst. Increasing the WHSV beyond these levels may significantly decrease the catalyst/reactor cycle length between regenerations, especially at higher levels of C_4 conversion. For the same reason, the WHSV for the combined fresh olefin feed and recycle to the reactor should no more than 14, 12, 11 or 9 based on the amount of molecular sieve in the oligomerization catalyst.

[0089] The oligomerization process can be conducted over a wide range of temperatures, although generally the temperature within the oligomerization reaction zone should be between about 150°C and about 350°C, such as between about 180°C and about 330°C, for example between about 210°C and 310°C.

[0090] It is, however, desirable to ensure that the temperature across the reaction zone is maintained relatively constant so as to produce the desired level of C_4 olefin conversion at a given WHSV and point in the reaction cycle. Thus, as discussed above, the difference between the highest and lowest temperatures within the reactor should be maintained at 40°F (22°C) or less, such as 30°F (17°C) or less, for example 20°F (11°) or less, conveniently 10°F (6°C) or less, or even 5°F (3°C) or less.

[0091] The oligomerization process can be conducted over a wide range of olefin partial pressures, although higher olefin partial pressures are preferred since low pressures tend to promote cyclization and cracking reactions, and are thermodynamically less favorable to the preferred oligomerization reaction. Typical olefin partial pressures of olefins in the combined olefinic feed and light olefinic/recycle stream as total charge to the reactor comprise at least 400 psig (2860 kPa), such as at least 500 psig (3550 kPa), for example at least 600 psig (4240 kPa), or at least 700 psig (4930 kPa), or at least 800 psig (5620 kPa) or even

900 psig (6310 kPa). It will, of course, be appreciated that the olefin partial pressure will be lower at the exit to the reactor as fewer moles of olefins exist due to the oligomerization reaction.

[0092] Typically, the conditions of the oligomerization process are controlled so as ensure that the conversion of C_4 olefins in the feed is at least 80 wt.%, or at least 85 wt.% or at least 90 wt.%, but no greater than 99%, or no greater than 96 wt.%, or no greater than 95 wt.% or no greater than 94 wt.%. During the course of the oligomerization process, the catalyst will lose activity due to the accumulation of carbonaceous deposits and hence the C_4 olefin conversion will tend to decline with time. Thus to sustain a given level of C_4 olefin conversion, the temperature at which the oligomerization reaction is conducted is continually raised until some limit, discussed above, is reached. At that point, the catalyst is generally regenerated, either in situ or ex situ, by combustion of the coke deposits with oxygen/air using methods and conditions that are well known in the art. The regenerated catalyst may then be used again in the oligomerization reaction at some initial temperature, with the continually increasing temperature cycle being repeated.

[0093] Conveniently, the oligomerization process is conducted in a plurality of serial adiabatic reactors with interstage cooling, such as is disclosed in U.S. Patent No. 4,560,536, the entire contents of which is incorporated herein by reference. In order to achieve the desired low ΔT within each reactor, more than three reactors, for example, about 4 to 10 reactors, may be required. Conveniently, the reactors employed are boiling water reactors, sometimes called heat exchanger reactors, e.g., such as is discussed in U.S. 4,263,141 and 4,369,255 (for methanol production), and "Petroleum Processing, Principles and Applications," R.J. Hengstebeck, McGraw-Hill, 1959, pages 208 - 218 (specifically for olefin oligomerization, using solid phosphoric acid).

[0094] The hydrocarbon composition produced by the oligomerization process described above can be blended, as described below to produce jet or diesel fuel, or can be saturated with hydrogen, e.g., according to the method of U.S. Patent Nos. 4,211,640 and 6,548,721, the entire contents of which are incorporated herein by reference, to produce an aliphatic product. The saturated product can

contain least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, or at least 95 wt% or at least 99 wt.% aliphatic hydrocarbons. All other characteristics of the saturated distillate product in terms of carbon number distribution, non-normal proportions and boiling point ranges will remain largely unchanged from the olefinic product.

[0095] Referring now to Figure 1, there is shown one example of an oligomerization process for producing a hydrocarbon composition according to the invention. The process shown in Figure 1 employs an olefin oligomerization system 10, comprising a heat exchanger reactor system 26 and a separation device 46, among other elements. A fresh feedstock stream containing at least one C_3 to C_8 olefin is provided in line 12, and an olefinic recycle stream containing no greater than 10 wt.% C_{10}+ olefins is provided in line 14, such that the mass ratio of the flow of olefinic recycle in line 14 to the flow of feedstock in line 12 is at least 0.5 and no greater than 2.0. The combined materials are provided via line 16 to feed/effluent heat exchanger 18 to form a first heated combined reactor feed in line 20. The first heated combined reactor feed in line 20 is passed through a preheat exchanger 22 to form a second heated combined reactor feed in line 24. The unnumbered line through preheat exchanger 22 represents a heating medium, for example 900 psig (6310 kPa) steam, and the second heated combined reactor feed in line 24 should be at a greater temperature than the first heated combined reactor feed in line 20, but have a temperature no greater than the desired oligomerization reaction temperature in heat exchanger reactor 27.

[0096] The second heated combined reactor feed in line 24 is provided to heat exchanger reactor 27, where it flows through tubes 28, coming into contact with catalyst contained within the tubes 28. The rate of flow of the second heated combined reactor feed in line 24 and amount of catalyst within the tubes 28 of heat exchanger reactor 27 are such that a WHSV of at least 2.3 is achieved, based on the content of olefin in the second heated combined reactor feed in line 24 and the amount of molecular sieve in the catalyst.

[0097] The oligomerization reaction thus occurs within tubes 28, generating heat, which passes through tubes 28 to be absorbed by boiling water flowing around the outside of the tubes in shell side 30 of the reactor 27. The boiling

water in shell side 30 is a mixture of steam and liquid water that passes through line 38 to disengaging vessel 34. Make-up liquid boiler feed water is provided in line 32 to disengaging vessel 34, and the combined liquid make-up boiler feed water and liquid water formed in the disengaging vessel 34 from the mixture of steam and liquid water that came through line 38 exit the bottom of disengaging vessel 34 through line 36. The steam generated in the heat exchanger reactor 27 emanates from the top of disengaging vessel 34 through line 40, and may be used, for example, to provide heat in fractionation tower reboilers or to make electricity in turbogenerators. The liquid water in line 36 is then provided to the shell side of heat exchanger reactor 27 to become the boiling water in shell side 30.

[0098] The presence of a relatively pure heat exchange component, such as water, in a boiling state on the shell side 30 provides an almost constant temperature within shell side 30 and can, given other appropriate design considerations of heat exchanger reactor 27, provide for a very close approach to isothermal conditions for the reaction occurring within the tubes 28. The difference between the highest and lowest temperature within and between all tubes 28 in heat exchanger reactor 27 is no greater than 40°F (22°C). Further, this configuration of heat exchanger reactor system 26 allows for good control of the reaction temperature within tubes 28 through controlling the pressure within the disengaging vessel 34 (sometimes called a "steam drum"). The pressure in the steam drum 34 controls the temperature at which the water will boil in shell side 30, one of the key factors governing the rate of absorption of the heat of reaction within tubes 28.

[0099] As the catalyst in tubes 28 deactivates with time on stream, a given level of conversion of olefins can be obtained by increasing the pressure in steam drum 34, thus increasing the boiling temperature of the fluid in shell side 30, and increasing the temperature of the oligomerization reaction within tubes 28. Of course, the temperature of the boiling fluid in shell side 30 must be kept lower than the desired oligomerization reaction temperature within tubes 28, conveniently at least 5°C lower, such as at least 10°C lower, including at least 15°C lower and even at least 20°C lower, but typically not exceeding 40°C lower to reduce the risk of introducing too great a radial temperature gradient within

tubes 28 and decreasing the isothermality of the oligomerization reaction within tubes 28.

[00100] One design consideration for approaching isothermal conditions in heat exchanger reactor 27 is a relatively small diameter for the tubes 28, for example, an outside diameter of less than about 3 inches (7.6 cm), conveniently less than about 2 inches (5.1 cm), such as less than about 1.5 inches (3.8 cm), and an inside diameter commensurate with the desired pressure rating for the inside of the tubes 28. This provides a relatively small resistance to heat transfer relative to the heat generated per unit volume of reaction space within tubes 28. Another such design consideration is a relatively long length for tubes 28, such as greater than about 5 meters, including greater than about 7 meters, conveniently greater than about 9 meters, which reduces the heat release per unit volume of reaction within tubes 28 and also promotes isothermality.

[00101] The oligomerization reaction product exits heat exchanger reactor 27 through line 42, and is provided to feed/effluent exchanger 18. The cooled reaction product exits feed/effluent exchanger 18 through line 44, and is provided to separation device 46. Separation device 46 may include one or more well known elements, such as fractionation columns, membranes, and flash drums, among other elements, and serves to separate the various components in the cooled reaction product in line 44 into various streams having differing concentrations of components than the cooled reaction product in line 44, including the desired hydrocarbon composition in line 48 and an olefinic recycle stream containing no greater than 10 wt.% C10 olefins in line 14. Additionally, one or more purge streams may be produced by separation device 46 and exit via line 50. Such purge streams in line 50 conveniently include streams richer in saturated hydrocarbons than the feedstock stream in line 12, such as a C_4- rich stream containing unreacted butylenes and relatively concentrated C_4- saturates, or a portion of material of identical or similar composition to that of the olefinic recycle in line 14 and relatively concentrated in C_5+ saturates. Providing such purge streams is convenient in controlling the partial pressure of olefins provided for reaction in heat exchanger reactor 27.

Fuel Blends

[00102] One preferred use of the hydrocarbon composition of the invention is in producing fuel blends, for example blends useful as jet fuels and diesel fuels.

[00103] In one embodiment of producing a fuel blend, the hydrocarbon composition of the invention is combined with a second hydrocarbon material having a specific gravity greater than 0.775 and/or having a having a freezing point of greater than -47 ^{O}C according to ASTM Test Method D2386. The blend meets all specifications for Jet Fuel A, or Jet Fuel A-1, as described in Table 1 of ASTM D1655-04. When used in such a blend, the hydrocarbon composition of the invention preferably has an end point (or final boiling point) of at least 270°C, or at least 290°C, or at least 300°C or at least 310°C.

[00104] More particularly, the second hydrocarbon material used in making a blend useful as Jet Fuel A or Jet Fuel A-1 can have one or more of the following additional or alternative properties:

(i) a 10 vol% recovered temperature (T10) of at least 170°C, or at least 190°C, or at least 210°C or at least 220°C;

(ii) an end point (or final boiling point) of at least 220°, or at least 240°C or at least 260°C, and no greater than 270°C, or no greater than 290°C, or no greater than 300°C or no greater than 320°C;

(iii) a freezing point of greater than -40°C;

(iv) a flash point of at least 40°C, or at least 50°C or even at least 60°C;

(v) an aromatics content of greater than 15 wt.%, or greater than 25 wt.%, or greater than 30 wt.%, or greater than 40 wt.% or greater than 50 wt.%; and

(vi) a smoke point less than 30 mm, or less than 25 mm, or less than 20 mm, or less than 18 mm or less than 15 mm according to ASTM Test Method 1322, the entire contents of which are incorporated herein by reference.

[00105] The jet fuel blend can further include an additive to increase its electrical conductivity, for example, Stadis 450, as described above. The blend

can also include other additives, the types and proportions of which may be found in Table 2 of ASTM D1655-04.

[00106] In another embodiment, the hydrocarbon composition of the invention is combined with a second hydrocarbon material having a specific gravity greater than 0.775 and less than 0.890 and/or having a kinematic viscosity at 40°C greater than 1.9 (mm^2/S). Depending on the sulfur content and/or viscosity of the hydrocarbon composition of the invention and the second hydrocarbon material, the resultant blend meets all specifications for No. 2-D S15, No. 2-D S500 or No. 2-D S5000 diesel fuel as described in Table 1 of ASTM D975-04a, Table 1. In particular, when the hydrocarbon composition of the invention has a sulfur content less than 15 wppm and the second hydrocarbon material has a sulfur content greater than 15 wppm, the blend meets all specifications for No. 2-D S15 diesel fuel as described in Table 1 of ASTM D975-04a. When the hydrocarbon composition of the invention has a sulfur content less than 500 wppm and the second hydrocarbon material has a sulfur content greater than 500 wppm, the blend meets all specifications for No. 2-D S500 diesel fuel as described in Table 1 of ASTM D975-04a. When the hydrocarbon composition of the invention has a kinematic viscosity at 40°C less than 1.5 mm^2/sec, or less than 2.0 mm^2/sec or less than 2.5 mm^2/sec, and the second hydrocarbon material has a kinematic viscosity at 40°C greater than 2.1 mm^2/sec, or greater than 2.5 mm^2/sec, or greater than 3.0 mm^2/sec, or greater than 3.5 mm^2/sec or greater than 4.1 mm^2/sec, the blend meets all specifications for a No. 2-D S5000 diesel fuel as described in Table 1 of ASTM D975-04a.

[00107] In yet another embodiment, the hydrocarbon composition of the invention has a kinematic viscosity at 40°C less than 1.3 mm^2/sec and is combined with a second hydrocarbon material having a kinematic viscosity at 40°C greater than 1.3 mm^2/sec. Depending on the sulfur content and/or viscosity of the hydrocarbon composition of the invention and the second hydrocarbon material, the resultant blend meets all specifications for No. 1-D S15, No. 1-D S500 or No. 1-D S5000 diesel fuel as described in Table 1 of ASTM D975-04a, Table 1. In particular, when the hydrocarbon composition of the invention has a sulfur content

less than 15 wppm and the second hydrocarbon material has a sulfur content greater than 15 wppm, the blend meets all specifications for No. 1-D S15 diesel fuel as described in Table 1 of ASTM D975-04a. When the hydrocarbon composition of the invention has a sulfur content less than 500 wppm and the second hydrocarbon material has a sulfur content greater than 500 wppm, the blend meets all specifications for No. 1-D S500 diesel fuel as described in Table 1 of ASTM D975-04a. When the hydrocarbon composition of the invention has a kinematic viscosity at 40°C less than 1.5 mm^2/sec, or less than 2.0 mm^2/sec or less than 2.5 mm^2/sec and the second hydrocarbon material has a kinematic viscosity at 40°C greater than 1.5 mm^2/sec, or greater than 2.0 mm^2/sec, or greater than 2.4 mm^2/sec, the blend meets all specifications for a No. 1-D S5000 diesel fuel as described in Table 1 of ASTM D975-04a,.

[00108] With respect to second hydrocarbon material used in making blends having the properties of No. 1 or No. 2 Diesel fuel, it conveniently has the following additional properties:

(i) a 90 vol% recovered temperature (T90) of at least 282°C, or at least 300°C, or at least 338°C or at least 345°C;

(ii) an aromatics content of greater than 25 wt.%, or greater than 30 wt.%, or greater than 35 wt.%, or greater than 40 wt %, or greater than 45 wt% or greater than 50 wt.%; and a

(iii) a flash point of at least 55°C, or at least 60°C, o at least 70°C.

[00109] The invention will now be more particularly described with reference to the following Examples.

EXAMPLE 1

[00110] Four separate commercial ZSM-5 samples having the properties summarized in Table 1 below as catalysts A to D were tested in the oligomerization of butenes. Catalyst D was a sample of COD-9 provided by Sud-Chemie AG, Lenbachplatz 6, D-80333 Munich, manufactured and used commercially to convert olefins to diesel and gasoline fuels. Each catalyst was loaded into a fixed bed pilot reactor and used to process a feedstock comprising

52-58 wt% butenes and 10-11 wt% isobutane, with the balance being heptane. In each case, the feedstock was initially saturated with water by passing the feedstock upwardly through a vessel containing water at a constant 40°C and was then preheated to the desired processing temperature. Processing conditions for each catalyst run included a pressure of 7,000kPa, a range of WHSV from 14 to 28 based on total feed to the reactor and total catalyst weight (zeolite plus binder). For catalysts A to C, the reactor inlet temperature was set at 210 to 215°C, whereas for catalyst D the reactor inlet temperature was set at 210 to 225°C. The product effluent was cooled to near room temperature and depressured to 2,000 kPa, at which pressure total reactor effluent samples were taken and analyzed by gas chromatography. The feed and product olefin/paraffin ratios were compared in order to measure conversion. The liquid product was analyzed by a gas chromatograph equipped with a platinum catalyst to hydrogenate product olefins to paraffins and the carbon number distribution and paraffin distribution were measured. The results are summarized in Figures 2 to 5, from which it will be seen that catalyst A exhibited the highest oligomerization activity, the lowest cracking activity, the highest C_8 selectivity, the lowest heavies (C_{16}+) selectivity and the lowest n-butane selectivity of the four ZSM-5 catalysts tested.

TABLE 1

Catalyst	% Alumina	% ZSM-5	Alpha G(102)	SiO_2/Al_2O_3	Crystal Size (μm)
A	35	65	200	50	<0.05 homogeneous
B	35	65	1100	18	0.02-0.05 homogeneous
C	35	65	200	55	0.06-0.12
D	unknown	Unknown	unknown	unknown	unknown

EXAMPLE 2

[00111] The performance of catalysts A and D from Example 1 were compared with that of a ZSM-12 catalyst using the feedstock and process conditions described in Example 1 except the inlet temperature was 190°C instead of 210 to

215°C. The ZSM-12 had a narrow crystallite size distribution centered on 0.05 microns (homogeneous crystals), an alpha value of 300, a silica to alumina of 45 and was formed into a catalyst comprising 65 wt% ZSM-12 and 35 wt% alumina. The results of the comparison are shown in Figures 6 to 9. As shown in Figure 6, the ZSM-12 catalyst achieved similar conversion to the most active ZSM-5 catalyst (catalyst A) at a 25°C lower set-point temperature. Moreover, the deactivation rate, as depicted by decreasing conversion at constant temperature, was lower for the ZSM-12 catalyst than that for either of catalysts A and D. As shown in Figure 7, the ZSM-12 catalyst made similar amounts of C_8 and C_{12} oligomers as the ZSM-5 catalysts A and D and also had a similar selectivity to C_{16}+ heavies. In contrast, the ZSM-12 catalyst showed decreased formation of light (C_5 to C_7) hydrocarbons as compared with the ZSM-5 catalysts (Figure 8) and a lower level of carbon number interconversion (Figure 9).

EXAMPLE 3

[00112] The performance of catalysts A and D from Example 1 were compared with that of an MCM-22 catalyst using the feedstock and process conditions described in Example 1 except the inlet temperature was 180 to 190°C instead of 210 to 215°C. The MCM-22 crystals were nearly two dimensional hexagonal platelets having a narrow particle size distribution (are homogeneous) centered on 1 micron, with the thickness of the platelets ranging between 0.005 and 0.01 microns. The MCM-22 had an alpha value of 300, a silica to alumina molar ratio of 24 and was formed into a catalyst comprising 100 wt% MCM-22 and 0 wt% alumina (selfbound). The results of the comparison are shown in Figures 10 to 13. As shown in Figure 10, the MCM-22 catalyst achieved similar conversion to the most active ZSM-5 catalyst (catalyst A) at a 35°C lower set-point temperature. Moreover, the deactivation rate, as depicted by decreasing conversion at constant temperature, was lower for the MCM-22 catalyst than that of either of catalysts A and D. As shown in Figure 11, the MCM-22 catalyst made less C_8 and C_{12} oligomers than the ZSM-5 catalysts A and D but showed an increased selectivity to C_{16}+ heavies. As shown in Figure 13, the lower selectivity to C_8 and C_{12} oligomers of the MCM-22 catalyst may be explained by its increased carbon

number interconversion. As shown in Figure 12, the ratio of the amount of C_5 to C_7 hydrocarbons to the amount of C_9 to C_{11} and C_{13} hydrocarbons produced by the MCM-22 catalyst was similar to that produced by the ZSM-5 catalysts.

EXAMPLE 4

[00113] Olefinic feedstock and recycle materials were prepared as shown in Table 2 and were oligomerized over a catalyst comprising 65 wt.% of 0.02 to 0.05 micron crystals of ZSM-5 having a SiO_2/Al_2O_3 molar ratio of 50:1, and 35 wt.% of an alumina binder, shown as catalyst A in Table 1. The catalyst was in the form of 1/16 inch extrudates and about 90 cc of catalyst was blended with about 202 cc of inert, silicon carbide beads to reduce the heat generation per unit volume of reaction and placed in the reaction bed of a tubular reactor equipped with a heat management system that allowed the oligomerization reaction to proceed under near isothermal conditions.

TABLE 2				
	Charge A		Charge B	
	Feed	Recycle	Feed	Recycle
Wt. %	49.5	50.5	41.8	58.2
Proportion	1.0	1.0	1.0	1.4
Comp. Wt.%				
Ethane	0.0	0.0	0.0	0.0
Ethylene	0.0	0.0	0.0	0.0
Propane	0.0	0.0	0.0	0.0
Propene	0.0	0.0	0.0	0.0
iso-butane	7.2	0.1	1.0	0.0
n-butane	0.1	0.0	11.6	0.0
t-butene-2	0.0	0.1	27.2	0.0
butene-1	72.3	0.0	16.3	0.0
iso-butene	2.9	0.0	2.7	0.0
c-butene-2	0.0	0.0	20.1	0.0
iso-pentane	0.0	0.1	0.8	0.0
n-pentane	1.7	0.0	1.6	0.0
1,3-butadiene	0.0	0.0	0.1	0.0
C5 olefins	15.8	0.1	17.3	0.2
C6 sats	0.0	0.0	0.2	0.0
C6 olefins	0.0	0.5	1.2	1.3
C7 olefins	0.0	1.3	0.0	3.2
n-heptane	0.0	8.1	0.0	10.6
C8 olefins	0.0	73.7	0.0	55.6
C9 olefins	0.0	15.1	0.0	27.7
C10 olefins	0.0	0.8	0.0	1.3
Total	100.0	100.0	100.0	100.0

[00114] Over the course of the experimental run, various charges were provided to the reactor to test performance under various conditions over an extended period of time. As the experimental run progressed, the catalyst activity declined, requiring an increase in reactor temperature later in the run to achieve a given conversion of feedstock olefins. In two particular experiments, the feedstock and recycle materials were blended in the proportions shown in Table 2, and the single blended stream ("Charge") was provided to the reactor at 1000 psig (7000 kPa) and other conditions shown in Table 3; wherein the WHSV is based on based on the olefin in the total charge (combined feed and recycle) and the total catalyst

composition (ZSM-5 and binder). Four thermocouples were available, positioned evenly through the reaction bed in the reactor, with one very near the first point where the charge and catalyst come into contact, and one very near the outlet of the reaction bed. The difference between the highest and lowest temperatures within the reactor was from 2 to 7°C. The reaction product was analyzed with a gas chromatograph, and the composition of the products is provided in Table 3. No products having a carbon number greater than 21 were detected.

TABLE 3		
Experiment (ca. Days On Stream)	23	59
Charge	A	B
Reactor T (°C)	235	274
WHSV (1/hr)	4.2	3.9
Product Comp. Wt.%		
Ethane	0.0	0.0
Ethylene	0.0	0.0
Propane	0.0	0.0
Propene	0.1	0.1
iso-butane	3.6	0.5
n-butane	0.1	4.3
t-butene-2	2.0	0.7
butene-1	0.6	0.2
iso-butene	0.2	0.2
c-butene-2	1.3	0.4
iso-pentane	0.1	0.4
n-pentane	0.1	0.6
1,3-butadiene	0.0	0.0
C5 olef	1.6	1.5
C6 sats	0.1	0.1
C6 olefins	0.9	1.0
C7 olefins	1.6	2.3
n-heptane	4.6	6.6
C8 olefins	40.2	29.8
C9 olefins	15.8	19.0
C10 olefins	2.8	4.0
C11 olefins	2.5	3.2
C12 olefins	12.4	12.1
C13 - C15 olefins	4.3	6.5
C16 olefins	4.4	4.9
C17 - C20 olefins	0.8	1.6
Total	100.0	100.0

EXAMPLE 5

[00115] The same apparatus and procedure as Example 4 was utilized for a further, extended experimental run with a fresh batch of catalyst and another set of

charge compositions as shown in Table 4. The olefinic feedstocks shown in Table 4 were produced by reacting methanol over a SAPO-34 catalyst generally according to the method of U.S. Patent No. 6,673,978, with separation of the methanol reaction products to provide a C_4+ olefin composition. Over 90 wt.% of the olefins in each feed composition were normal in atomic configuration, and the feed composition further contained about 1000 wppm oxygenates, such as methanol and acetone (not shown in Table 4). Some minor adjustments of some components in the feed compositions were made by additions of reagent grade materials to test certain aspects of the operation.

[00116] The olefinic recycle compositions shown in Table 4 were produced by taking accumulated batches of the reaction products from Example 4 and this further experimental run and periodically providing those batches to a fractionation tower to separate a distillate product from a light olefinic recycle material, collecting those fractionated materials, and using the fractionated light olefinic recycle material for subsequent experiments. Over 90 wt.% of the olefins in each recycle composition were non-normal in atomic configuration. Some minor adjustments of some components in the recycle compositions were made via addition of reagent grade materials to account for unavoidable losses in the fractionation step and test certain other aspects of the operation.

TABLE 4

	Charge C		Charge D		Charge E		Charge F	
	Feed	Recycle	Feed	Recycle	Feed	Recycle	Feed	Recycle
Wt. %	38.3	61.7	45.5	54.5	49.7	50.3	47.6	52.4
Proportion	1.0	1.6	1.0	1.2	1.0	1.0	1.0	1.1
Comp. Wt.%								
Butane	2.0	16.6	2.3	10.0	2.8	9.3	2.1	7.5
Butenes	63.5	3.1	64.4	2.7	64.6	3.0	64.9	3.1
Dienes	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0
Pentane	0.5	4.7	1.8	0.2	1.4	1.0	1.5	1.9
Pentenes	21.8	1.7	20.8	2.3	20.7	2.5	21.1	2.3
Hexanes	0.3	0.1	0.3	0.1	0.2	0.3	0.2	0.5
Hexenes	11.8	1.3	10.4	3.1	10.3	3.5	10.1	4.3
Heptenes	0.0	3.0	0.0	3.4	0.0	3.2	0.0	3.4
n-Heptane	0.0	6.6	0.0	7.5	0.0	7.6	0.0	8.1
Octenes	0.0	44.1	0.0	49.6	0.0	48.9	0.0	52.8
Nonenes	0.0	18.6	0.0	21.0	0.0	20.5	0.0	16.2
Decenes	0.0	0.2	0.0	0.2	0.0	0.2	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[00117] For a number of particular experiments using the charge material and proportions shown in Table 4, the butylene conversion and yield of C_{10}+ material in the reactor product for each of the charge compositions under a variety of temperatures and approximate days on stream are provided in Table 5. In all of the experiments shown in Table 5, the total reactor pressure was about 1000 psig (7000 kPa), the WHSV was between 3.5 and 4.0 based on the olefin in the total charge (combined feed and recycle) and the total catalyst composition (ZSM-5 and binder), and the difference between the highest and lowest temperatures within the reactor was 10°C or less.

TABLE 5

Experiment (Days on Stream)	Charge	Reactor T (°C)	C4= conversion (wt.%)	C10+ yield (wt.%)
2	C	207	93.3	38.0
3	C	212	97.9	43.4
5	C	211	91.9	36.0
8	C	211	87.9	32.1
13	D	221	98.4	46.3
14	D	220	96.3	41.6
15	D	220	95.5	40.2
17	D	220	92.4	37.1
20	E	225	95.6	40.1
24	E	227	94.6	38.3
32	E	233	95.1	37.4
41	E	244	96.2	37.6
46	E	247	96.2	37.5
51	E	253	97.2	38.7
55	F	252	94.9	33.0
57	F	255	96.0	33.5
59	F	259	97.0	37.0
62	F	259	96.8	36.0

EXAMPLE 6

[00118] Several batches of distillate materials were produced from the fractionation of various batches of reactor product obtained in Examples 4 and 5. The carbon number distribution of these non-hydrogenated distillate material batches are provided in Tables 6 and 6A. Distillates 1 and 2 in Tables 6 and 6A were obtained from fractionation operations using the aggregate reactor product from Example 4, while Distillate 3 was obtained from fractionation operations of

the aggregate reactor product from Charges C, D and E used in Example 5. All of the distillate materials contain all of the C_{11}+ and almost all of the C_{10} material present from the reaction products, i.e., no separation of any components heavier than C_{11} was conducted on the reactor product in obtaining the distillate materials. As obtained directly from the reactor product via the fractionation tower, all the distillate materials are over 90 wt.% non-normal olefins, and further contain very low amounts of aromatics (<100 wppm).

EXAMPLE 7

[00119] The batches of distillate materials obtained in Example 6 were hydrogenated in discrete batches by reacting them with hydrogen over a hydrogenation catalyst. Distillates 1 and 2 were hydrogenated over a nickel-containing catalyst while Distillate 3 was hydrogenated over a platinum/palladium-containing catalyst, each according to operations and conditions well known. The carbon number distribution of the hydrogenated distillates is provided in Table 6. Hydrogenation did not significantly change the non-normal character of distillate compositions although, following hydrogenation, the distillate materials were almost completely aliphatic. No products having a carbon number greater than 21 were detected. Table 6 provides the carbon number distribution according to the Linear Paraffin method, which defines carbon number between two adjacent linear paraffins and integrates each normal peak separately.

[00120] In Table 6A the carbon distribution of the non-hydrogenated distillate samples is given. It gives the carbon or isomer distribution. Cn is then defined as all isomers with carbon number "n". With the Linear Paraffin method what is defined as Cn, can contain e.g. a Cn-1 or Cn+1 isomer due to overlapping GC peaks. As a result, there are differences between the carbon distribution in Table 6 and 6A for the same distillate samples.

[00121] The GC analysis data for both Table 6 and 6A were collected on a PONA Gas Chromatograph. On this GC, the distillate sample, prior to entering the GC separation column, is coinjected with hydrogen across a small reactor bed containing saturation catalyst. All the olefinic material in the distillate sample to

the GC separation column is thus saturated (if not yet saturated before by hydrogenation). However, it is believed that the carbon number distribution (CND) measured herein are accurate.

TABLE 6			
Distillate	1	2	3
	Before and after hydrogenation		
Comp (wt.%)			
C4-C7	0.1		0.1
C8	0.0		0.1
C9	4.8		12.6
C10	8.7		12.6
C11	16.2		14.3
C12	32.0		22.8
C13	12.8		11.6
C14	5.7		6.9
C15	8.1		7.7
C16	5.8		5.3
C17	2.2		2.5
C18	1.5		1.7
C19	1.2		1.1
C20	1.0		0.7
Total	100.0	0.0	100.0
% normal paraffins	3.17		2.75

TABLE 6A			
Distillate	1	2	3
	Before hydrogenation		
Comp (wt.%)			
C4-C7	0.3	0.4	0.7
C8	0.4	1.0	1.0
C9	4.9	19.8	13.3
C10	8.7	9.4	13.0
C11	8.5	7.5	8.1
C12	39.1	32.4	29.2
C13 - C15	16.7	14.9	16.0
C16	15.9	11.2	13.8
C17 - C20	5.6	3.6	5.0
Total	100.0	100.0	100.0

[00122] Table 7 provides composition and other physical and fuel performance properties of the hydrogenated distillate materials.

TABLE 7				
Distillate	1	2	3	
	After hydrogenation			
Distillation T10 (°C)	188	165	171	ASTM D86
Distillation T90 (°C)	265	250	269	ASTM D86
Distillation End Point (°C)	304	293	308	ASTM D86
Flash Point (°C)	57	42	47	ASTM D94
Density @ 15 °C (kg/l)	0.767	0.756	0.765	ISO 12185
Viscosity @ 40 °C (mm2/s)	1.53	1.26	1.42	ASTM D445
Viscosity @ 20 °C (mm2/s)	2.16	1.72		ASTM D445
Viscosity @ -20 °C (mm2/s)	6.06	4.15		ASTM D445
Freeze Point (°C)	-56	-62	< -50	ASTM D2386
Aromatics (wppm)	25		49	Ultra-violet
Sulfur (wppm)	<0.1	<0.1	<0.1	ASTM D2622
Olefins (wt.%)	<0.01	<0.01	<0.01	ASTMD2710

[00123] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

What is Claimed is:

1. A hydrocarbon composition comprising at least 90 wt.% of C_9 to C_{20} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition, at least 2 wt.% and not greater than 25 wt.% of C_9 hydrocarbons based on the weight of the hydrocarbon composition, and less than 15 wt.% of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition, wherein said hydrocarbon composition has a specific gravity at 15°C of at least 0.730 and less than 0.775.

2. The hydrocarbon composition of claim 1 and comprising at least 92 wt.%, preferably at least 95 wt.%, of C_9 to C_{20} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition.

3. The hydrocarbon composition of claim 1 or claim 2 and comprising 50 wt.% to 75 wt.% of C_{12} to C_{16} non-normal olefins, non-normal saturates or combinations thereof based on the weight of the hydrocarbon composition.

4. The hydrocarbon composition of any preceding claim and comprising 3 wt.% to 20 wt.%, preferably 4 wt.% to 15 wt.%, of C_9 hydrocarbons based on the weight of the hydrocarbon composition.

5. The hydrocarbon composition of any preceding claim and comprising less than 10 wt.%, preferably less than 5 wt.%, of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition.

6. The hydrocarbon composition of any preceding claim and comprising at least 1 wt.%, preferably at least 3 wt.%, of C_{17}+ hydrocarbons based on the weight of the hydrocarbon composition.

7. The hydrocarbon composition of any preceding claim and comprising no greater than 12 wt.%, preferably no greater than 7 wt.%, of C_{17} to C_{20} hydrocarbons based on the weight of the hydrocarbon composition.

8. The hydrocarbon composition of any preceding claim and comprising no greater than 8 wt.%, preferably no greater than 5 wt.%, of C_{19} to C_{20} hydrocarbons based on the weight of the hydrocarbon composition.

9. The hydrocarbon composition of any preceding claim and comprising no greater than 3 wt.%, preferably no greater than 1 wt.%, of C_{21}+ hydrocarbons based on the weight of the hydrocarbon composition.

10. The hydrocarbon composition of any preceding claim and comprising no greater than 5 wt.%, preferably no greater than 3 wt.%, more preferably no greater than 1 wt.%, of C_8- hydrocarbons based on the weight of the hydrocarbon composition.

11. The hydrocarbon composition of any preceding claim and comprising less than 5000 ppm wt., preferably less than 500 ppm wt., more preferably less than 15 ppm wt., of sulfur.

12. The hydrocarbon composition of any preceding claim and having a specific gravity at 15°C of 0.740 to 0.770, preferably 0.750 to 0.765.

13. The hydrocarbon composition of any preceding claim and having a flash point of at least 38°C, preferably at least 40°C, more preferably at least 45°C.

14. A process for producing a hydrocarbon composition, the process comprising:

(a) contacting a feed comprising at least one C_3 to C_8 olefin and an olefinic recycle stream with a molecular sieve catalyst in at least

one reaction zone under olefin oligomerization conditions such that the recycle to feed weight ratio is about 0.5 to about 2.0, the WHSV is at least 1.5 based on the olefin in the feed, and the difference between the highest and lowest temperatures within the or each reaction zone is 40°F (22°C) or less, said contacting producing a oligomerization effluent stream; and

(b) separating said oligomerization effluent stream into at least a hydrocarbon product stream and said olefinic recycle stream, wherein the olefinic recycle stream contains no more than 10 wt.% of C_{10}+ non-normal olefins, and the hydrocarbon product stream contains at least 1 wt.% and no more than 30 wt.% of C_9 non-normal olefins.

15. The process of claim 14 wherein the recycle to feed weight ratio in said contacting (a) is about 0.7 to about 1.3.

16. The process of claim 14 or claim 15 wherein the contacting (a) is conducted at a WHSV of about 1.8 to about 9 based on the olefin in the feed.

17. A process for producing a hydrocarbon product, the process comprising:

(a) contacting a feed comprising at least one C_3 to C_8 olefin and an olefinic recycle stream rich in C_9- hydrocarbons with a crystalline molecular sieve catalyst having an average crystal size no greater than 0.15 micron and an alpha value between about 100 and about 600 in at least one reaction zone under olefin oligomerization conditions including an inlet temperature between about 180°C and about 350°C, a pressure of at least 2,860 kPa and a recycle to feed weight ratio of about 0.1 to about 3.0, said contacting producing a oligomerization effluent stream; and

(b) separating said oligomerization effluent stream into at least a hydrocarbon product stream rich in C_9+ hydrocarbons and said olefinic recycle stream.

18. The process of claim 17 wherein the recycle to feed weight ratio in said contacting (a) is about 0.5 to about 2.0, preferably about 0.7 to about 1.3.

19. The process of claim 17 or claim 18 wherein the contacting (a) is conducted at a WHSV of at least 1.5, preferably about 1.8 to about 9, based on the olefin in the feed.

20. The process of any one of claims 14 to 19 wherein the contacting (a) is conducted at a WHSV of about 2.3 to about 14 based on the olefin in the combined feed and olefinic recycle stream.

21. The process of any one of claims 14 to 20 wherein said feed comprises a mixture of C_3 to C_5 olefins comprising at least 5 wt.% of C_4 olefin.

22. The process of any one of claims 14 to 21 wherein said mixture comprises at least 40 wt.% of C_4 olefin and at least 10 wt.% of C_5 olefin.

23. The process of any one of claims 14 to 22 wherein said feed contains C_4 olefin and the contacting (a) is conducted so as to convert about 80 wt.% to about 99 wt.% of the C_4 olefin in the feed.

24. The process of any one of claims 14 to 23 wherein said catalyst comprises an aluminosilicate molecular sieve having a silica to alumina molar ratio of about 20 to about 150, preferably about 45 to about 90.

25. The process of any one of claims 14 to 24 wherein said catalyst comprises a molecular sieve having a Constraint Index of about 1 to about 12.

26. The process of any one of claims 14 to 25 wherein said molecular sieve comprises ZSM-5, ZSM-12, and/or MCM-22.

27. The process of any one of claims 14 to 26 wherein said olefinic recycle stream contains no more than 7 wt.% of C_{10}+ non-normal olefins.

28. The process of claim 27 wherein said olefinic recycle stream has a final boiling point of no greater than 340°F (170°C).

29. The process of any one of claims 14 to 26 wherein said olefinic recycle stream contains no more than 30 wt.% of C_9+ non-normal olefins.

30. The process of claim 29 wherein said olefinic recycle stream has a final boiling point of no greater than 290°F (140°C).

31. A blend useful as a fuel and comprising (a) the hydrocarbon composition as claimed in any one of claims 1 to 13 (b) a second hydrocarbon composition different from the first-mentioned hydrocarbon composition and having at least one of the following properties (i) a specific gravity at 15°C greater than 0.775, (ii) a freezing point greater than -47 °C and (iii) a kinematic viscosity at 40°C greater than 1.3 mm^2/s.

32. The blend of claim 31 wherein said second hydrocarbon composition has a specific gravity at 15°C less than 0.890.

33. The blend of claim 31 or claim 32 wherein said second hydrocarbon composition has a freezing point greater than -40°C.

34. The blend of any one of claims 31 to 33 wherein said second hydrocarbon composition has a kinematic viscosity at 40°C greater than 1.9 mm^2/s.

35. The blend of any one of claims 31 to 34 wherein said first hydrocarbon composition has a final boiling point of at least 270°C.

36. The blend of any one of claims 31 to 35 wherein said second hydrocarbon composition has a final boiling point of at least 220°C and no greater than 320°C.

FIGURE 1

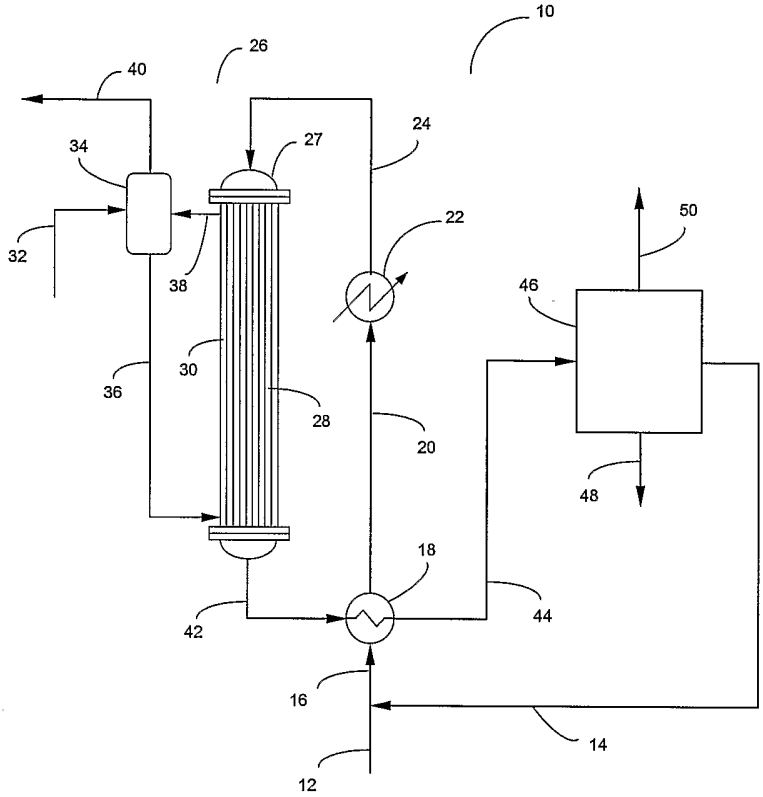


Figure 2

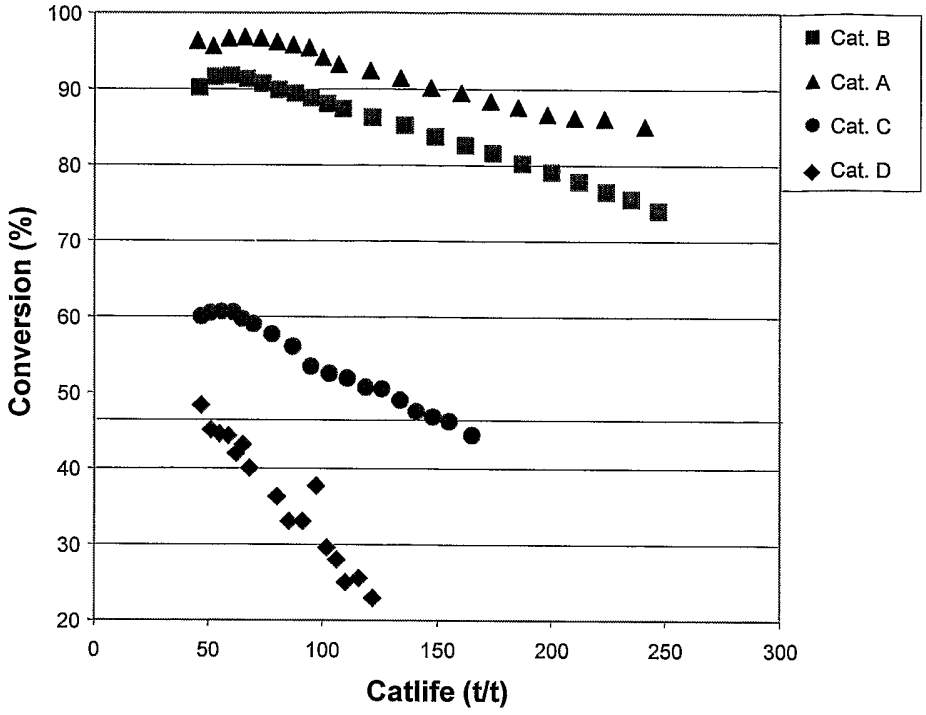

100
90
80
70
60
50
40
30
20
Conversion (%)
0
50
100
150
200
250
300
Catlife (t/t)
Cat. B
Cat. A
Cat. C
Cat. D

Figure 3

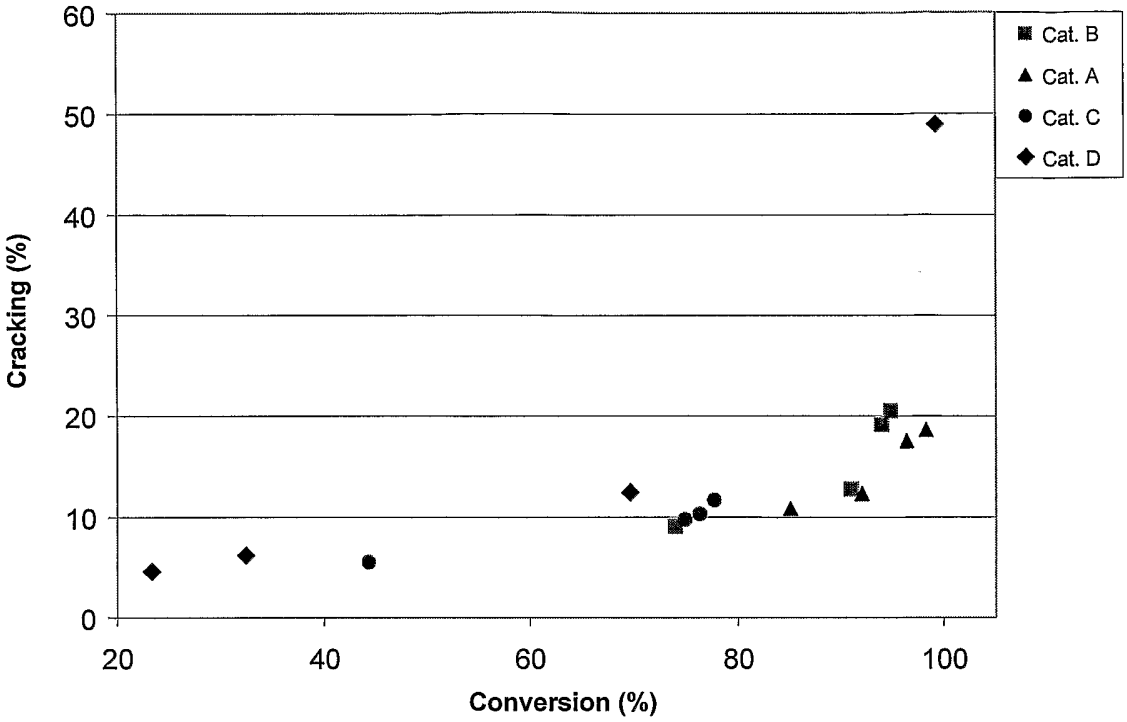

60
50
40
30
20
10
0
Cracking (%)
20
40
60
80
100
Conversion (%)
Cat. B
Cat. A
Cat. C
Cat. D

Figure 4

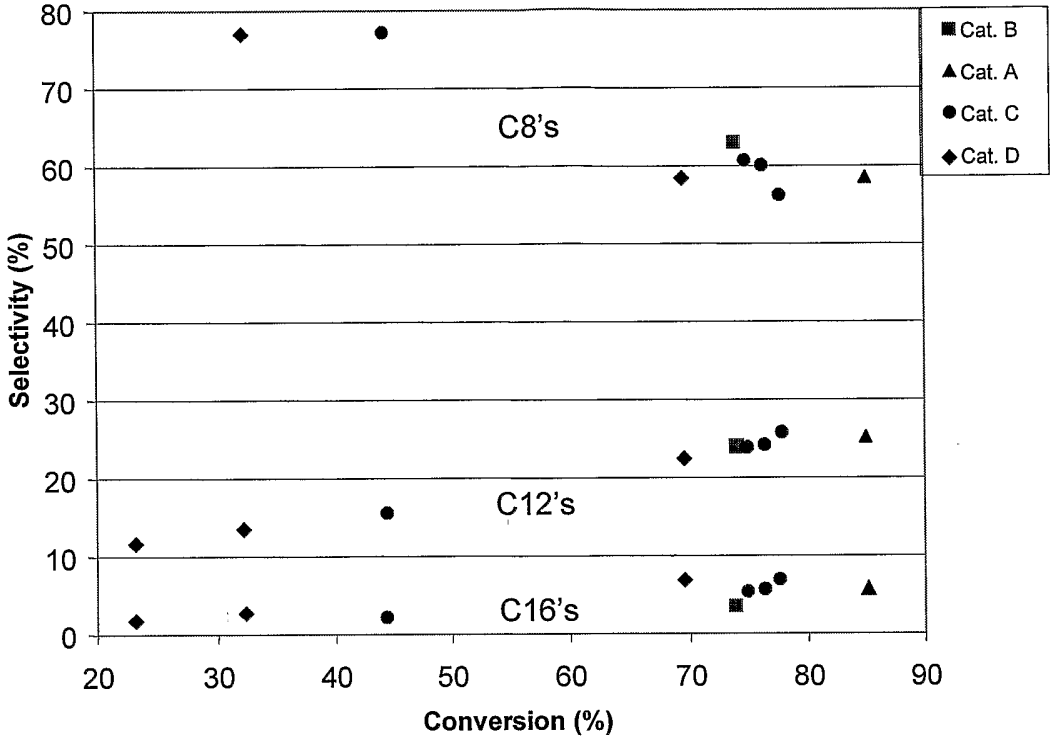

80
70
60
50
40
30
20
10
0
Selectivity (%)
C8's
C12's
C16's
20
30
40
50
60
70
80
90
Conversion (%)
Cat. B
Cat. A
Cat. C
Cat. D

Figure 5

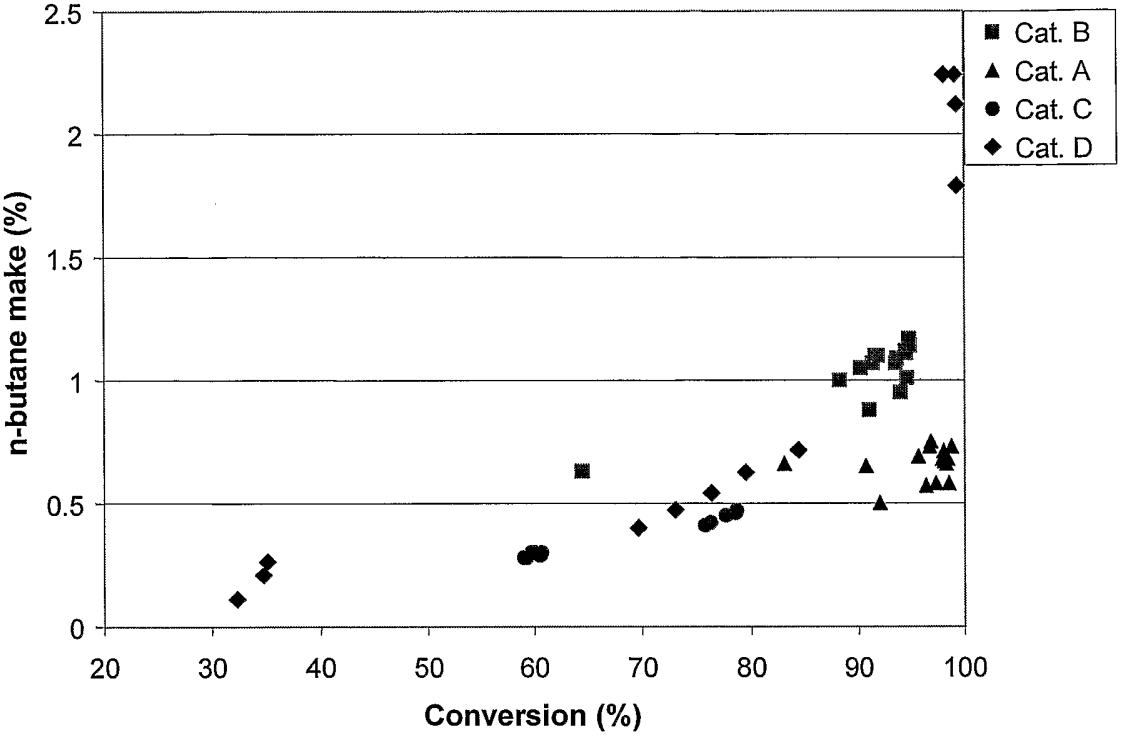

2.5
2
1.5
1
0.5
0
n-butane make (%)
20
30
40
50
60
70
80
90
100
Conversion (%)
Cat. B
Cat. A
Cat. C
Cat. D

Figure 6

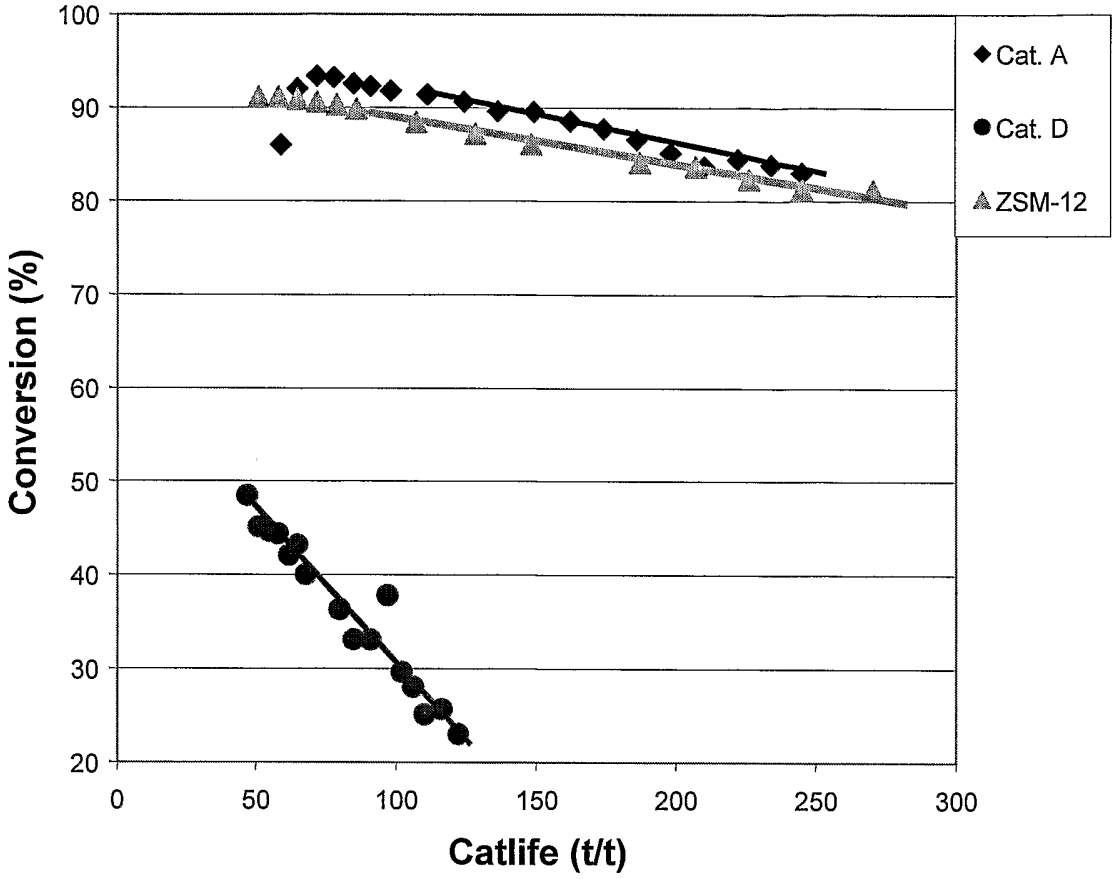

100
90
80
70
60
50
40
30
20
Conversion (%)
0
50
100
150
200
250
300
Catlife (t/t)
Cat. A
Cat. D
ZSM-12

Figure 7

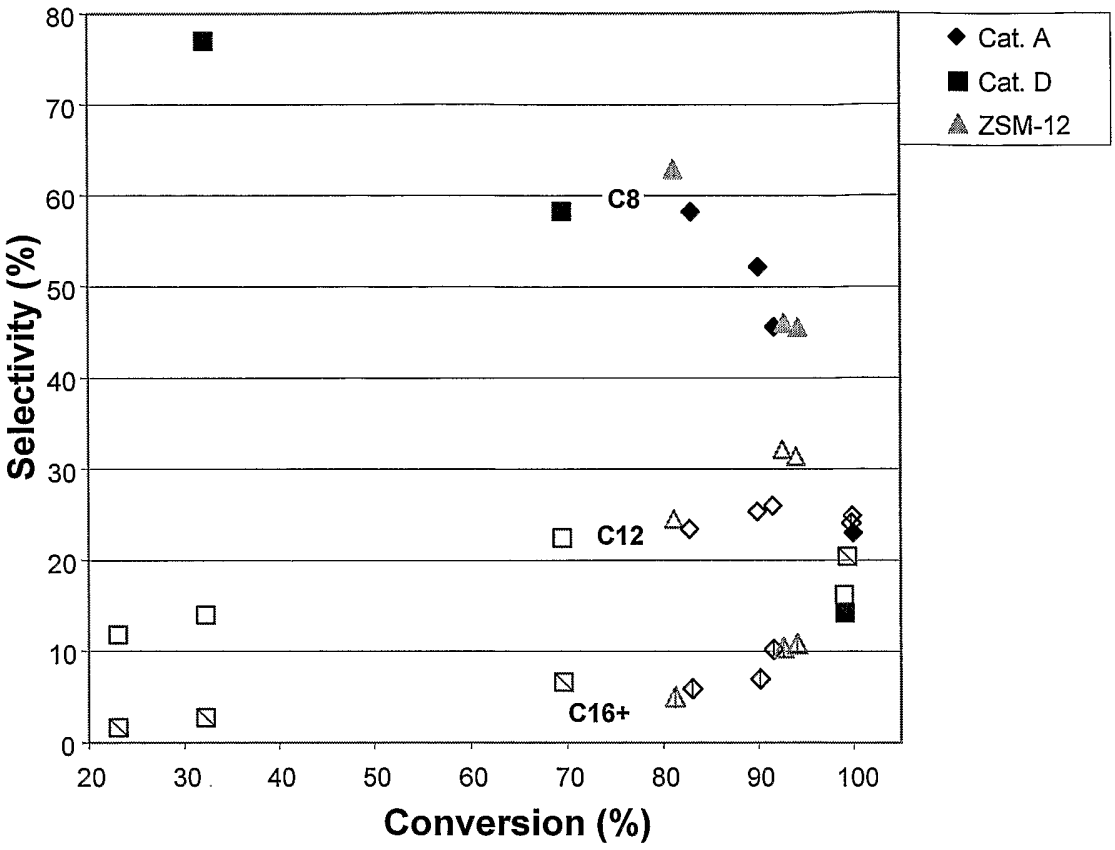

Cat. A
Cat. D
ZSM-12
C8
C12
C16+
Selectivity (%)
Conversion (%)
0
10
20
30
40
50
60
70
80
20
30
40
50
60
70
80
90
100

Figure 8

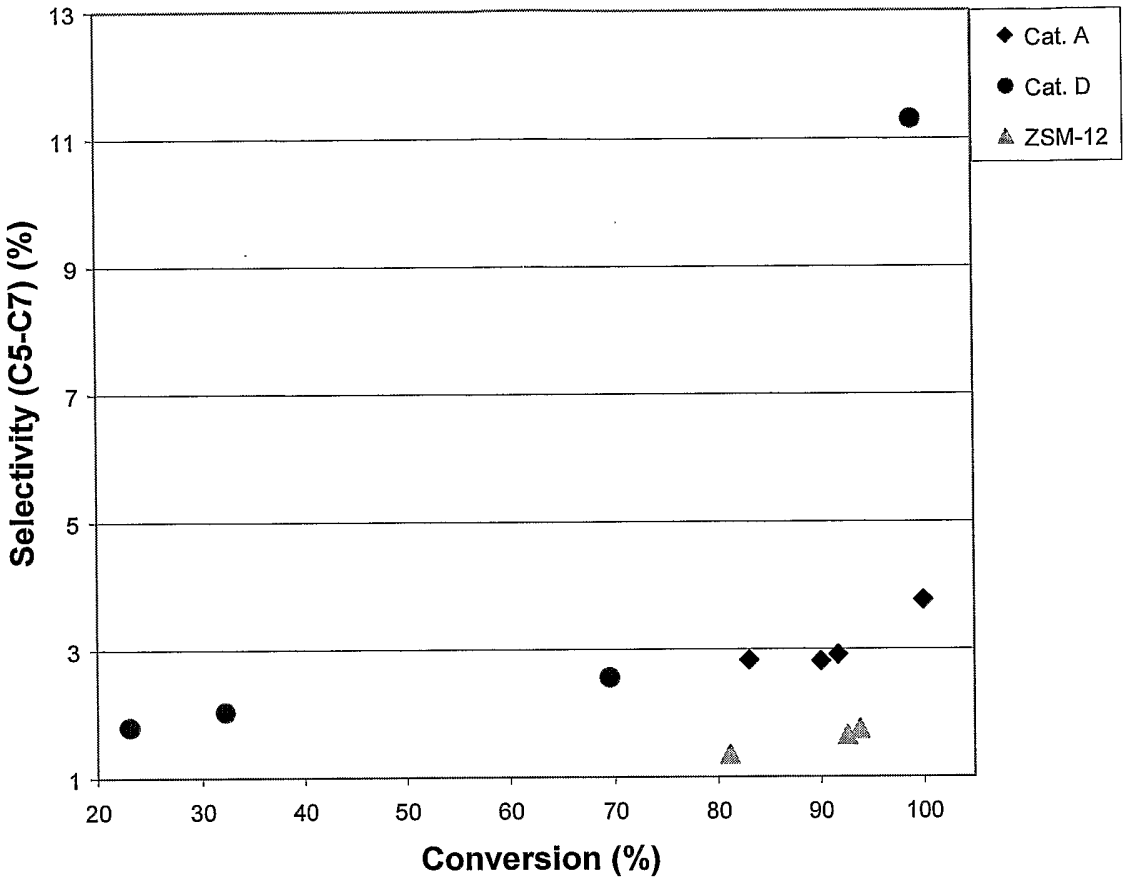

13
11
9
7
5
3
1
Selectivity (C5-C7) (%)
20
30
40
50
60
70
80
90
100
Conversion (%)
Cat. A
Cat. D
ZSM-12

Figure 9

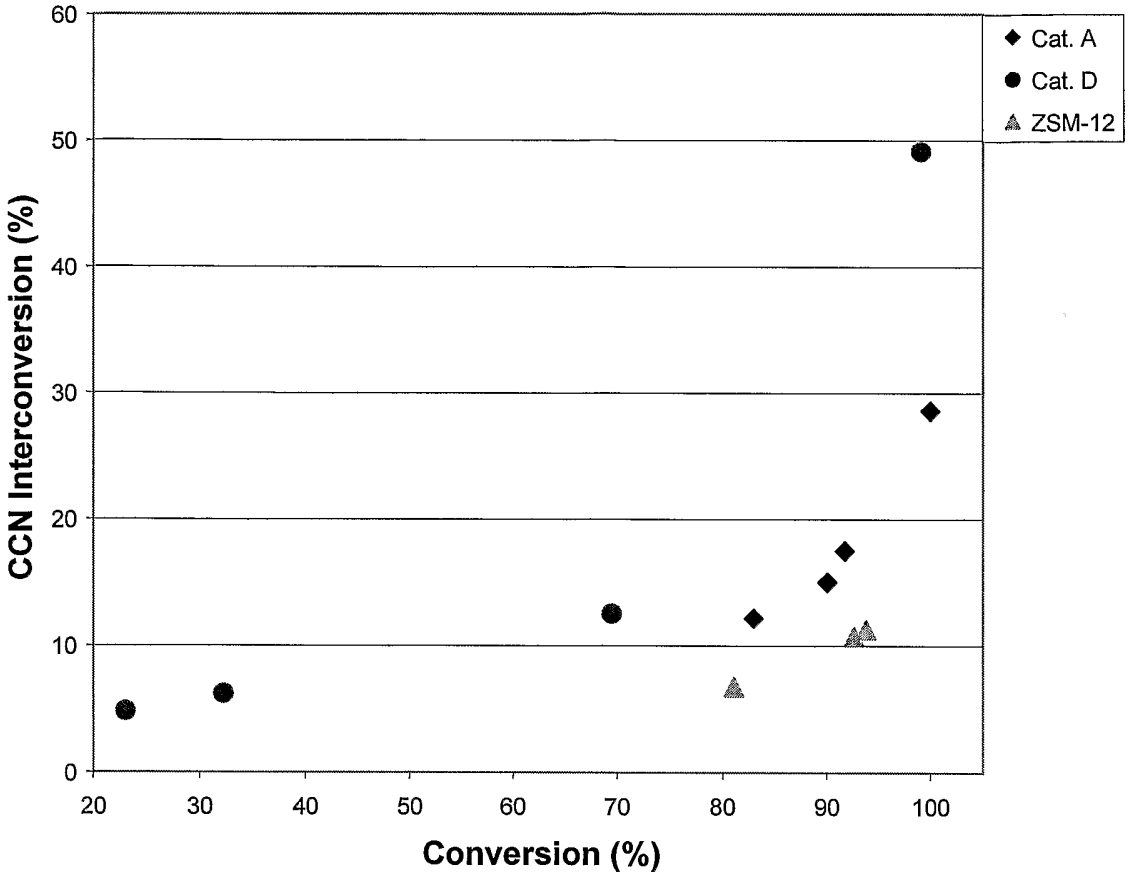

60
50
40
30
20
10
0
CCN Interconversion (%)
20
30
40
50
60
70
80
90
100
Conversion (%)
Cat. A
Cat. D
ZSM-12

Figure 10

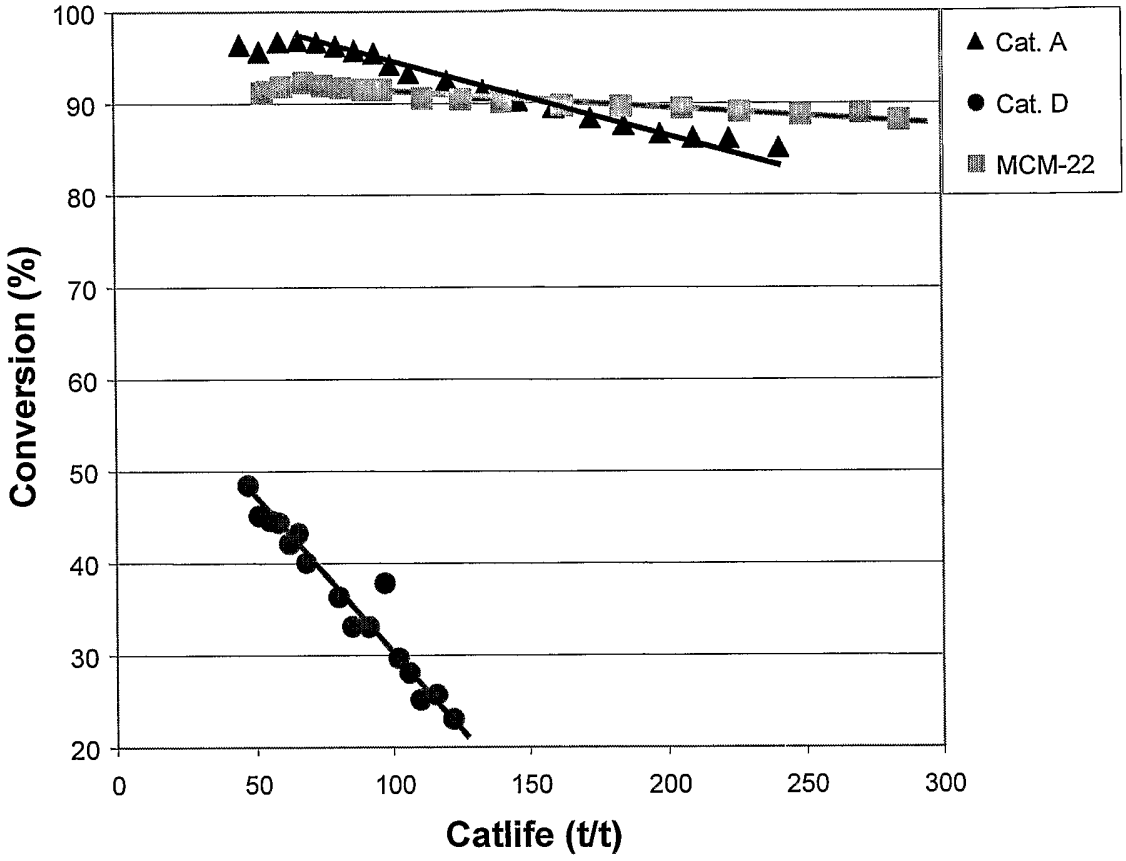

100
90
80
70
60
50
40
30
20
Conversion (%)
0
50
100
150
200
250
300
Catlife (t/t)
Cat. A
Cat. D
MCM-22

Figure 11

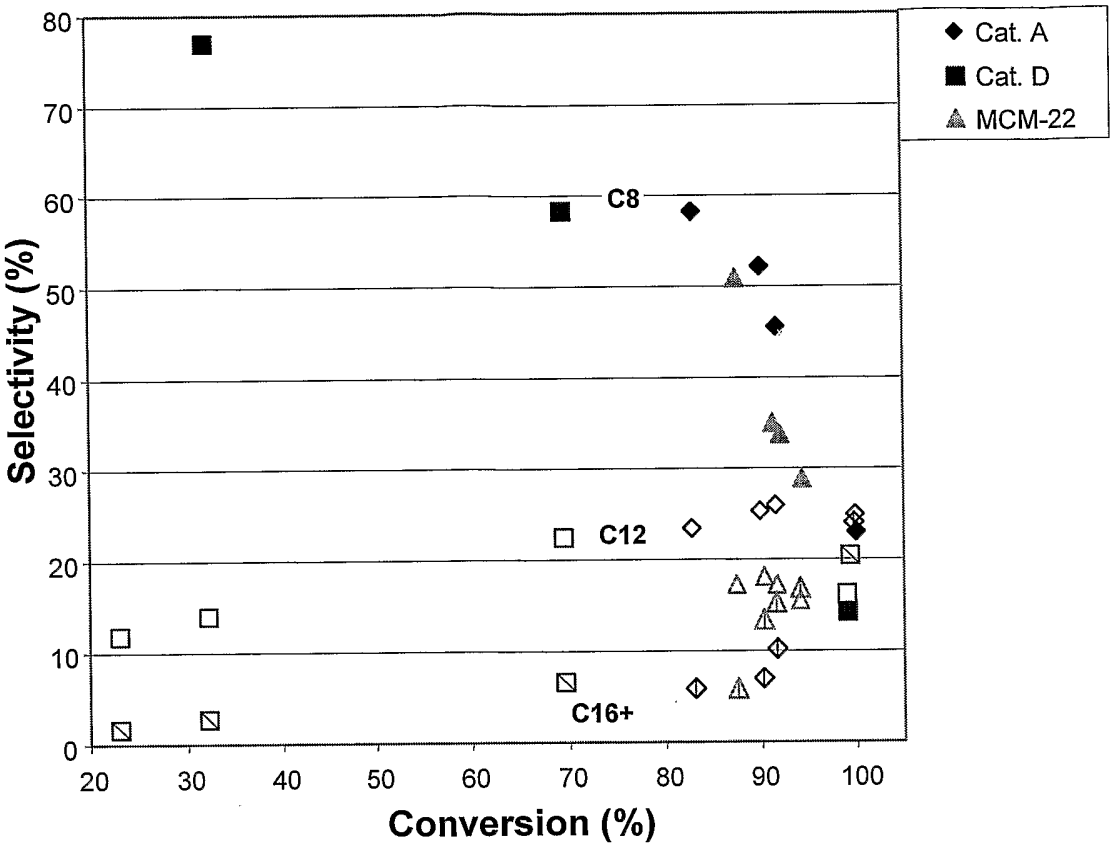

Cat. A
Cat. D
MCM-22
C8
C12
C16+
Selectivity (%)
Conversion (%)
0
10
20
30
40
50
60
70
80
20
30
40
50
60
70
80
90
100

Figure 12

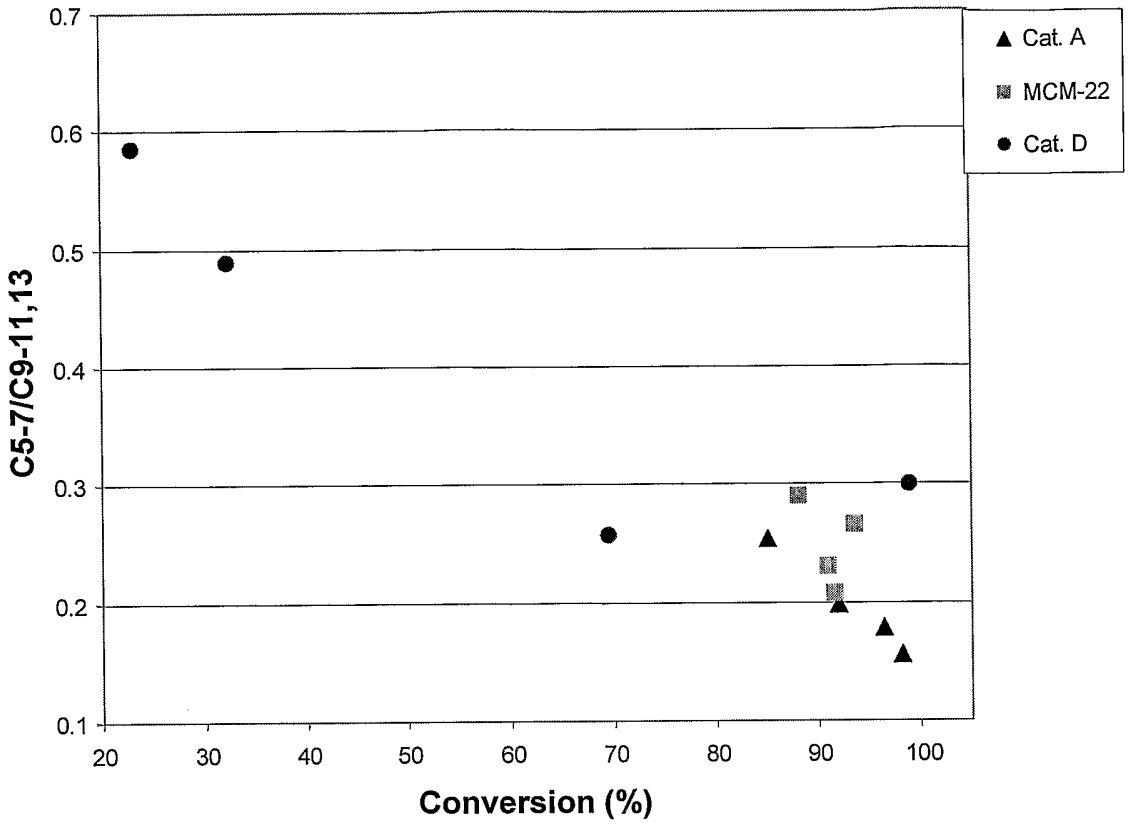
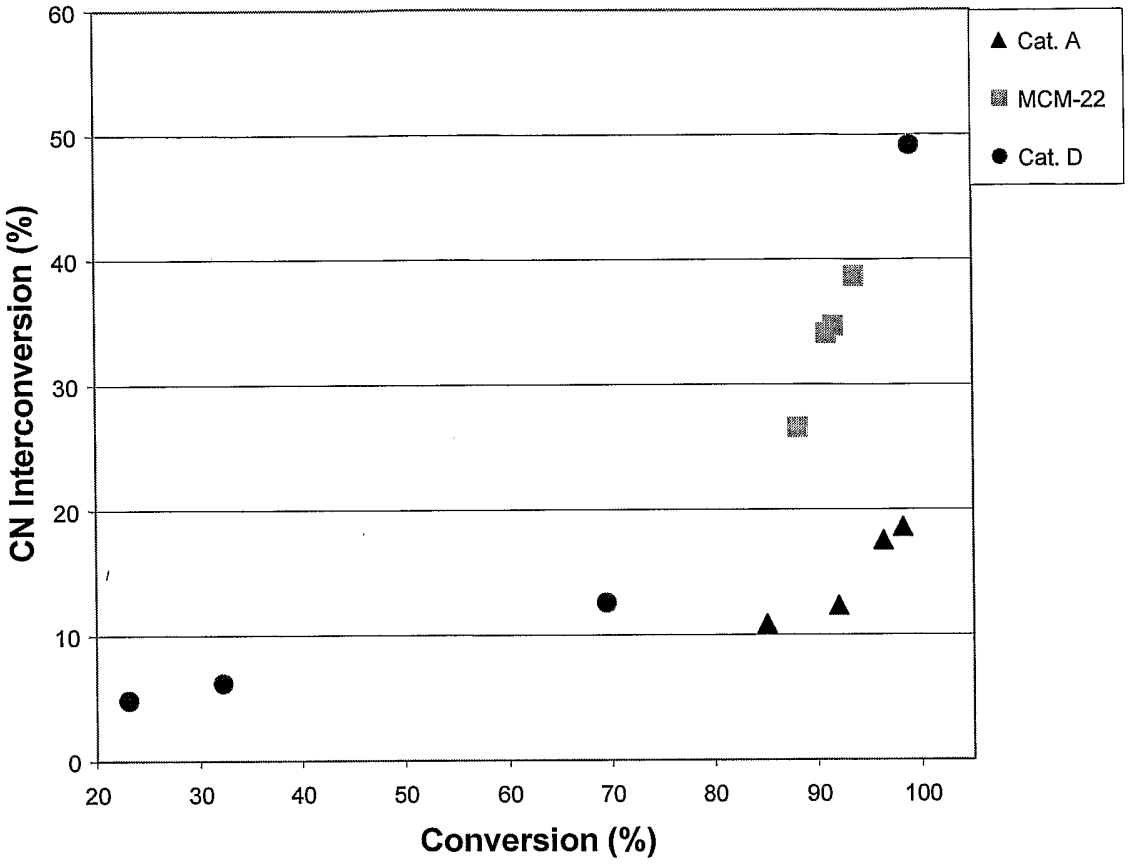

0.7
0.6
0.5
0.4
0.3
0.2
0.1
C5-7/C9-11,13
20
30
40
50
60
70
80
90
100
Conversion (%)
Cat. A
MCM-22
Cat. D

Figure 13


60
50
40
30
20
10
0
CN Interconversion (%)
20
30
40
50
60
70
80
90
100
Conversion (%)
Cat. A
MCM-22
Cat. D