

CONVERSION OF MIXTURES OF C₂-C₈ OLEFINS TO JET FUEL AND/OR DIESEL FUEL IN HIGH YIELD FROM BIO-BASED ALCOHOLS

PRIORITY INFORMATION

[0001] This application claims the benefit of U.S. Provisional Application Nos. 62/408,476, filed on Oct. 14, 2016; 62/412,046, filed on October 24, 2016; 62/426,787, filed on November 28, 2016; 62/484,580, filed on April 12, 2017; 62/489,756, filed on April 25, 2017; 62/500,892, filed on May 3, 2017; 62/521,664, filed on June 19, 2017, and 62/539,287, filed on July 31, 2017; each of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This disclosure relates to a process for converting lower linear and branched mono-olefins derived from C₂-C₅ bio-based alcohols to higher hydrocarbons, which are useful as precursors towards Jet or Diesel fuel production. In certain embodiments, Gevo researchers have developed technology converting bio-based C₂-C₅ alcohols to their respective linear and branched olefins in high yield, followed by subsequent oligomerization of branched and/or linear C₂-C₈ olefins to renewable Jet Fuel and/or Diesel fuel in overall yields of at least 70% in the presence of tungstated zirconium catalysts, nickel and/or cobalt doped tungstated zirconium catalysts, zeolites, or metal (Group IB-VIIB) doped zeolites and/or catalyst combinations thereof.

BACKGROUND

[0003] Bioethanol is a significant commodity chemical product. With the increased availability and reduced cost of bioethanol, researchers have explored bioethanol as a feedstock for making a variety of downstream hydrocarbons, including the aforementioned Jet Fuel and/or Diesel Fuel. Additionally, Gevo researchers have developed a fermentative process facilitating bio-isobutanol production, thereby providing a new route to bio-based fuels based on mixtures of bio-based alcohols.

[0004] Dehydration of C₂-C₅ alcohols and in some cases their subsequent isomerization is documented in the literature (*Materials* **2013**,6,101-115; *Catalysis Communications* **10**, **2009**, 567-571; US 20130131411; US 2017/0050896; EP 2374781), but few reports target catalysts

aimed at dehydrating mixtures of bio-based C₂-C₅ alcohols directly followed by oligomerization to hydrocarbon Jet and/or Diesel fuel in a fully integrated mode.

[0005] The oligomerization of gaseous mono-olefins so as to form gasoline-type hydrocarbons is known, and has been disclosed in the patent literature (US 4613719; US 9688590). However, there is an ever present need to develop new oligomerization processes employing more effective and/or less expensive catalyst compositions.

[0006] The oligomerization reaction of olefins has been carried out by using acid catalysts such as supported phosphoric acid, and olefin dimers have been generally obtained for gasoline additive after hydrogenation of the dimers (USP 6689927, 6284938).

[0007] Recently, several oligomerization methods to prepare trimers are reported. Olefin trimerization has been mainly carried out by using solid acid catalysts such as heteropoly acid (JP 2005015383), zirconia (JP 2005015384), zeolite called AI-TS-I (USP 6914165) and sulfated titania (J. Molecular Catalysis A, 228, 333, 2005). Ionic liquids are also used for the reaction (CN 1379005).

[0008] Additionally, numerous examples have been reported that utilize cation exchange resins for the oligomerization. It has been claimed that a cation exchange resin can be used in a dimerization (USP 2005/011911 IAI). USP 5789643 taught that oligomerization could be catalyzed by zeolites, aluminas and ion exchange resins. Tetramers or pentamers could be obtained by the oligomerization of pre-formed dimers with ion exchange resins (US 6239321).

[0009] Moreover, an ion exchange resin called Amberlyst-15 was used in the oligomerization of isobutene (Catalysis Today, 100, 463, 2005). However, the conversion was less than 40%, and dimers rather than trimers were the main products. Similarly, Amberlyst-35 ion exchange resin affords higher levels of trimers, but dimers are present in 30-40% levels.

[0010] Additionally, nickel based heterogeneous catalysts are routinely used for ethylene oligomerization in order to provide mixtures of C₂-C₈ olefins which are secondarily oligomerized to C₈-C₂₀ olefins (US 2381198, US 2581228, US 3527839).

[0011] Most industrial processes produce oligomers in a non-selective manner by the oligomerization of C₂-C₆ olefins. Such processes typically generate a mathematical distribution (Schulz-Flory or Poisson) of oligomers, which very often does not match market demand.

SUMMARY OF THE INVENTION

[0012] This disclosure relates to a process for converting lower linear and branched mono-olefins derived from C₂-C₅ bio-based alcohols to higher hydrocarbons, which are useful as precursors towards Jet or Diesel fuel production. In certain embodiments, a process for converting one or more C₂-C₈ linear or branched olefins to jet and/or diesel fuel, including contacting a feed stream comprising the one or more C₂-C₈ linear or branched olefins with a first catalyst to afford a mixture comprising at least 70 wt % C₁₂ or greater alkenes is described.

[0013] In some embodiments, the one or more C₂-C₈ linear or branched olefins comprise at least about 50 wt% of butenes, at least about 75 wt% of butenes, and at least about 90 wt% of butenes. Said butenes may comprise at least about 75 wt% isobutene or 75 wt% of linear butenes.

[0014] The process can further comprise dehydrating one or more C₂-C₈ linear or branched alcohols to provide the feed stream comprising one or more C₂-C₈ linear or branched olefins. The feed stream comprising one or more C₂-C₈ linear or branched olefins includes at least 0.5 wt% oxygenates, at least 1 wt% oxygenates, at least 2 wt% oxygenates, and at least 3 wt% oxygenates. The oxygenates can comprise water and one or more C₂-C₈ linear or branched alcohols. The yield of said C₁₂ or greater alkenes can be at least about 50%, at least about 60%, at least about 70%, and at least about 75%.

[0015] In some embodiments, the first catalyst comprises tungstated zirconium catalysts, molybdenum zirconium catalysts, nickel and/or cobalt doped tungstated zirconium catalysts, nickel and/or cobalt doped molybdenum zirconium catalysts, zeolites, Group IB-VIIB metal doped zeolites) doped zeolites, or combinations thereof. The tungstated zirconium catalyst can comprise about 85 wt% zirconium and about 15 wt% tungsten. The tungstated zirconium catalyst can further comprise from about 0.01 to about 3 wt% of nickel. The tungstated zirconium catalyst can further comprises from about 0.01 to about 3 wt% of cobalt. The molybdenum zirconium catalyst can comprise about 85 wt% zirconium and about 15 wt% molybdenum. The molybdenum zirconium catalyst can further comprise from about 0.01 to about 3 wt% of nickel. The molybdenum zirconium catalyst can further comprise from about 0.01 to about 3 wt% of cobalt. The first catalyst can comprise an acidic zeolite catalyst. The first catalyst can comprise an acidic ZSM-5 catalyst. The acidic ZSM-5 can further comprise from about 0.01 wt% to about 5 wt% zinc. The acidic ZSM-5 can further comprise from about 0.01 wt% to about 20 wt% zirconium. The first catalyst can comprise an acidic Ferrierite catalyst. The acidic Ferrierite can further comprise from

about 0.01 wt% to about 5 wt% zinc. The acidic Ferrierite can further comprise from about 0.01 wt% to about 20 wt% zirconium.

[0016] In some embodiments, the second catalyst comprises Zeolites, Group IB-VIIB metal doped zeolites) doped zeolites, or combinations thereof. The second catalyst can comprise an acidic ZSM-5 catalyst. The acidic ZSM-5 can further comprise from about 0.01 wt% to about 5 wt% zinc. The acidic ZSM-5 can further comprise from about 0.01 wt% to about 20 wt% zirconium. The second catalyst can comprise acidic Ferrierite catalyst. The acidic Ferrierite can further comprise from about 0.01 wt% to about 5 wt% zinc. The acidic Ferrierite further comprises from about 0.01 wt% to about 20 wt% zirconium.

[0017] It should be appreciated that all combinations of the foregoing concepts and additional concepts discussed in greater detail below (provided such concepts are not mutually inconsistent) are contemplated as being part of the inventive subject matter disclosed herein. In particular, all combinations of claimed subject matter of this disclosure are contemplated as being part of the inventive subject matter disclosed herein. It should also be appreciated that terminology explicitly employed herein that also may appear in any disclosure incorporated by reference should be accorded a meaning most consistent with the particular concepts disclosed herein.

DETAILED DESCRIPTION

[0018] In the following description, certain specific details are set forth in order to provide a thorough understanding of various embodiments. However, one skilled in the art will understand that the disclosure may be practiced without these details. In other instances, well-known structures have not been shown or described in detail to avoid unnecessarily obscuring descriptions of the embodiments. Unless the context requires otherwise, throughout the specification and claims which follow, the word “comprise” and variations thereof, such as, “comprises” and “comprising” are to be construed in an open, inclusive sense, that is, as “including, but not limited to.” Further, headings provided herein are for convenience only and do not interpret the scope or meaning of the claimed disclosure.

[0019] Reference throughout this specification to “one embodiment” or “an embodiment” means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrases “in one embodiment”

or “in an embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. Also, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the content clearly dictates otherwise. It should also be noted that the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

[0020] The word ‘about’ when immediately preceding a numerical value means a range of plus or minus 10% of that value, e.g., “about 50” means 45 to 55, “about 25,000” means 22,500 to 27,500, etc. Furthermore, the phrases “less than about” a value or “greater than about” a value should be understood in view of the definition of the term “about” provided herein.

[0021] The present inventors have made intensive research to overcome the shortcomings described above, and as a result, have developed novel oligomerization processes in which a tungstated (or molybdenum doped) zirconium, nickel or cobalt doped tungstated zirconium, zeolite or metal doped zeolite, and/or combinations of catalysts are used in the reaction resulting in mixed olefin conversions to either Jet fuel or Diesel fuel hydrocarbons in yields exceeding 60%. Accordingly, the object of this invention is to provide a process for producing olefinic C₁₂+ oligomers in high selectivity, high throughput, and long catalyst life that meet or exceed Jet and/or Diesel fuel specifications. Those skilled in the art will recognize that in order to meet Jet fuel and/or Diesel fuel specifications the appropriate balance of branched and/or linear oligomers is desirable in the oligomerization feedstock, and as such catalysts that concurrently isomerize and/or oligomerize mixtures of branched and/or linear C₂-C₈ olefins in high yield and conversion are desired. In certain embodiments, depending on the bio-based alcohol (C₂-C₅) feedstock mixture introduced, catalysts that additionally facilitate isomerization and/or structural rearrangement during the dehydration step are desirable in order to produce the C₂-C₈ olefinic feedstock for oligomerization. The ability to selectively oligomerize branched olefins, in the presence of linear olefins, increases process flexibility towards either Jet and/or Diesel fuel production depending on market fluctuations.

[0022] The present invention is directed to novel processes for i) preparing a mixture of branched and/or linear C₂-C₈ olefins via novel dehydration catalysts, and ii) preparing C₁₂+ olefins via oligomerizing mixtures of linear and/or branched C₂-C₈ olefins, wherein tungstated zirconium,

nickel or cobalt doped tungstated zirconium, zeolite or metal doped zeolite, and/or combinations of catalysts are used as catalysts. The present invention will be described in more detail as follows:

[0023] The olefins described in this invention are any olefins composed of C₂ or higher carbon, preferentially to be branched and/or linear C₂-C₈ mixtures of unsaturated hydrocarbons, and more preferentially to be mixtures of ethylene (C₂H₄), propylene (C₃H₆), butylenes (C₄H₈), pentenes (C₅H₁₀), and hexenes (C₆H₁₂) as the most suitable olefins.

[0024] The preferential dehydration temperature of mixtures of branched and/or linear C₂-C₅ alcohols is from 250°C to 400°C, with reaction pressures ranging from 0-100 psig.

[0025] The dehydration reaction is performed in continuous mode for mass production of olefins. The continuous mode is operated by using a fixed bed reactor, and reactant flows can be upward or downward.

[0026] The preferential oligomerization temperature is from 100°C to 300°C (e.g., about 100 °C, about 110 °C, about 120 °C, about 130 °C, about 140 °C, about 150 °C, about 160 °C, about 170 °C, about 180 °C, about 190 °C, about 200 °C, about 210 °C, about 220 °C, about 230 °C, about 240 °C, about 250 °C, about 260 °C, about 270 °C, about 280 °C, about 290 °C, about 300 °C), with reaction pressures ranging from 200-600 psig (e.g., about 220 psig, about 240 psig, about 260 psig, about 280 psig, about 300 psig, about 320 psig, about 340 psig, about 360 psig, about 380 psig, about 400 psig, about 420 psig, about 440 psig, about 460 psig, about 480 psig, about 500 psig, about 520 psig, about 540 psig, about 560 psig, about 580 psig, about 600 psig).

[0027] The oligomerization reaction is performed in continuous mode for mass production of oligomers. The continuous mode is operated by using a fixed bed reactor, and reactant flows can be upward or downward. It is advisable to use a recycle stream consisting of oligomerized reaction product to control the heat of reaction, as the oligomerization reaction is very exothermic.

[0028] Granular or extrudated catalysts are suitable for the reaction even though no specific size and morphology are mandatory. Catalyst with size greater than 0.1 mm is more suitable, and the size of 0.2-1.0 mm is most suitable for the operation ability and low pressure drop.

[0029] C₂-C₅ alcohol conversion through dehydration is typically higher than about 90% (e.g., about 91%, about 92%, about 93%, about 94%, about 95%, about 96%, about 97%, about 98%, about 99). Typical olefin conversion is higher than about 60% (e.g., about 65%, about 70%, about 75%, about 80%, about 85%, about 90%). In some embodiment, the conversion is higher than about 90%, because selectivity to olefin trimers increases with increasing olefin conversion. If

olefin conversion is too low, the formation of lower molecular weight oligomers, such as olefin dimers cannot be avoided, whereas olefin tetramers can be increased slightly when the olefin conversion is too high.

[0030] Productivity is low, and the concentration of high molecular weight oligomers is high when the flow rate or space velocity of reactant is too low. On the other hand, the olefin conversion and trimers selectivity are low if the space velocity is too high. The suitable space velocity, based on the olefin WHSV (weight hourly space velocity), is 2-100 h⁻¹, and more preferably the velocity is 5-20 h⁻¹.

[0031] The trimers and tetramers obtained from the olefin oligomerization can be utilized directly for the production of Jet and Diesel fuel post hydrogenation. Hydrogenation catalysts can be selected from any supported catalysts such as Pd/C, Pd/alumina, Pd/silica, Pd/silica-alumina, Pt/C, Pt/alumina, Pt/silica, Pt/silica-alumina, Ru/C, Ru/alumina, Ru/silica, Ru/ silica-alumina, Ni/C, Ni/alumina, Ni/silica, Ni/silica-alumina.

[0032] Efforts aimed at making Renewable Jet in high yields from mixtures of bio-based ethylene, propylene, and/or butylenes identified a selective oligomerization process resulting in mass yields to Jet Fuel and/or Diesel fuel exceeding at least 70%. Surprisingly, the oligomerization process can be operated at relatively low temperatures and pressures with WO_x/ZrO_y catalysts, or Mo_xZrO_y catalysts with 15 wt% W or Mo loading on ZrO_y support, which are relatively inexpensive and commercially available catalysts.

[0033] Specifically, the oligomerization of liquefied linear C₂-C₈ olefins with WO_x/ZrO_y catalyst proceeds smoothly at reaction pressures of 250-600 psig, reaction temperatures of 125-350°C, and a liquid hourly space velocity (LHSV) of 1.5-2.5 resulting in a single pass C₂-C₈ olefin conversion of at least 70% with a product oligomer distribution of 1% C₄, 18% C₈, 65% C₁₂, 14% C₁₆, and 1.5% C₂₀, as exemplified in the examples below. Removal and recycle of the 'light' C₂-C₈ oligomer fraction provides an overall isolated Jet yield of at least 70% based on olefins fed. The WO_x/ZrO_y catalysts are stable, and extended reaction on-stream times have been demonstrated both in the lab and at demo plant scale. In addition, the WO_x/ZrO_y catalyst can be regenerated via air to regain activity.

[0034] Previous work (Lee et al, Applied Catalysis A: General, 366, 2009, 299-303) utilizing these WO_x/ZrO_y catalyst were aimed at oligomerizing isobutylene to a mixture of C₁₂ and C₁₆ olefins utilizing n-butane as a diluent (50:50, isobutylene:n-butane). However, this is the first report using

a similar catalyst for the production of Jet or Diesel fuel, via linear C₂-C₈ olefin oligomerization with or without the presence of isobutylene, and with no diluent present.

[0035] The C₂-C₈ Olefin Oligomerization process with WO_x/ZrO_y catalysts results in high yield and selectivity to bio-based Jet or Diesel fuel at relatively low temperatures and pressures, and tolerate high levels of oxygenates. Other known catalysts for C₂-C₈ linear Olefin oligomerization (Zeolites, modified Zeolites, SPA's, Nafion Resins, etc) deactivate rapidly requiring re-activation, are relatively expensive, have poor tolerance for the presence of oxygenates, and result in higher levels of oligomer cracking/isomerization as evidenced by higher levels of C₅₋₇ dimers and lesser amounts of isolated yields to Jet and/or Diesel fractions.

[0036] Likewise, the isobutylene oligomerization process utilizing WO_x/ZrO_y (10 wt% W) catalysts results in high yield and selectivity to bio-based Jet fuel at relatively low temperatures and pressures. Surprisingly, the WO_x/ZrO_y (10 wt% W) catalyst results in an extremely 'clean' oligomer distribution with high single-pass yield to Jet Fuel, as exemplified by the 'water' clear olefinic product, as compared to a 'yellowish' colored oligomerization product when utilizing other known oligomerization catalysts.

[0037] The WO_x/ZrO_y (10 wt% W) catalyst is an improvement over the previously reported WO_x/ZrO_y catalyst with 15 wt% W loading (Lee et al, Applied Catalysis A: General, 366, **2009**, 299-303), as exemplified by a 'cleaner' olefinic product, and higher single-pass yield to Jet in comparison. Another surprising feature of the WO_x/ZrO_y (10 wt% W) catalyst is the isomeric purity of the C₈ olefinic 'light' fraction, which consists of at least 90% to the preferred 2,4,4-trimethylpentene isomer with <10% of the undesirable 2,3,4-trimethylpentene. The 2,4,4-trimethylpentene is i) the C₈ olefinic isomer required for formation of p-Xylene in high selectivity via dehydrocyclization reaction, ii) is the precursor to the pure high octane 2,2,4-trimethylpentane compound, and iii) most easily dimerizes to the C₁₆ olefin which is necessary for producing other grades of Jet Fuel (eg JP5).

[0038] Dehydration of biobased C₂-C₆ alcohols results in significant levels of C₂-C₈ linear plus branched C₄-C₈ olefins, aromatics, and with minor amounts of paraffins depending upon catalysts employed. In certain embodiments, Gevo researchers have identified metal doped Zeolite catalysts that result in i) significant levels of isomerization to C₄ linear olefins from C₄ branched alcohols with minimal amounts of aromatics and C₅+ olefins, ii) significant levels of isomerization to C₄ linear olefins from C₄ branched alcohols along with significant levels of aromatics and C₅+ olefins,

iii) improved on-stream stability, iv) complete dehydration of ethanol to ethylene at a relatively low reaction temperature of 300°C, and v) catalyst regeneration via air.

[0039] Catalyst preparations are accomplished via impregnation or co-precipitation techniques depending upon selectivity desired and/or feedstock compositions. The ability to control the level of skeletal isomerization along with the amount of aromatics and C₅+ olefins across the dehydration step maximizes process flexibility and plant economics.

[0040] The subsequent oligomerization of these 'crude' olefinic streams, without purification to remove oxygenates and/or water, results in formation of Diesel, Jet, and/or Gasoline fractions in high yields via a WO_x/ZrO_y (15 wt% W or 15 wt% Mo) catalyst impregnated with Nickel and/or Cobalt, or combinations incorporating type IB-VIIB metals. Additionally, a physical mixture of the impregnated WO_x/ZrO_y catalyst with type H⁺ZSM-5 Zeolite catalyst provides additional benefits with regard to maximizing both conversion and extent of reaction of the olefinic mixtures to a C₁₂+ fraction. As required, the impregnated WO_x/ZrO_y catalyst, and nickel or cobalt impregnated WO_x/ZrO_y catalyst physically mixed with a H⁺ZSM-5 Zeolite catalyst, or a H⁺ZSM-5 Zeolite catalyst can be regenerated via air to regain activity.

[0041] Gevo has developed catalytic technology that converts bio-based isobutanol and/or ethanol to isobutylene or propylene in high yields with significant levels of linear and branched C₂–C₆ olefins. The isobutylene containing C₂–C₆ linear and branched olefins can subsequently be oligomerized utilizing these novel WO_x/ZrO_y based catalysts and/or catalyst combinations to renewable Diesel (C₁₂+ fraction), Jet fuel (C₁₂+ fraction) or Gasoline (C₈'s) fuel in overall yields of at least 70%, and more preferably 90%, depending upon temperature, pressure, and flow rates (eg WHSV). One skilled in the art will immediately recognize the applicability of this catalyst and oligomerization technology for converting 'crude' un-deoxygenated petro-based refinery streams containing mixtures of C₂–C₈ olefins to higher value liquid fuel fractions in a single step.

[0042] Data in the graphs 1 and 2 below exemplifies the surprising impact on linear olefin conversion and mass accountability, via doping tungstated zirconium catalyst with Cobalt and/or Nickel, in combination with H⁺ZSM-5 Zeolites at 180°C and 230°C (Graphs 1-2), versus the undoped tungstated zirconium catalyst and versus H⁺ZSM-5 by itself.

[0043] In accordance with the invention, there is provided a process for producing Diesel, Jet and/or Gasoline fractions from predominately olefinic compounds, preferably having a Cetane number of 35 or above, a research octane number (RON) of 80 or above, meeting Jet Fuel

specifications, and having therein no more than about 1-5% by weight of aromatics. Said process comprising contacting C₂–C₈ olefins with a H⁺ZSM-5 type Zeolite, at a WHSV of from about 0.1 to about 25 and at a temperature of from about 80°C to about 350°C, whereby said Diesel, Jet, or Gasoline fractions containing predominantly higher olefins is obtained. Data in the graphs 1 and 2 below exemplifies the surprising impact on linear and branched olefin conversion, and mass accountability utilizing the H⁺ZSM-5 catalyst.

[0044] Efforts aimed at making Renewable Jet in high yields from bio-based isobutanol and/or ethanol identified a selective oligomerization process resulting in exemplary mass yields to Diesel Fuel exceeding at least 70%. Surprisingly, the oligomerization process can be operated at relatively low temperatures and pressures with Nickel or Cobalt impregnated WO_x/ZrO_y catalysts containing 15 wt% W loading on ZrO_y support, which are relatively inexpensive and commercially available catalysts from Clariant and others. Specifically, the oligomerization of liquefied isobutylene with 0.05-5 wt% Cobalt and/or Nickel on WO_x/ZrO_y catalyst proceeds smoothly at reaction pressures of 250-600 psig, reaction temperatures of 170-350°C, and a liquid hourly space velocity (LHSV) of 1.5-2.5 resulting in a single pass olefin conversion of at least 70% with a 'typical' oligomer distribution reflective of significant levels of isomerization and rearrangement as depicted by the Diesel Fuel distillation profile, versus Jet Fuel distillation profiles shown in Figure 1. Removal and recycle of the C₄-C₈ oligomer fraction results in overall isolated Diesel yields of at least 70% based on olefins fed. Alternatively, the 'lights' C₄-C₈ oligomer fraction could be removed, via distillation, and marketed as high octane gasoline due to level of branched and linear olefins as a result of isomerization and rearrangement during oligomerization. The Cobalt and/or Nickel impregnated WO_x/ZrO_y catalysts are stable and extended reaction on-stream times have been demonstrated. In addition, the Cobalt and/or Nickel impregnated WO_x/ZrO_y catalyst can be regenerated via air to regain activity.

[0045] Oligomerization of crude renewable butylenes containing high levels of water, alcohols, and oxygenates to Jet Fuel proceeds smoothly over 15 wt% tungstated zirconium catalyst. The Capex and Variable cost of a commercial Jet Unit is significantly reduced by not requiring purification of the 'crude' olefin stream, obtained from the dehydration of renewable isobutanol, prior to oligomerization. Typically, so-called 'modifiers,' including of alcohols, water, and oxygenates, are purposely added to the feed of the oligomerization unit to reduce catalytic activity therein, enabling selective formation of high levels of C₈ olefins in proportion to C₁₂ and larger

oligomers. As such, the addition of modifiers, typically results in unacceptably low yields to Jet Fuel (C_{12} and higher olefins) with a corresponding high yield to C_8 olefins.

[0046] Surprisingly, we have found the presence of high levels of alcohol, water, and oxygenates, which would be expected to result in commercially unacceptable low yields, does not result in catalyst deactivation of a tungstated zirconium catalyst, and yields to Jet Fuel ($C_{12}+$ oligomers) of at least 75% can be maintained without pre-purification of an isobutylene feed to an oligomerization unit. Moreover, near complete single-pass isobutylene conversion can be effected.

[0047] Additionally, by adjusting the weight hourly space velocity (WHSV), in conjunction with adjustment of the recycle ratio of the oligomerization reactor effluent, an on-stream 80% yield of Jet Fuel can be sustained while simultaneously “tuning” or adjusting the $C_{12}/C_{16}/C_{20}$ oligomer ratios required to meet Jet fuel specifications (e.g., Jet A, Jet A-1, JP-5, JP-9, *etc.*) with regard to boiling point and viscosity. Operating outside optimal WHSV and recycle ratios can be problematic. For example, operating at too high a WHSV, with too low a recycle ratio, results in over oligomerization as observed by unacceptably high levels of C_{16} and larger oligomers relative to the C_{12} oligomers in a product stream. These higher levels of C_{16} and larger oligomers result in a higher viscosity product that does not meet typical Jet Fuel specification viscosity requirements, and necessitates an additional separation step (e.g., vacuum distillation) to remove a portion of the C_{16} oligomers, thus resulting in lower overall yields to Jet Fuel.

[0048] Additionally, we were surprised to learn that by tuning the WHSV of the fresh feed of ‘crude’ isobutylene in relation to the reactor effluent recycle ratio, the $C_{12}/C_{16}/C_{20}$ oligomer ratio can be ‘fixed’ (e.g., held relatively constant), while still being able to control the extent of the oligomerization process to increase Jet Fuel yield to at least 75%. Furthermore, adjusting oligomerization reaction temperature lower in conjunction with adjustments in WHSV had a minimal impact on the oligomer distribution exemplifying robustness of the WO_x/ZrO_y catalyst. Another unexpected finding of the present oligomerization process is that the isomeric purity of co-produced 2,4,4-trimethylpentenes (C_8 olefins) in ~15-20% yield exceeds 90% selectivity of all C_8 oligomers produced, while still maintaining at least 75% yield of Jet fuel. Typically, in order to increase the extent of oligomerization to maximize isobutylene conversion and concomitantly maximize yield of Jet Fuel, higher temperatures and more active catalysts are generally needed, resulting in higher levels (~35-40%) of isomerized 2,3,4-trimethylpentene. Isomeric purities of

>90% for 2,4,4-trimethylpentene is necessary to obtain high octane, renewable iso-octane. Moreover, high isomeric purity of 2,4,4-trimethylpentene formation can afford high isomeric purity renewable p-xylene via dehydrocyclization of the 2,4,4-trimethylpentene isomer. **Table 3** below provides yield, composition, and selectivity data taken over a 7 day period from a bench scale oligomerization reactor system.

Reactor Set-Up

[0049] The dehydration reaction of alcohols was carried out at 280-350°C via a fixed bed reactor containing 2.5 g of specified catalyst, and flowing preheated (180°C) vaporized alcohol in downward flow over the fixed catalyst bed. The flow rates of alcohols were controlled by Teledyne Model 500D syringe pumps coupled with D-Series pump controllers, and the alcohol flow rate was adjusted to obtain the targeted olefin WHSV (weight hourly space velocity). The reaction temperature was maintained constant via a Lindberg Blue M furnace as manufactured by Thermo-Scientific. Alcohol conversion was determined by analysis of condensed liquid phases of the reactor effluent by GC for residual alcohol content, and by weight of water phase collected in comparison to the theoretical amount of water expected for the overall reaction time and total amount of alcohol fed. Olefin isomeric distribution was determined by i) online gas analysis via SRI Instrument fitted with thermal conductivity detector and olefins calibrated relative to nitrogen flow across the reactor, and ii) sparging gaseous reactor effluent into chilled ethanol and injection on GC fitted with FID detector.

[0050] The oligomerization reaction of olefins was carried out at 110-280°C by using a fixed bed reactor containing 2.9 g of specified catalyst, and flowing the liquefied olefins downward. The flow rates of hydrocarbons were controlled by Teledyne Model 500D syringe pumps coupled with D-Series pump controllers, and the olefin flow rate was adjusted to obtain the targeted olefin WHSV (weight hourly space velocity). The reaction temperature was maintained constant via a Lindberg Blue M furnace as manufactured by Thermo-Scientific. Olefin conversion was calculated by analysis of the liquid phase reactor effluent by GC for olefin content, and comparing mass accountability fed versus liquid mass collected. Catalyst screening required that mass accountabilities exceeded 90% for continued development and evaluation

EXAMPLES

Example 1a: Co-precipitated Zn/Zr-Zeolite H⁺ (Zeolyst CP-914C, Si/Al=20) Catalyst Preparation:

[0051] Zeolyst CP-914C (6 g) was calcined at 550°C for 4 hours to convert from ammonium cation to protonated H⁺ form. The precursor metal salts (Sigma Aldrich) 2.84 g Zirconium (IV) oxynitrate hydrate and 0.57 g Zinc nitrate hexahydrate were added to deionized water (70 ml) resulting in a Zn/Zr metal molar ratio of 1/6.5. Upon salt dissolution, the salt solution was added to a 250ml flask with magnetic stir bar and 6 g of Zeolyst CP-914C-H⁺ was added to the salt solution. The Zeolite was stirred for 10 minutes to assure complete wetting, and dropwise addition of 20% NaOH (4.5 g) was added to the slurry until pH=7.5. The resulting pH adjusted slurry was allowed to stir at room temperature for an additional 60 minutes. The slurry was filtered, washed with hot water (3x 100ml), dried at 150°C for 2hrs and afterwards calcined at 500°C for 4hrs.

Example 1b: Nickel Impregnated WO_x/ZrO_y Catalyst Preparation:

[0052] WO_x/ZrO_y + 1.25% Ni catalyst was prepared by incipient wetness technique as described. Briefly, the precursor nickel salts (Sigma Aldrich) were added to deionized water in an amount to produce a nickel loading of 1.25 wt% upon addition to a known amount of WO_x/ZrO_y catalyst (15% W) as support. The impregnated WO_x/ZrO_y catalyst was dried at 140°C for 4 h, and afterwards calcined at 550°C for 4 h.

Example 2: Jet/Diesel formation:

[0053] Oligomerization of mixed C₄-C₈ Olefin Feed derived from initial ethylene oligomerization (48% C₄'s, 36% C₆'s, 16% C₈'s, 0.8% C₁₀'s) over WO_x/ZrO_y + 1.25% Ni. Reaction Conditions: 200°C, P=300 psig, WHSV=7.1, Recycle Ratio 3:1 (reactor effluent:mixed C₄-C₈ olefin feed), 98% mass accountability (Mass In/Mass Out), Isolated 67% Jet/Diesel Fraction post vacuum distillation. As per GC, the overhead 'lights' fraction representing 32% of the total oligomerization product mass was 16% C₅-C₇, 70% C₈, and 13% C₉-C₁₁ as a mixture of branched and linear olefins as per GC/MS.

Example 3: Jet/Diesel Formation:

[0054] Oligomerization of mixed C₄ Olefin Feed (16.5% n-Butene, 16.5% cis-Butene, 16.5% trans-Butene, 50.5% Isobutylene) over WO_x/ZrO_y + 1.25% Ni. Reaction Conditions: 200°C, P=300 psig, WHSV=7.1, Recycle Ratio 6:1 (product:fresh butenes feed), >97% mass accountability (Mass In/Mass Out), Isolated 67% Jet/Diesel Fraction post vacuum distillation. As per GC, the overhead 'lights' fraction representing 32% of the total oligomerization product mass was 16% C₅-C₇, 70% C₈, and 13% C₉-C₁₁ as a mixture of branched and linear olefins as per GC/MS.

Example 4: Jet formation:

[0055] Oligomerization of mixed C₄ Olefin Feed (16.5% n-Butene, 16.5% cis-Butene, 16.5% trans-Butene, 50.5% isobutylene over un-doped Tungstated Zirconium (T=195°C, P=340 psig, WHSV=1.6). Single pass yields; Tabulated GC Area% of Oligomer Distribution

% C ₄	% C ₅ -C ₇	% C ₈	% C ₉ -C ₁₁	% C ₁₂	% C ₁₃ -C ₁₅	% C ₁₆	% C ₂₀
20.76	0.61	55.73	0.31	20.39	0.27	1.82	0.11

Mass Accountability = 50%; Overall C₄ Olefin Conversion = 51%

Area% C₈ Fraction = 54%; Area% C₁₂+ Fraction = 23%

Example 5: Diesel formation:

[0056] Oligomerization of mixed C₄ Olefin Feed (16.5% n-Butene, 16.5% cis-Butene, 16.5% trans-Butene, 50.5% Isobutylene) over H⁺ZSM-5 (Type CBV-2314). Reaction Conditions: 280°C, WHSV=1.8, 95% Mass accountability (Mass In/Mass Out), Isolated 70% Diesel Fraction post vacuum distillation resulting in Cetane Value of >40.

Example 6: Diesel formation:

[0057] Oligomerization of Propylene Feed over H⁺ZSM-5 (Type CBV-2314). Reaction Conditions: 280°C, WHSV=1.4, 95% Mass accountability (Mass In/Mass Out), Isolated 75% Diesel Fraction post vacuum distillation resulting in Cetane Value of >40.

Example 7: Diesel formation:

[0058] Oligomerization of mixed linear butenes feed (33.3% n-Butene, 33.3% cis-Butene, 33.3% trans-Butene) over $\text{WO}_x/\text{ZrO}_y + 1.25\% \text{ Ni} + \text{H}^+\text{ZSM-5}$ (Type CBV-5524). Reaction Conditions: 230°C , $\text{WHSV}=1.8$, 95% Mass accountability (Mass In/Mass Out), Isolated 65% Diesel Fraction post vacuum distillation resulting in Cetane Value of >40 .

Example 8: Jet Formation:

[0059] Oligomerization of mixed linear butenes feed (33.3% n-Butene, 33.3% cis-Butene, 33.3% trans-Butene) over $\text{WO}_x/\text{ZrO}_y + 1.25\% \text{ Ni} + \text{H}^+\text{ZSM-5}$ (Type CBV-5524). Reaction Conditions: 180°C , $\text{WHSV}=1.8$, 95% Mass accountability (Mass In/Mass Out), Isolated 70% Jet Fraction post vacuum distillation.

Example 9: Jet Formation:

[0060] Selective Oligomerization of mixed butenes feed (16.5% n-Butene, 16.5% cis-Butene, 16.5% trans-Butene, 50.5% Isobutylene) over WO_x/ZrO_y (15wt% W) Reaction Conditions: 110°C , $\text{WHSV}=3.2$, Table 1: 65% liquid mass accountability (mass in/mass out), 60% Jet selectivity ($\text{C}_{12}+$ oligomers); Table 2: 40% butenes unreacted consisting of $\sim 90\%$ linear C_4 's and $\sim 10\%$ isobutylene.

Table 1:

Product Composition: Case i (mixed butenes only, 250 psig)									
	% C4	% C8	% C12	% C16	% C20	% C24	Jet Selectivity	C4 Conversion	Mass Accountability
0.21 ml/min, 110 deg C	13.3	29.4	40.8	11.8	1.9	0.3	56.2%	57%	66%
	8.9	31.6	43.4	11.9	1.5	0.1	53.4%	61%	66%
	19.8	31.6	42.4	11.3	1.4	0.1	56.6%	60%	67%
	11.5	30.9	42.5	11.4	1.4	0.0	56.6%	62%	70%

Table 2:

<i>Vented mass and composition: Case I (mixed butenes only, 250 psig)</i>				
	total recoverable butenes (% of total initial butenes mass)	composition, recoverable butenes (mass %)		
		iC4	linears	butanes
0.21 ml/min, 110 deg C	43%	10	88	1.3
	39%	7	92	0.8
	40%	7	92	0.7
	38%	7	92	0.7

Example 10

[0061] Concurrent Dehydration/Isomerization of Fuel Grade Isobutanol over co-precipitated Zn/Zr-Zeolite-H⁺ (Zeolyst CP-914C) Reaction Conditions: T=300°C, 2.5 g catalyst, WHSV=9.1, P=50 psig, >99% conversion of isobutanol, 75% linear butenes/25% isobutylene, trace amounts of organic phase containing C₄+ olefins.

Example 11

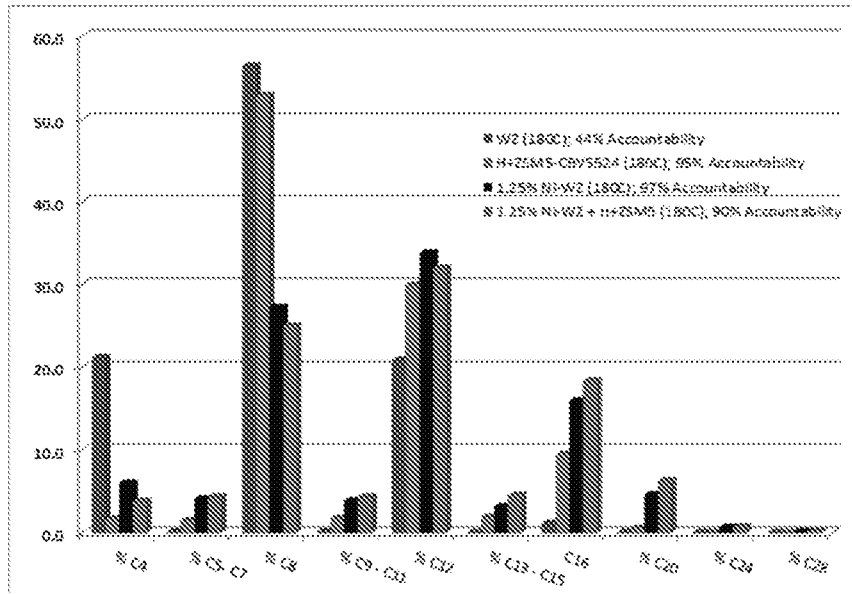
[0062] Dehydration of Fuel Grade Ethanol over co-precipitated Zn/Zr-Zeolite-H⁺ (Zeolyst CBV-5524, Si/Al=50) Reaction Conditions: T=300°C, 2.5 g catalyst, WHSV=1.0, P=50 psig, >98% conversion of ethanol, >90% yield to ethylene with trace amounts of C₃ and C₄ olefins.

Example 12

[0063] Dehydration of a 75/25 wt% mixture of Fuel Grade Isobutanol and Fuel Grade Ethanol over co-precipitated Zn/Zr-Zeolite-H⁺ (Zeolyst CBV-5524, Si/Al=50) Reaction Conditions: T=350°C, 2.5 g catalyst, WHSV=3.1, P=50 psig, >99% conversion of isobutanol and >90% conversion of ethanol. Vapor composition: 11% ethylene, 11% propylene, 45% isobutylene, 32% linear butenes.

Graph 1: Oligomerization of mixed C₄ Olefin Feed (16.5% n-Butene, 16.5% cis-Butene, 16.5% trans-Butene, 50.5% Isobutylene) over Tungstated Zirconium doped with 1.23% Nickel

(T=180°C, P=345 psig, WHSV=1.8), Tungstated Zirconium without Ni, H⁺ZSM-5, and Tungstated Zirconium doped with 1.23% Nickel in combination with H⁺ZSM-5.



Graph 2: Oligomerization of mixed C4 Olefin Feed (16.5% n-Butene, 16.5% cis-Butene, 16.5% trans-Butene, 50.5% Isobutylene) over Tungstated Zirconium doped with 1.23% Nickel (T=230°C, P=345 psig, WHSV=1.8), Tungstated Zirconium without Ni, H⁺ZSM-5, and Tungstated Zirconium doped with 1.23% Nickel in combination with H⁺ZSM-5.

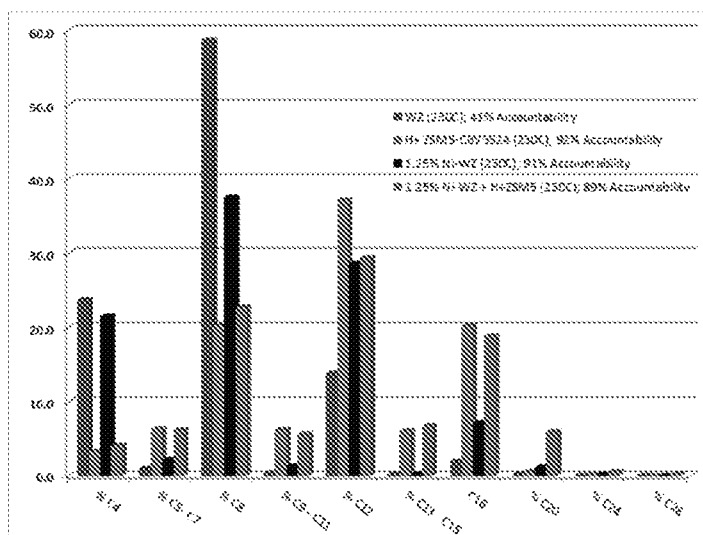


Table 3: Oligomerization of mixed butylenes feed (3% n-Butene, 4% cis-Butene, 6% trans-Butene, 88% Isobutylene) over Tungstated Zirconium (T=130°C, P=225 psig, WHSV=6), Tungstated Zirconium (15% W), Recycle Ratio 6:1, Water level 1500 ppm, Alcohol level 6000 ppm.

Table 3:

	Beginning						
Day	Recycle Jet Yield		Avg % Jet Yield in Reactor Effluent		C12/C16/C20 Ratio	%244-C8	%234-C8
1	74.7		79.7		79.8/16.4/2.2	74.5	25.5
2	80.1		80.4		80.7/15.8/2.0	79.3	20.7
3	80.1		80.4		81.6/15.2/1.9	83.0	17.0
4	80.5		79.9		82.3/14.7/1.7	85.9	14.1
5	79.8		80.1		82.8/14.3/1.7	88.3	11.7
6	80.6		78.7		84.3/12.9/1.4	90.4	9.6
7	80.0		80.0		84.2/13.2/1.4	91.6	8.4

[0064] The following specific examples are intended to be illustrative of the invention and should not be construed as limiting the scope of the invention as defined by appended claims.

[0065] The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations should be understood there from as modifications will be obvious to those skilled in the art.

[0066] While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth and as follows in the scope of the appended claims.

[0067] The disclosures, including the claims, figures and/or drawings, of each and every patent, patent application, and publication cited herein are hereby incorporated herein by reference in their entireties.

CLAIMS

1. A process for converting one or more C₂-C₈ linear or branched olefins to jet and/or diesel fuel, comprising contacting a feed stream comprising the one or more C₂-C₈ linear or branched olefins with a first catalyst and a second catalyst to afford a mixture comprising at least 70 wt % C₁₂ or greater alkenes, wherein the first catalyst comprises tungstated zirconium, molybdenum zirconium, or a combination thereof and the second catalyst comprises an acidic ZSM-5 catalyst.
2. The process of claim 1, wherein the one or more C₂-C₈ linear or branched olefins comprise at least about 50 wt% of butenes.
3. The process of claim 2, wherein the one or more C₂-C₈ linear or branched olefins comprise at least about 75 wt% of butenes.
4. The process of claim 3, wherein the one or more C₂-C₈ linear or branched olefins comprise at least about 90 wt% of butenes.
5. The process of claim 4, wherein said butenes comprises at least about 75 wt% isobutene.
6. The process of claim 4, wherein said butenes comprises at least about 75 wt% of linear butenes.
7. The process of claim 1, further comprising dehydrating one or more C₂-C₈ linear or branched alcohols with a third catalyst to provide the feed stream comprising one or more C₂-C₈ linear or branched olefins.
8. The process of claim 7, wherein the feed stream comprising one or more C₂-C₈ linear or branched olefins comprises at least 0.5 wt% oxygenates.

9. The process of claim 8, wherein the feed stream comprising one or more C₂-C₈ linear or branched olefins comprises at least 1 wt% oxygenates.
10. The process of claim 9, wherein the feed stream comprising one or more C₂-C₈ linear or branched olefins comprises at least 2 wt% oxygenates.
11. The process of claim 10, wherein the feed stream comprising one or more C₂-C₈ linear or branched olefins comprises at least 3 wt% oxygenates.
12. The process of claim 8, wherein said oxygenates comprise water and one or more C₂-C₈ linear or branched alcohols.
13. The process of claim 1, wherein a single-pass conversion of said C₂-C₈ olefin is at least about 50%.
14. The process of claim 13, wherein the single-pass conversion of said C₂-C₈ olefin is at least about 60%.
15. The process of claim 14, wherein the single-pass conversion of said C₂-C₈ olefin at least about 70%.
16. The process of claim 15, wherein the yield of said C₁₂ or greater alkenes is at least about 75%.
17. The process of claim 1, wherein said first catalyst comprises nickel and/or cobalt doped tungstated zirconium catalysts, nickel and/or cobalt doped molybdenum zirconium catalysts, or combinations thereof.
18. The process of claim 1, wherein said first catalyst is tungstated zirconium catalyst.

19. The process of claim 18, wherein said tungstated zirconium catalyst comprises about 85 wt% zirconium and about 15 wt% tungsten.
20. The process of claim 18, wherein said tungstated zirconium catalyst further comprises from about 0.01 to about 3 wt% of nickel.
21. The process of claim 18, wherein said tungstated zirconium catalyst further comprises from about 0.01 to about 3 wt% of cobalt.
22. The process of claim 1, wherein said first catalyst is nickel and/or cobalt doped molybdenum zirconium catalyst.
23. The process of claim 22, wherein said molybdenum zirconium catalyst comprises about 85 wt% zirconium and about 15 wt% molybdenum.
24. The process of claim 22, wherein said molybdenum zirconium catalyst further comprises from about 0.01 to about 3 wt% of nickel.
25. The process of claim 22, wherein said molybdenum zirconium catalyst further comprises from about 0.01 to about 3 wt% of cobalt.
26. The process of claim 1, wherein said first catalyst further comprises acidic Ferrierite, zeolites, Group IB-VIIB metal doped zeolites, doped zeolites, an acidic zeolite catalyst, or combinations thereof.
27. The process of claim 1, wherein said acidic ZSM-5 further comprises from about 0.01 wt% to about 5 wt% zinc.
28. The process of claim 1, wherein said acidic ZSM-5 further comprises from about 0.01 wt% to about 20 wt% zirconium.

29. The process of claim 1, wherein said first catalyst further comprises an acidic Ferrierite catalyst.
30. The process of claim 29, wherein said acidic Ferrierite further comprises from about 0.01 wt% to about 5 wt% zinc.
31. The process of claim 30, wherein said acidic Ferrierite further comprises from about 0.01 wt% to about 20 wt% zirconium.
32. The process of claim 7, wherein said third catalyst comprises Zeolites, Group IB-VIIB metal doped zeolites) doped zeolites, or combinations thereof.
33. The process of claim 7, wherein said third catalyst comprises an acidic ZSM-5 catalyst.
34. The process of claim 33, wherein said acidic ZSM-5 further comprises from about 0.01 wt% to about 5 wt% zinc.
35. The process of claim 33, wherein said acidic ZSM-5 further comprises from about 0.01 wt% to about 20 wt% zirconium.
36. The process of claim 7, wherein said third catalyst comprises an acidic Ferrierite catalyst.
37. The process of claim 36, wherein said acidic Ferrierite further comprises from about 0.01 wt% to about 5 wt% zinc.
38. The process of claim 36, wherein said acidic Ferrierite further comprises from about 0.01 wt% to about 20 wt% zirconium.