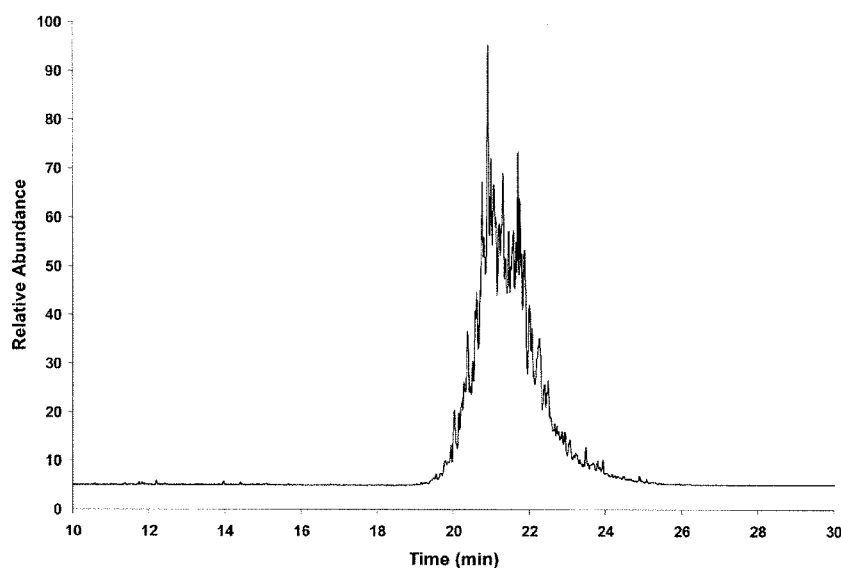




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(54) **Title:** TURBINE AND DIESEL FUELS AND METHODS FOR MAKING THE SAME



(57) **Abstract:** A process for making diesel and turbine fuels includes providing an amount of one or more branched olefins and adding active heterogeneous acid catalyst(s) to the branched olefins to produce a mixture, which can be solvent-free. The process further includes heating the solvent-free mixture to a temperature greater than about 80°C for a sufficient time to produce a dimers/catalyst mixture, removing the catalysts from the dimers/catalyst mixture, and adding hydrogenation catalyst(s) to the dimers under hydrogen atmosphere to produce a mixture of stable fuels.

TURBINE AND DIESEL FUELS AND METHODS FOR MAKING THE SAME

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The invention described herein may be manufactured and used by or for the government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

[0002] The invention generally relates to turbine and diesel fuels and methods for making the same, and more specifically, methods to convert renewable branched chain olefins including 2-ethyl-1-hexene to fuels suitable for use in turbine and diesel engines.

BRIEF DESCRIPTION OF THE DRAWINGS

[0003] **FIG. 1** is a GC/MS chromatogram of a dimerized β -pinene product mixture, according to embodiments of the invention.

[0004] **FIG. 2** is a plot of a GC-MS total ion chromatogram for the oligomers produced from 1-butene, according to embodiments of the invention.

[0005] **FIG. 3** is a graph of the relative area integration for each of the oligomers by carbon number for the GC-MS chromatogram of Figure 2 above, according to embodiments of the invention.

[0006] **FIG. 4** is an ^1H NMR spectrum of butene oligomers, according to embodiments of the invention.

[0007] **FIG. 5** is an ^1H NMR spectrum of hydrogenated butene oligomers, according to embodiments of the invention.

[0008] **FIG. 6** is a Gas Chromatogram of hydrogenated butene oligomers, according to embodiments of the invention.

[0009] **FIG. 7** is a Gas Chromatogram of distilled fuel, according to embodiments of the

invention.

[0010] **FIG. 8** is a ^1H (top) and ^{13}C (bottom) NMR spectra of the product mixture derived from sulfuric acid dimerization of 2-ethyl-1-hexene, according to embodiments of the invention.

[0011] **FIG. 9** is a gas chromatogram (GC) of 2-ethyl-1-hexene dimers, according to embodiments of the invention.

[0012] **FIG. 10** is a mass spectrum of a typical hydrogenated 2-ethyl-1-hexene dimer, according to embodiments of the invention.

[0013] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments, which are illustrated schematically in the accompanying drawings and in the appended claims.

DETAILED DESCRIPTION OF THE EMBODIMENTS OF THE INVENTION

[0014] Embodiments of the invention generally relate to turbine and diesel fuels and methods for making the same, and more specifically, methods to convert renewable branched chain olefins to fuels suitable for use in turbine and diesel engines.

[0015] Embodiments of the invention generally relate to a process for making fuels including providing an effective amount of one or more branched olefins and adding active heterogeneous acid catalyst(s) to the branched olefins to produce a mixture. The process further includes heating the (solvent-free) mixture to greater than about 80°C for a sufficient amount of time which may depend on various conditions, such as temperature and reactants, to produce a dimers/catalyst mixture. The catalyst is removed from the dimers/catalyst mixture and a hydrogenation catalyst(s) added to the dimers under a hydrogen atmosphere to produce a mixture of stable fuels.

[0016] The branched olefin(s) can be branched alkenes having from 5-15 carbon atoms, including 2-ethyl-1-hexene. The branched olefins can be derived from products produced by fermentation of biomass. The branch (i.e., the shortest chain can be from 1 to 4 carbons in length, such as 1-2 (methyl, ethyl) or simply one carbons in length. The olefin can have more than one branch. The branched olefin can be an alpha olefin or can be internally unsaturated. The olefin can be

monounsaturated or di- or poly-unsaturated.

[0017] The branched olefin mixture can be solvent-free, by which it is meant that the mixture consists only of the branched olefin, catalyst and optionally dimers of the branched olefin. Or, it can be substantially solvent free, by which it is meant that the mixture includes up to 5 wt. %, or up to 1 wt. %, or up to 0.1 wt. % of solvent.

[0018] In embodiments, the step of providing branched olefins further includes a mixture of branched olefins. In embodiments, the step of adding active heterogeneous acid catalyst(s) to the branched olefins is performed under a N₂ atmosphere. In other embodiments, another step further includes the step of purifying the stable fuels by removing short chain branched olefins remaining in the stable fuels. The purifying step can include filtration and/or distillation.

[0019] In embodiments, at least one branched olefin is a C₅-C₁₅ branched olefin such as a C₇ or above, e.g., a C₈ branched olefin, such as 2-ethyl-1-hexene.

[0020] The heating step can be performed at a temperature of at least 100°C, such as in the range of from about 110°C to about 120°C. In embodiments, the catalyst includes a Ziegler-Natta catalyst. In other embodiments, the catalyst further includes a co-catalyst.

[0021] In embodiments, fuels are formed in accordance with the processes described herein. Furthermore, butene oligomer fuels are formed in accordance with the processes herein.

[0022] In embodiments, the catalysts are selected from the group consisting of cation exchange resins, acid clays, zeolites, polyoxometallates, sulfated metal oxides, and other heterogeneous acids. In embodiments, the fuels are selected from the group consisting of 5,7-diethyl-5-methylundecane, 8-ethyl-5,6-dimethyldodecane, 6-ethyl-3-methyl-4-propyldecane, 5-ethyl-5,6,7-trimethylundecane, and 5-ethyl-3,5-dimethyl-4-propylnonane and similar molecules, and molecules produced from the coupling of any two structural isomers of 2-ethyl-1-hexene.

[0023] Another aspect of the invention generally relates to a process for making fuels including providing an effective amount of branched olefins including 2-ethyl-1-hexene, adding active heterogeneous acid catalyst(s) to the branched olefins to produce a solvent-free mixture, heating the solvent-free mixture greater than about 80°C for a desired amount of time to produce C₁₆ dimers/catalyst mixture, removing the catalyst(s) from the dimers/catalyst mixture, and adding hydrogenation catalyst(s) to the dimers under hydrogen atmosphere to produce a mixture of stable

fuels.

[0024] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments which are illustrated schematically in the accompanying drawings and in the appended claims.

[0025] High density fuel candidates have been synthesized by the present Applicant in up to 90% yield from β -pinene, a renewable, strained, bicyclic compound derived from wood and plant sources. These novel syntheses are based on heterogeneous acidic catalysts (also referred to as heteropolyacidic catalysts) including Montmorillonite-K10 and Nafion® NR-50 which promote selective isomerization and dimerization of pinenes under moderate conditions (100°C, atmospheric pressure). Montmorillonite clays have been used as catalysts for a number of organic reactions and offer several advantages over classical acids. For example, they are highly acidic, non-corrosive, can be utilized under mild reaction conditions, and typically result in high yields with good selectivity. Additionally they are low cost, simple to use, and can be conveniently separated from reaction mixtures by decantation or filtration. Mesoporous Montmorillonite clays, which are dioctahedral phyllosilicates, are composed of hydrated sodium, calcium, aluminum, magnesium, silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$, with an octahedral layer (AlO_6 units) sandwiched between two tetrahedral layers (SiO_4 units). Potassium, iron, and other cations are common impurities. These clays typically have a surface area of 220-270 m^2/g . Montmorillonite-K10 is a strong Bronsted and Lewis acidic catalyst shown to be highly active for the dimerization of β -pinene concomitant with ring opening followed by dehydrogenation to produce *p*-cymene. Use of this catalyst resulted in a dimer yield of dimer to about 75%. Nafion® NR-50 was capable of producing dimers in up to 90% yield but was less active than the acidic clay. Amberlyst-15, a common industrial catalyst had very poor activity and conversion even at 150 °C.

[0026] The dimer mixtures were upgraded through hydrogenation over PtO_2 and fractional distillation. The synthesized fuels have a density of about 0.94 g/cc, and a net volumetric heating value of about 39.5 MJ/L (~141,745 BTU/gal). These values are nearly identical to those of the

widely used tactical fuel JP-10 (which is primarily composed of exo-tetrahydrodicyclopentadiene), suggesting that these renewable fuels may have applications for rocket propulsion.

β -pinene dimerization

[0027] Note of caution: the dimerization reaction is very exothermic, particularly when MMT-K10 is used as the catalyst. Runaway reactions can occur with both MMT-K10 and Nafion, especially with concentrated solutions or in the absence of a suitable heat sink. Slow addition of β -pinene to a refluxing reaction mixture at 100 °C was determined to be the safest method of addition. In a typical procedure, the solid acid catalyst (100 mg Nafion or 500 mg MMT-K10) was slurried in 10 mL of n-heptane under a nitrogen atmosphere and heated to reflux. β -pinene (35 g) was then added dropwise to the slurry and the reflux was maintained with external heat for the remainder of the reaction; additional reactions were conducted over a range of temperatures from 0 °C up to the reflux temperature of β -pinene. Dimer mixtures were hydrogenated with 1 wt% PtO₂ under 1-2 psig (about 108-115 kpa) of hydrogen for a period ranging from about 12 hours to about 24 hours. Subsequent distillations were carried out under reduced pressure (4 mm Hg).

Table 1. Catalysts for the Dimerization of β -pinene.

<u>Catalyst</u>	<u>Temperature</u>	<u>Time</u>	<u>Products</u>
MMT-K10	0-30 °C	4 h	isomers
MMT-K10	100 °C	1h	dimer/isomers
MMT-K10	150 °C	1h	dimer/trimer/isomers
Amberlyst-15	ambient	24h	NR
Amberlyst-15	150 °C	3h	isomers
Nafion	ambient	24h	NR
Nafion	100 °C	6h	dimer/isomers
Nafion	150 °C	2h	dimer/isomers/trimer
H2SO4 (98%)	0 °C	10 min	polymer
H2SO4 (50%)	0 °C	10 min	polymer

[0028] Nafion® NR-50 (Aldrich) was precipitated from a 5% water/alcohol dispersion by addition of dichloromethane (CH₂Cl₂) and ether, followed by filtration and drying under vacuum (4 Torr) at ambient temperature (adapted from Kim, T. K.; Kang, M.; Choi, Y. S.; Kim, H. K.; Lee, W.; Chang, H.; Seung, D. *J. Power Sources* 2007 165, 1-8). The MMT-K10 (Aldrich) and dry

Amberlyst-15 (Aldrich) were used directly from the bottle. (1S)-(-)- β -pinene (Aldrich) typically was used without further purification, or after an extended storage time, it was distilled from CaH_2 under a nitrogen atmosphere. Product mixtures were analyzed with an Agilent 6890-GC/5973-MS (gas chromatography mass spectrometer) to determine chemical compositions. The density of the product mixtures was measured with an Anton Parr DMA-35N density meter. Heat of combustion and elemental analyses were conducted under standard protocols by Southwest Research Institute.

[0029] α - and β -pinene have net heats of combustion of 132,300 and 132,500 BTU/gal respectively as calculated based on the experimental heat of formation as reported on <http://webbook.nist.gov> and by others (Hawkins, J. E.; Eriksen, W. T. *J. Am. Chem. Soc.* **1954** 76, 2669 and Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds* Academic Press, New York **1970**). In comparison, the net heat of combustion of JP-10 is 142,000 BTU/gal (**Table 2**) (Burdette, G. W.; Lander, H. R.; McCoy, J. R. *J. Energy* **1978**, 2, 289-292). It should be noted that both pinene molecules also have positive gas phase heats of formation due to strain energy. A path to improving the volumetric heating value of these natural products is selective dimerization that would both increase the density and maintain the ring strain of these molecules. Two target dimer molecules are shown in **Diagram 1**. Semi-empirical calculations for both of these molecules give positive gas phase heats of formation and impressive values for net heat of combustion (based on a density of 0.94 g/mL); 146,900 BTU/gal and 146,500 BTU/gal for the hypothetical hydrogenated α - and β -pinene dimers, respectively. The gas phase data was calculated utilizing MOPAC, while a liquid phase net heat of combustion was calculated assuming a density of 0.94 g/mL and utilizing double the value of the heat of vaporization of β -pinene according to Hawkins and Armstrong (Hawkins, J. E.; Armstrong, G. T. *J. Am. Chem. Soc.* **1954** 76, 3756). These calculations clearly suggest that dimerized pinenes have the potential to have heating values exceeding that of JP-10.

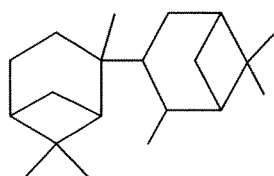
Table 2. Selected properties of JP-10 and α - and β -pinene

	β -pinene	α -pinene	JP-10
Density	0.859	0.858	0.94
$\Delta H_f(g)$ (kJ/mole)	35.8	30.2	-96.6a
$\Delta H_f(l)$ (kJ/mole)	-7.66	-16.4	-133.8b
$\Delta H_c(\text{BTU/gal})_c$	132,500d	132,300d	142,000

a. semi-empirical calculation (MOPAC AIM1). b. calculated from the experimental heat of combustion. c. net heat of combustion. d. calculated from the experimental

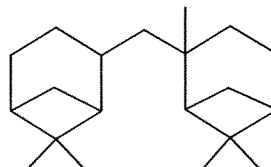
heat of formation.

Diagram 1. Structures of target dimer molecules and selected calculated properties.



Hydrogenated α -pinene dimer

Calculated $\Delta H_f(g) = 48.6$ kJ/mol
 Calculated $\Delta H_f(l) = -44.6$ kJ/mol
 Calculated $\Delta H_c(net) = 146,900$ BTU/gal



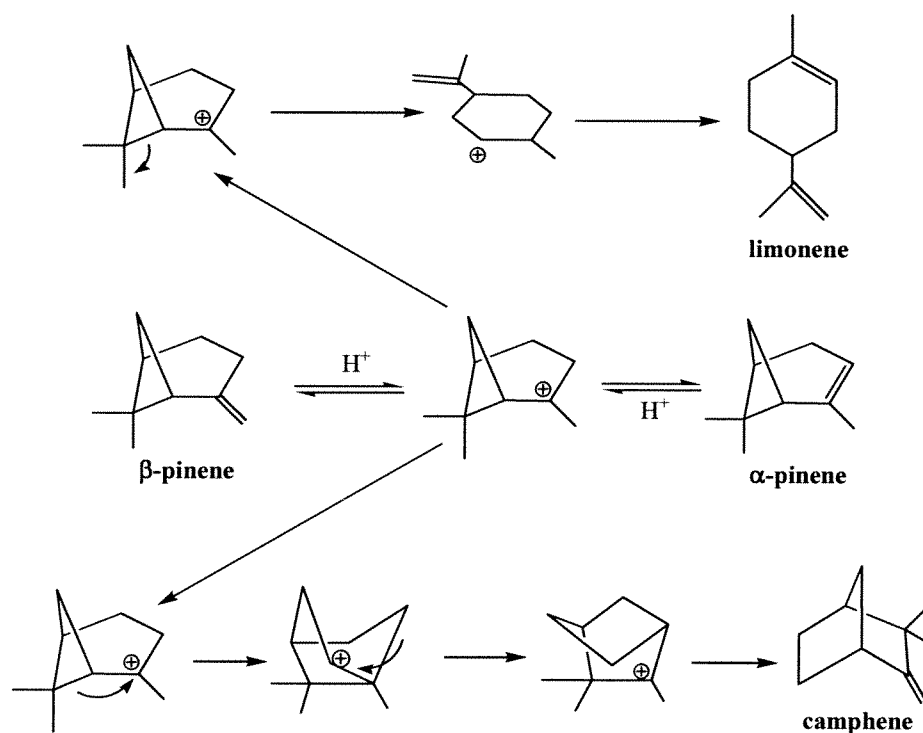
Hydrogenated β -pinene dimer

Calculated $\Delta H_f(g) = 4.2$ kJ/mol
 Calculated $\Delta H_f(l) = -82.7$ kJ/mol
 Calculated $\Delta H_c(net) = 146,500$ BTU/gal

Montmorillonite K10

[0030] Initially MMT-K10 was targeted as a catalyst due to its low cost, abundance, and well established reactivity (Madhavan, D.; Murugalakshmi, M.; Lalitha, A.; Pitchumani, K. *Catalysis Letters* **2001** 73, 1). MMT-K10 is a layered aluminosilicate functionalized with additional acidic sites through treatment with sulfuric acid. Its acidity can vary several orders of magnitude based on the amount of water present in the sample and it has both Lewis and Bronsted acidic sites (Pillai, S.M.; Ravindranathan, M. *J. Chem. Soc. Chem. Commun.* **1994** 1813-1814). The clay can delaminate or separate into particles as little as 1 nm in width and several hundred nanometers in length. Upon addition of MMT-K10 to a flask containing β -pinene at room temperature, a vigorous reaction occurs, with the catalyst immediately turning red accompanied by a rapid exotherm. Without a heat sink, the reaction rapidly reaches the boiling point of β -pinene. In an effort to more effectively control the reaction, slow addition of β -pinene to a slurry of the catalyst in heptane at 0 °C under an inert atmosphere resulted in only a trace amount of isomers (detected by NMR) and no dimers, suggesting that the isomerization reaction is very slow at that temperature. Removal of the ice bath led to an exotherm that was controlled by sequentially submerging the rapidly stirred flask in an ice bath and then removing the flask and allowing the internal temperature to warm up to 30 (+/- 5) °C. This was repeated several times until the temperature was stable at ambient temperature. At this point the reaction was monitored by both NMR and GC/MS revealing that the principal

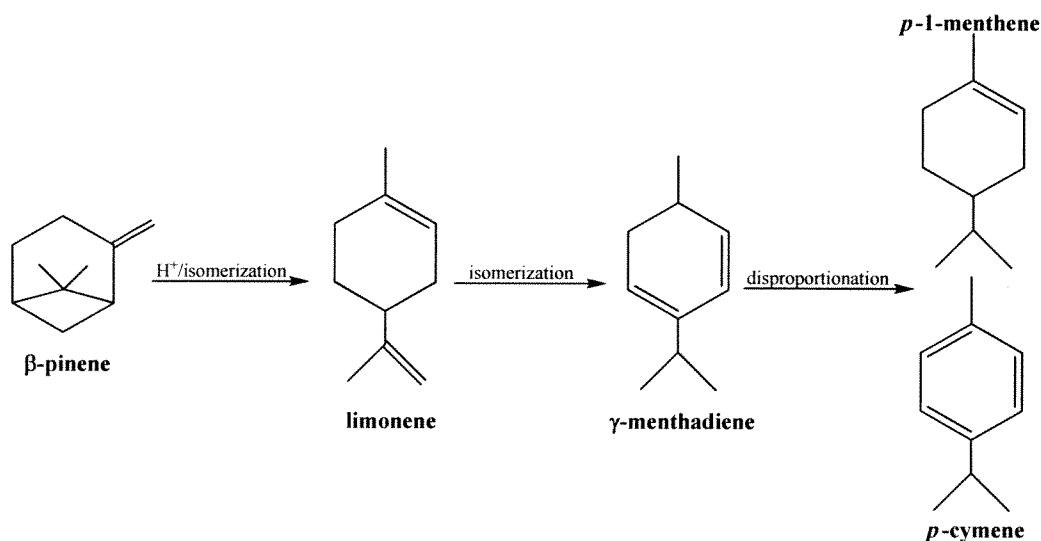
reaction was isomerization to a mixture of camphene, limonene and α -pinene, with some β -pinene remaining (**Scheme 1**). Small amounts of dimer, α - and γ -terpinene, and *p*-cymene were also observed, as well as a trace of oxidation products. The relative ratio of α -pinene:camphene: β -pinene:limonene was 3:5:2:4. Heating the mixture to the reflux temperature of heptane led to a vigorous reaction with production of significant amounts of hydrogen. After 1 h the overall yield of dimer molecules was 80% by GC/MS, with the balance of the product represented by primarily *p*-cymene, camphene, and tricyclene. Extended heating times at the reflux temperature of heptane did not change the concentration of camphene in the reaction mixture, suggesting that MMT-K10 is a poor catalyst for camphene dimerization. Although camphene represents 35% of the initial isomerized product, it represents only about 10% of the final product mixture.



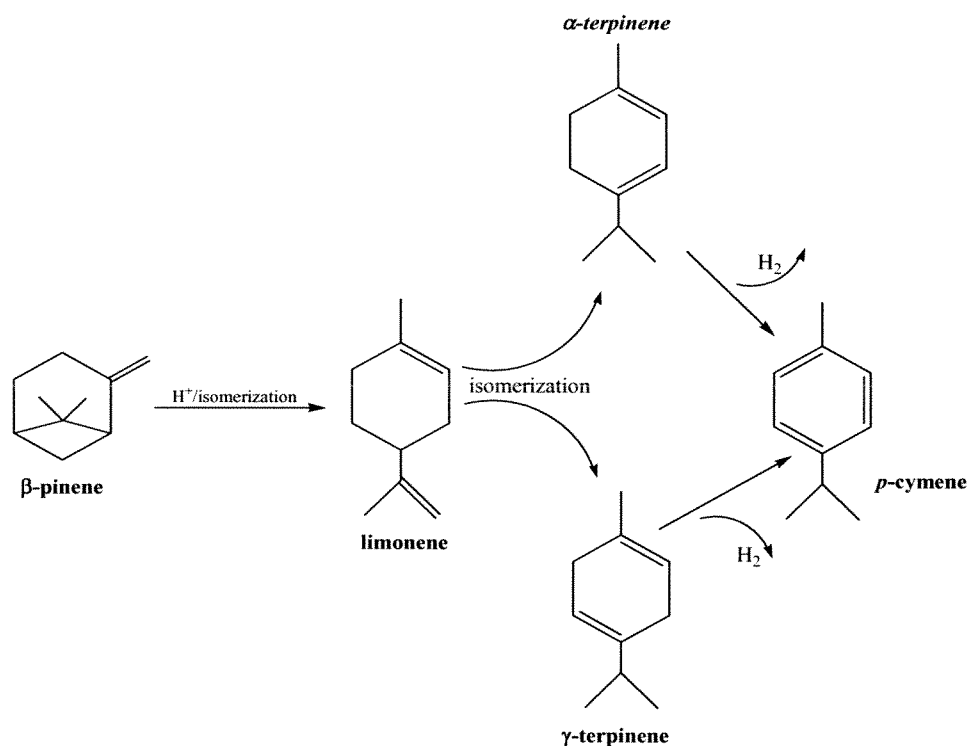
Scheme 1. Mechanism for the isomerization of β -pinene over MMT-K10.

[0031] This suggests that although MMT-K10 is inefficient for the dimerization of camphene, it does promote the cross coupling of camphene with other isomers in solution. Another important product is *p*-cymene which is derived from limonene. Previous studies suggest that the mechanism for formation of *p*-cymene proceeds through a rearrangement/disproportionation reaction in which

limonene rearranges to terpinenes which then disproportionate to *p*-cymene and a menthenes such as *p*-1-menthene (**Scheme 2**) (Fernandes, C.; Catrinescu, C.; Castilho, P.; Russo, P.A.; Carrott, M.R.; Breen, C. *Applied Catalysis A* **2007** 318, 108-120). However, it was observed that copious production of hydrogen was evident at the reflux temperature of heptane. This supports a direct dehydrogenative mechanism (**Scheme 3**) that could be catalyzed by the clay or possibly by polyaromatic coke deposits on the catalyst surface (Arnano, H.; Sato, S.; Takahashi, R.; Sodesawa, T. *Phys. Chem. Chem. Phys.* **2001** 3, 873-879).

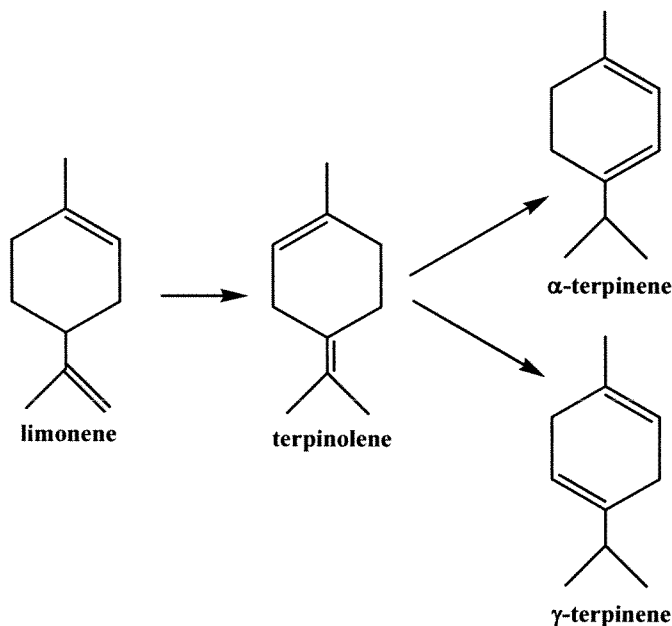


Scheme 2. Potential mechanism for the conversion of β -pinene to *p*-cymene.



Scheme 3. Potential mechanism for the conversion of β -pinene to *p*-cymene.

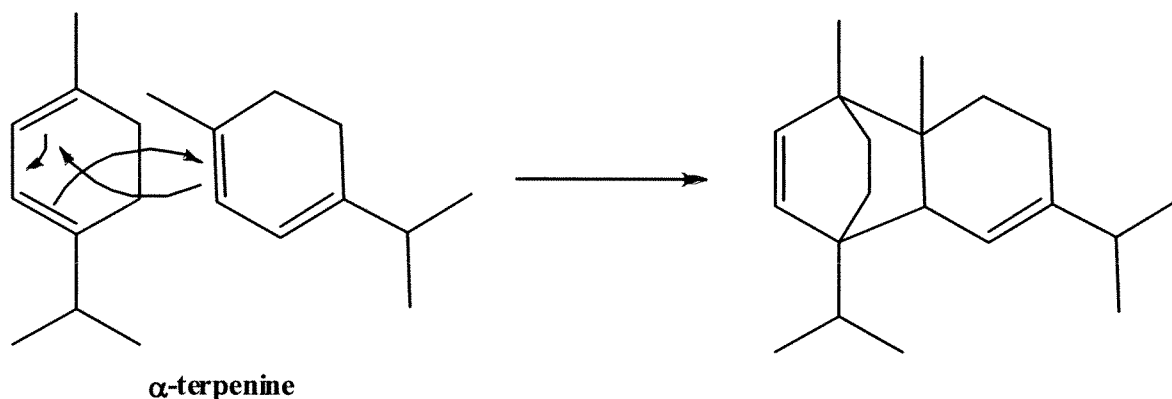
[0032] To shed some light on the mechanism, (R)-(+)-limonene was added dropwise to a stirred slurry of MMT in refluxing heptane. After one hour an NMR spectrum was collected and it was observed that limonene, *p*-cymene, α - and γ -terpinene and terpinolene were the primary low molecular weight components present. This result supports the second mechanism (**Scheme 3**), given that no evidence was observed for any menthene products. It is also of interest that the intermediate terpinolene was observed in the reaction mixture, suggesting that the isomerization reaction progresses in a step-like fashion (**Scheme 4**).



Scheme 4. Stepwise conversion of limonene to terpinenes through terpinolene.

[0033] Although no menthene products were observed in the NMR spectrum, GC/MS analysis of an MMT limonene mixture in heptanes that had been refluxed overnight revealed the presence of *p*-cymene and residual menthenes, primarily *p*-menth-3-ene and *p*-menth-1-ene. The presence of these particular menthenes was expected based on the carbocationic mechanism of isomerization and the stability of intermediates with tertiary cationic centers. The data suggest that a competition exists between the first and second mechanism, with some disproportionation occurring through a dehydrogenative/hydrogenative mechanism and some direct loss of hydrogen ostensibly due to the slower rate of hydrogenation under these conditions. Additionally, many other potential reactants in solution including dimer molecules could react with the released hydrogen. The GC/MS analysis reveals that the dimer region is a complex mixture of peaks mainly with molecular weights of 272, while some peaks have $m/z = 274$. It is unclear whether the molecule(s) represented by the $m/z = 274$ peaks are produced by hydrogenation after dimerization of two monomers, or if they are produced from the coupling of a monoolefin and a diolefin. A recent report has suggested that under somewhat harsher conditions (150 °C, acidic clay catalyst), terpinenes and other olefins undergo a Diels Alder reaction (**Scheme 5**) that is promoted by the Lewis acidity of the catalyst (Fernandes, C.; Catrinescu, C.; Castilho, P.; Russo, P.A.; Carrott, M.R.; Breen, C. *Applied*

Catalysis A **2007** 318, 108-120).



Scheme 5. Example of a potential Diels Alder dimerization reaction of α -terpinene.

[0034] Similar reactions could occur between terpenines and a variety of olefins in solution. Although the conversion to *p*-cymene is of interest, it limits the conversion of β -pinene to dimer products. In an attempt to efficiently control the heat of reaction and to selectively produce dimers incorporating ring strained cyclobutanes, β -pinene was added dropwise to a stirred slurry of MMT-K10 in refluxing heptane under a nitrogen atmosphere. Upon addition of the first drop the slurry turned green and then rapidly converted to a red/brown suspension. After the addition, the mixture was refluxed for an additional hour. Interestingly, the NMR spectra and GC-MS chromatograms were indistinguishable from those obtained when β -pinene was added slowly at room temperature and then heated to refluxing heptane temperatures. This result suggests that the rate of isomerization at the elevated temperature is faster than the rate of dimerization of β -pinene. To determine the effect of even higher temperatures, β -pinene was added neat to the clay catalyst in an open flask maintaining a slow flow of nitrogen. The mixture was vigorously stirred and rapidly rose in temperature until vigorous gas evolution was evident. After the bubbling had mostly subsided, the flask was placed in an oil bath at 150 °C and further evolved gas was allowed to slowly escape through a bubbler. The distribution of products was similar to that observed at 100 °C with the addition of about 10% trimer, leading to a 70/10/20 ratio for dimer/trimer/low molecular weight products. This result suggests that the intermediate temperature is ideal, leading to a high conversion to dimer while limiting the formation of trimer or other heavier oligomers.

The clay catalyst can be removed with some difficulty from the reaction mixture by filtration, however as the catalyst is remarkably well dispersed it was often more convenient to separate the clay by centrifugation followed by decantation.

Amberlyst-15

[0035] Although MMT-K10 was found to be an efficient dimerization catalyst, in an attempt to produce a dimer mixture with less isomerized products and more molecules maintaining strained ring systems, Amberlyst-15, a sulfonic acid functionalized cross-linked polystyrene resin was investigated to determine its catalytic activity for the dimerization of β -pinene. Unlike MMT-K10, upon addition of neat β -pinene to beads of Amberlyst-15 under nitrogen, no reaction at room temperature occurred even upon reaction times of 48 hours. This difference in activity may be due to the presence of Lewis acidic sites present in MMT-K10 which may allow for coordination and isomerization of β -pinene at low temperature (Fernandes, C.; Catrinescu, C.; Castilho, P.; Russo, P.A.; Carrott, M.R.; Breen, C. *Applied Catalysis A* **2007** 318, 108-120). Upon heating to 140 °C for 3 h, a mixture of primarily β -pinene and camphene were present with traces of *p*-cymene and dimer. Given the slow reaction rate, negligible conversion to dimer and high reaction temperature, Amberlyst-15 was not studied in further detail.

Nafion[®]

[0036] Nafion[®] is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone, and may be considered to be a perfluorinated sulfonic acid resin. The combination of fluorinated backbone, sulfonic acid groups, and the stabilizing effect of the polymer matrix render Nafion[®] a very strong acid (i.e., superacid), with $H_0 = (-11 \text{ to } -13)$. Nafion[®] has various chemical configurations and thus several chemical names, including: ethanesulfonyl fluoride, 2-[1-[difluoro-[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2,-tetrafluoro-, with tetrafluoroethylene; and, tetrafluoroethylene-perfluoro-3,6-dioxo-4-methyl-7-octenesulfonic acid copolymer, for example. Nafion[®] is insoluble in non-polar solvents. It will be clear to those of skill in the art that polyacidic or heteropolyacidic catalysts other than MMT-K10, and perfluorinated sulfonic acid resins other than Nafion[®] NR50 may be suitable to facilitate the synthesis of pinene dimers, and the use of such other catalysts in the synthetic schemes disclosed

are within the scope of this disclosure. For convenience in discussion, we refer herein to the sulfonated tetrafluoroethylene based fluoropolymer-copolymer incorporating perfluorovinyl ether groups terminated with sulfonate groups class of catalysts, suitable for use in synthesis of β -pinene dimer, including the Nafion[®] catalysts, as well as the acidic clays, simply as solid heterogeneous acidic catalysts or solid heteropolyacidic catalysts.

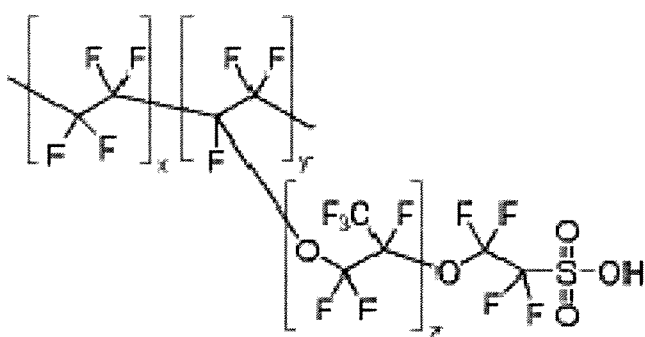


Diagram 2. Structure of Perfluorinated Sulfonic Acid Resin Catalysts.

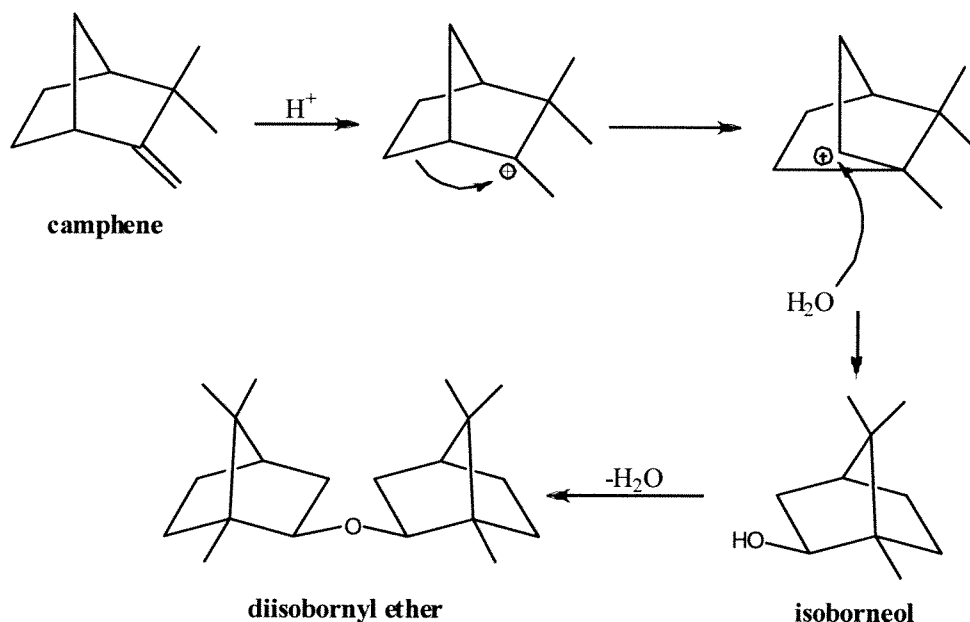
[0037] With respect to the catalysts of the structure shown in Diagram 2, the variables x , y , and z are mutually independent integers greater than 1. That is, any one of the variables x , y , z may have an integer value which is not dependent on the value of any other variable. Unlike MMT-K10 which maintains a high surface area and can delaminate at elevated temperature to yield easily dispersible nanosized catalyst particles, Nafion does not disperse well in non-polar solvents (Botella, P.; Corma, A.; López-Nieto, J. M. *J. Catal.* **1999** 185, 371-377). This limits the surface area of the catalyst and the relative amount of active sites in contact with the reaction medium. Nafion can be well dispersed on inorganic supports including silica or alumina, but the presence of the support can often influence the reactivity and in the case of β -pinene may lead to more isomerization products and lower ring strain dimers (Kumar, P.; Vermeiren, W.; Dath, J.; Hoelderich, W. F. *Energy Fuels* **2006** 20, 481-487). The catalyst was prepared by precipitation of a Nafion dispersion from water/alcohol and was dried under vacuum (4 mmHg) at ambient temperature to yield a flocculent white powder. In a manner similar to Amberlyst-15, Nafion showed virtually no reaction at room temperature for reaction times as long as 24 h. When neat solutions of β -pinene were heated with Nafion to 90 °C with stirring, no reaction occurred for an

extended period of time, typically 20-50 minutes, and then without warning, the Nafion turned a dark red color and a rapid exothermic reaction ensued with evolution of gas. Upon an additional hour at 90 °C, ¹H NMR spectroscopy revealed that the only remaining low molecular weight molecules were camphene and a small amount of *p*-cymene. In fact when MMT-K10 was used as a catalyst nearly 10 times more *p*-cymene was produced. This result suggested that either the ring opening mechanism that converts β-pinene to limonene does not readily occur with Nafion at these reaction temperatures, or that the rate of dimerization of limonene over Nafion is substantially faster than the dehydrogenation reaction to produce *p*-cymene. To differentiate between the two possibilities, a reaction was stopped prior to completion and an NMR spectrum was collected. Camphene was the dominant monomeric olefin, with small, nearly equal amounts of β-pinene and limonene. At this point in the reaction, *p*-cymene was not observed in the ¹H NMR spectrum. It appears from the data that the primary mechanism over Nafion is conversion to camphene concomitant with homo- and cross-dimerization of the olefin mixture. Upon further reaction it was observed that the last olefin remaining is camphene which dimerizes somewhat sluggishly over Nafion, however, unlike MMT-K10, continued reaction at 100 °C led to the conversion of camphene to dimer molecules. In order to determine the effect of temperature, the reaction was run neat at 140 °C using Nafion as the catalyst. Interestingly, *p*-cymene was formed in amounts similar to that observed for MMT-K10, in addition to the observance of about 10 wt% trimer. This suggests that for Nafion the dehydrogenation of limonene to *p*-cymene is favored at higher temperatures, while dimerization is favored at lower/intermediate temperatures. As with MMT-K10, it appears that a temperature of 100 °C is ideal for maximizing the amount of dimer produced. For all of the Nafion reactions, the catalyst could be removed by simple decantation and reused at least 3 times without significant loss of activity and given sufficient reaction time, yields of dimer as high as 90% were obtained. As mentioned previously, at the conclusion of the reaction the Nafion takes on a deep red hue. Washing the Nafion 5 times with CH₂Cl₂ did not remove the color, but only weak C-H stretches were observed in the IR spectrum of the washed and dried catalyst. With respect to **Figure 1**, the GC/MS chromatogram of the product mixture revealed a broad distribution of dimer molecules with the majority having *m/z* = 272. Small amounts of other molecular weights such as 274 and 288 were also observed, with the former being attributed to the

coupling of terpinenes and menthenes and the latter attributed to isobornyl ether which has been shown to be an oxidation product produced from camphene with heteropolyacidic catalysts (**Scheme 6**) (Lana, E.J.L.; da Silva Rocha, K. A.; Kozhevnikov, I. V.; Gusevskaya, E. V. *J. Molec. Catal. A* **2006** 243, 258-263).

Upgrading of Dimer Mixtures

[0038] The dimer yield varied depending on the catalyst and conditions. Yields of dimer were reduced when MMT-K10 was utilized due to an increase in the amount of *p*-cymene produced and the inability of MMT-K10 to efficiently homodimerize camphene. The amount of dimer was also heavily influenced by the reaction temperature in that higher temperatures produced trimer molecules and potentially other higher oligomers. Reactions run at greater than 140 °C produced colored solutions ranging from dark yellow to orange-red depending on the reaction time, suggesting that polymeric or conjugated mixtures were being produced. Reactions controlled at about 100 °C with refluxing heptanes gave colorless mixtures when MMT-K10 was utilized as the catalyst and pale yellow mixtures when Nafion was utilized.



Scheme 6. Acid catalyzed conversion of camphene to diisobornyl ether.

[0039] For potential use as fuels, these dimer mixtures must be hydrogenated to increase their

stability. The reaction mixtures were simply decanted and transferred to another flask for hydrogenation; no workup or caustic treatment was required. Platinum dioxide (PtO_2) was utilized as the hydrogenation catalyst under mild H_2 pressures as it has been shown to be a very efficient catalyst for hindered olefins (Wright, M. E.; Harvey, Benjamin G.; Quintana, R. *Energy and Fuels* **2008**, 22, 3299) (Harvey, B.G.; Wright, M.E.; Quintana, R.L. *Preprints of Symposia-ACS Div. Fuel Chem.* **2009** 54 305-306). The resulting dimer mixtures were then placed under reduced pressure to remove n-heptane and low molecular weight products including camphane (MMT-K10 catalyst) and then vacuum distilled to produce a dimer cut. Fractional vacuum distillation gave a trace of a low boiling fraction consisting of primarily camphane, and p-cymene, followed by a colorless dimer fraction (bp 116-122 °C, 4 mmHg) and leaving a small amount of resinous solid pot residue including a mixture of dimer and traces of other heavier oligomers. Isolated, distilled yields of the dimer fraction were greater than 80% on a 30 g scale, while for larger operations, a yield of up to 90% based on the GC/MS data seems reasonable due to more efficient distillations. Although higher oligomers limit the yield of dimer molecules they have uses in a variety of industries as resins and glues. (Goldschmidt, S.; McBride, J. J. in *Polymeric Materials Encyclopedia Vol. 9*; Salamone, J. C. Ed. CRC Press **1996** 6878-6884). The properties of the fuel are listed in **Table 3**. The density of the hydrogenated dimer mixture prepared with Nafion was 0.938 g/cm^3 , similar to JP-10 at 0.94 g/cm^3 . The net heat of combustion of the dimer mixture was 141,745 BTU/gal, virtually identical to JP-10 (142,000 BTU/gal), while the pour point was determined to be -30 °C, substantially higher than JP-10 with a freezing point of -79 °C.

Table 3. Selected Properties of Hydrogenated Pinene Dimers.

Property	Value
Density, g/cm^3	0.938
Heating Value, MJ/L	39.5
(BTU/gal)	141,745
Pour Point, °C	-30
Sulfur, ppm	0.5
Carbon, %	87.72 (calc. for $\text{C}_{20}\text{H}_{34}$: 87.52)
Hydrogen, %	12.12 (calc. for $\text{C}_{20}\text{H}_{34}$: 12.48)

[0040] Given recent advances in the conversion of starch (Ramey, D. E. U.S. Patent 5,753,474) and cellulosic biomass to biobutanol (Qureshi, N.; Sahaa, B. C.; Hector, R. E.; Hughes,

S. R.; Cotta, M. A. *Biomass Bioenergy* **2008**, 32 (2), 168–175. Qureshi, N.; Sahaa, B. C.; Cotta, M. A. *Biomass Bioenergy* **2008**, 32 (2), 176–183), the C4 alcohol was explored as a pivotal and versatile starting point for the creation of new fuels. Because 1-butene can be easily derived from 1-butanol (Berteau, P.; Delmon, B.; Dallons, J. L.; Vangysel, A. *Appl. Catal.* **1991**, 70 (2), 307–323. Bautista, F. M.; Delmon, B. *Appl. Catal., A* **1995**, 130 (1), 47–65), this versatile starting material has been investigated as a precursors to a biojet fuel that will meet the required energy content and key performance specifications of JP-5. Disclosed herein are methods for converting 1-butene into a variety of useful saturated hydrocarbon fuels using a highly efficient batch-catalysis process. The new approach affords a product that is composed of 100% iso-paraffins, retains good fuel density, possesses attractive cold-flow properties, and can be easily tailored to have a high flash point.

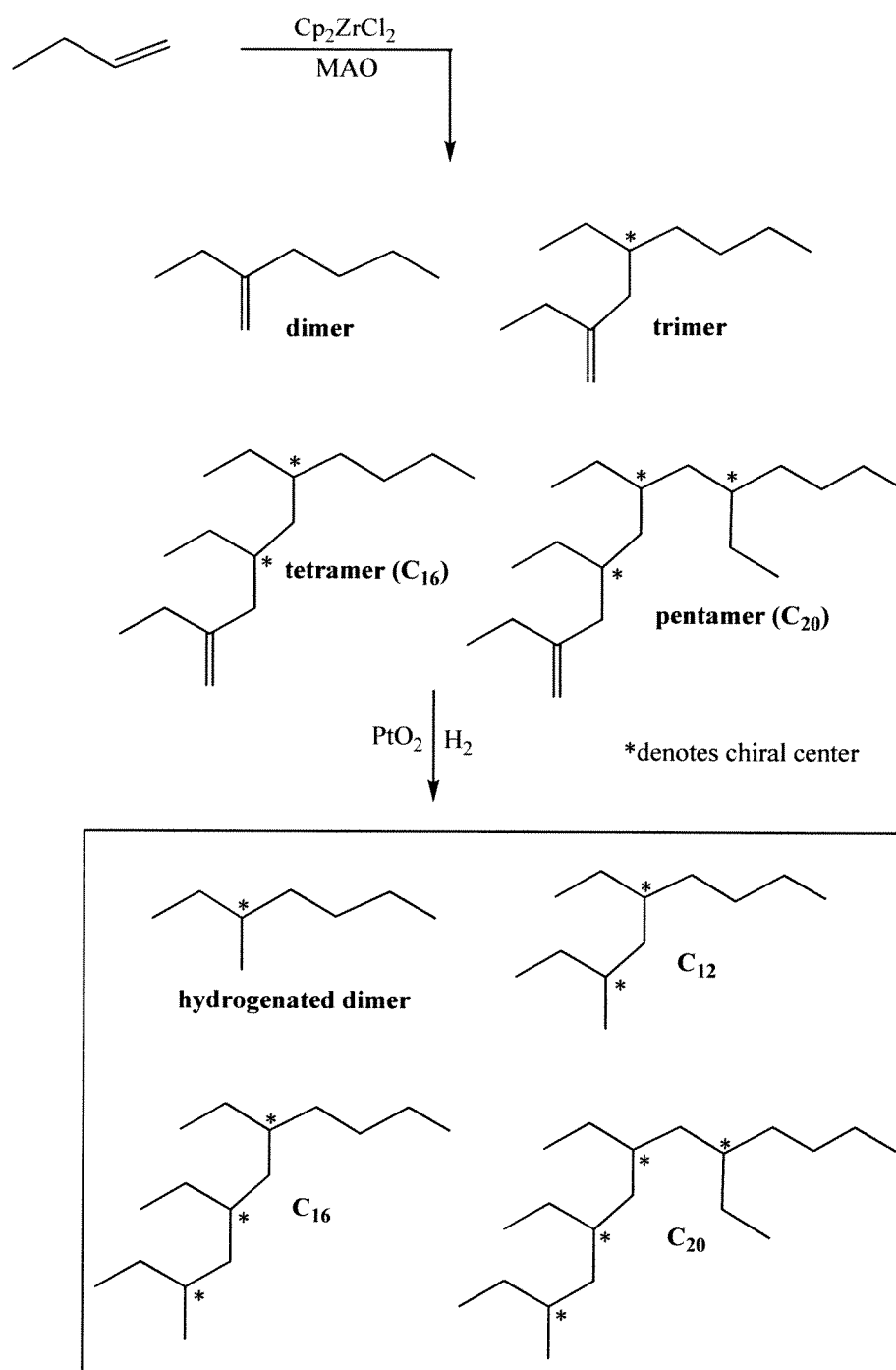
[0041] The synthetic fuel experiments were initiated using the commercially available precatalyst bis(cyclopentadienyl)zirconium dichloride. The precatalyst is activated by treatment with a toluene solution of methylaluminoxane (MAO) followed by removal of the toluene under reduced pressure.

The MAO may also be prepared in a solution of any aromatic solvent able to solvate the MAO and the precatalyst such as, without limitation, for example xylene, cumene, and mesitylene. Of course, coordinating solvents with heteroatoms are not appropriate. Removal of solvent after catalyst activation also removes any residual trimethylaluminum, creating “dried” MAO. The “dried” MAO has been shown to have a significant affect on catalyst activity for olefin oligomerization/polymerization reactions for several non-metallocene catalysts. (Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, 34 (10), 3142–3145) (Hagimoto, H.; Shiono, T.; Ikeda, T. *Macromol. Rapid Commun.* **2002**, 23, 73) (Furayama, R.; Saito, J.; Ishii, S.; Mitani, M.; Matsui, S.; Tohi, Y.; Makio, H.; Matsukawa, N.; Tanaka, H.; Fujita, T. *J. Mol. Catal. A: Chem.* **2003**, 200, 31) (Long, R. J.; Gibson, V. C.; White, A. J. P. *Organometallics* **2008**, 27 (2), 235–245). The catalyst was prepared using an aluminum/zirconium ratio of 100 (mol/mol). It may be noted that here the MAO is an oligomer of formula $[\text{CH}_3\text{AlO}]_n$ and there is one mole of aluminum for every mole of MAO repeat unit. Similarly, there is one mole of Zr per mole of Cp_2ZrCl_2 . Conveniently, both the molar ratio of MAO/ Cp_2ZrCl_2 and Al/Zr is 100:1. The turnover number (TON) here is at least about 17,000 and may be pushed to as high as on the order of 10^7 whereas the TON achieved by Christoffers and Bergman was only about 10 or less. It is well

known that use of very high Al/M ratios on the order of 10,000:1 results in the production of polymers, whereas significantly lower ratios can lead to oligomeric mixtures. Our use of the Al/M ratio of 100:1 is an approximate first optimization of the system based upon previous observations.

[0042] 1-butene (375 mL, about 240 g) is condensed onto CaH_2 and then transferred over the course of 3 h to a chilled (dry ice bath) pressure reaction vessel containing “activated” catalyst. Reactions were performed in a Parr stainless steel pressure reaction vessel lined with a glass insert and stirring was accomplished using a Teflon coated stirring bar. The 1-butene [Specialty Gas Concepts, Lancaster, CA, 98% Chemically Pure (CP) grade] was transferred after drying (over CaH_2) to the chilled reaction vessel through Tygon tubing. Once the pressure vessel was charged, the port was sealed, the cooling bath was removed, and the reaction vessel was kept at ambient temperature for 16 h (**Scheme 7**). At completion of the reaction, a partial vacuum exists in the reaction vessel. This observation is consistent with complete consumption of the 1-butene (bp -6.3°C). Gas chromatography-mass spectrometry (GC-MS) analysis indicates a Schultz-Flory distribution of products consisting primarily of C_8 , C_{12} , and C_{16} oligomers with small amounts of heavier oligomers. GC-MS analyses were performed using an Agilent 6890 gas chromatography (GC) system equipped with a Restek RTX-5MS 30 m column coupled to an Agilent 5973 mass selective detector system. After quenching as described herein below, a distillation using a vigreux column is used to remove the C_8 dimer, which accounts for about 25 wt % of the product mixture. Roughly 90% of the butene oligomer mixture consists of C_8 dimer and C_{12} , C_{16} , C_{20} , and C_{24} oligomers, and there are essentially no oligomers larger than C_{32} . After removing the C_8 dimer, hydrogenation (about 0.08 wt % PtO_2/H_2 , 2 psig (about 115 kpa)) of the remaining oligomers yields a potential fuel mixture that has a flash point (ASTM D93) of 59°C , viscosity of 103 cSt (ASTM D445 at -20°C), and a lubricity value of 0.45 mm [ASTM 6079, high frequency reciprocating rig (HFRR)]. All ASTM tests herein were performed at the Southwest Research Institute, San Antonio, TX 78238 (www.swri.org). Interestingly, this fuel does not show any sign of freezing (or cloudiness) when cooled to -60°C . When this fuel blend is subjected to a second high-temperature distillation, a colorless viscous oil residue is left behind that accounts for about 11% of the total fuel production. It is this oil fraction that leads to the good lubricity value for the fuel. It is important to note that incremental jumps are made in 4-carbon units, the reaction is highly regioselective based

on GC-MS data, and the fuels generated in this process are 100% iso-paraffinic. The branching is quite distinctive in that ethyl groups are located at regular positions along the carbon main chain of the oligomer. Furthermore, not only does this fuel have extensive branching, it contains a mixture of diastereoisomers that are produced as a consequence of the chiral carbon centers (marked with an asterisk in **Scheme 7**) present at the branch points. The diastereoisomers have different physical properties (e.g., boiling point) and can be clearly observed in both the nuclear magnetic resonance (NMR) spectra and GC-MS chromatograms. For example, the hydrogenated tetramer has three chiral centers. Using the standard formula of 2^n (where n is the number of chiral centers), the tetramer will have 8 possible stereoisomers. This consists of 4 pairs of enantiomers and 4 different diastereoisomers. Hence, after hydrogenation of the trimer and generation of a second chiral center, two major peaks in the GC-MS chromatogram are observed. This observation is consistent with the structures shown in **Scheme 7** and the regiochemistry anticipated from the earlier work of Kaminsky (above) on the ZN-catalyzed reactions of 1-butene.



Scheme 7.

[0043] By making a change in catalyst preparation, it is now possible to produce a significant change in the resulting oligomer distribution toward lighter oligomers; however, the complete, or near complete, conversion of 1-butene remains unchanged. The catalyst is first formed in solution,

then dried under vacuum and suspended in a small volume of hydrogenated butene dimer (3-methyl-heptane) derived from a previous run. This allows for reaction in which the solvent is primarily the reactant, 1-butene, without the need for addition of other solvent. This approach results in a mostly heterogeneous catalyst (i.e., the catalyst is dispersed in the solvent, but is not in solution, or is present in solution in only very low concentration). Using this heterogeneous, unsupported catalyst in the reaction results in a remarkable product distribution consisting primarily of dimer, trimer, and tetramer, but without production of heavy oligomers and polymer. This metallocene based unsupported heterogeneous catalyst method is a novel approach that results in a unique product distribution. It was discovered that if, after removal of the toluene, the aluminum/zirconium catalyst is slurried in hydrogenated dimer and then delivered to the reactor, the surprising result is: (1) complete, or essentially complete, conversion of 1-butene to oligomers as evidenced by a partial vacuum after completion of the reaction and the yield of oligomers obtained from the initial reactants; (2) an about 12 wt % increase in 2-ethyl-1-hexene dimer produced; and, (3) a decrease of high-molecular-weight oligomer generated, with the distribution defined by $M_n = 176$, $M_w = 211$, and $M_w/M_n = 1.2$, where, M_n is number average molecular weight, M_w is weight average molecular weight, and M_w/M_n is the polydispersity (**Figure 2**). This distribution can be observed in **Figure 2** which is a plot of a GC-MS total ion chromatogram for the oligomers produced from 1-butene (Al/Zr: 100) using the catalyst made by removal of the toluene and delivering the zirconium/MAO as a slurry in hydrogenated dimer (3-methyl heptane). It will be understood by one of ordinary skill in the art that any lower molecular weight C_4 to about C_{10} alkane may be used in place of 3-methyl-heptane, such as for example, butane, pentane, hexane, heptane, octane, and branched chain alkanes. **Figure 3** is a relative area integration for each of the oligomers by carbon number for the GC-MS chromatogram of **Figure 2**. The relative abundance areas are derived from the total ion count for the peaks of that particular set of oligomers (e.g., C_{24}). Yields of 98% or more with some loss of product due to filtration, handling and transfer were obtained. This advantageously also enables the entire procedure to be performed using simple Schlenk techniques while avoiding using a glovebox. At this time, the exact chemical differences/changes in the new active catalyst are not specified; however, the results are very consistent from run to run for this new catalyst preparation. As before, distillation is used to remove

the 2-ethyl-1-hexene dimer, and the resulting fuel blend of oligomers minus the dimer is subjected to hydrogenation. Using the new catalyst formulation, a significant decrease in viscosity is observed, down to 12.5 cSt, (entry 1 in **Table 3**) compared to products prepared using our earlier catalyst formulation. The cold-flow viscosity by back-addition of hydrogenated C₈ dimer can be further tailored. Thus, by adding 6.6 wt % (entry 2 in **Table 3**) of the dimer, the viscosity decreases to 8.5 cSt, which is quite close to JP-8 (8.0 cSt) and does meet the JP-5 (8.5 cSt) specification. Further dilution with the C₈ dimer brings the viscosity down to an impressive 6.0 cSt at -20 °C (entry 4 in **Table 3**). As anticipated, there is a decrease in fuel density as the dimer concentration increases.

Table 3. Viscosity Data (ASTM D445, -20 °C) for Fuel Blends^a

fuel blend	viscosity (cSt)	dimer (%)	fuel density (g/mL)
1	12.5	0	0.78
2	8.5	6.6	0.77
3	7.2	11.5	0.77
4	6.0	17	0.76

^a Catalyst delivered as a slurry in hydrogenated dimer.

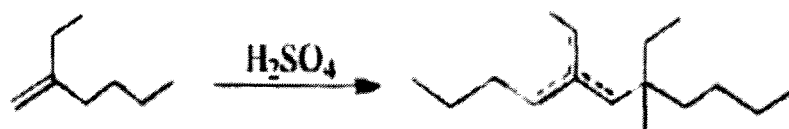
[0044] Carrying out a high-temperature distillation of the high flashpoint fuel mixture (no dimer) to 313 °C leaves a colorless pot residue of less than 1 wt % and physically/experimentally confirms the decrease in high-molecular-weight oligomer content. For the fuel blend of entry 1 in **Table 3**, elemental analysis indicates 85% carbon and 15 wt % hydrogen, which is consistent with a fully saturated hydrocarbon. It follows that the calculated heat of combustion is greater than 44+ MJ/kg or 34.3+ MJ/L. The heat of combustion is calculated for the stoichiometric reaction with oxygen to form carbon dioxide and water using an average formula of C₁₆H₃₄. The elemental analysis was performed at Atlantic Microlab, Inc., Atlanta, GA.

[0045] To demonstrate an overall efficient use of the reduced-carbon source (i.e., 1-butene), a means of converting the dimer (2-ethyl-1-hexene) to a higher boiling fuel component [e.g., C₁₆ compound(s)] was developed. The latter could then be blended with little negative effect on the flash point of the fuel. Thus, treatment of 2-ethyl-1-hexene with concentrated sulfuric acid leads to rapid conversion to a complex mixture of monounsaturated C₁₆ alkenes (**Scheme 8**). Figure 9 is

dimerized 2-ethyl-1-hexene, but by Nafion, not sulfuric acid. The proton and carbon NMR spectral data for the product mixture are quite complicated (**Figure 9**); however, the GC-MS data (**Figure 8**) is consistent with an elution time that is expected for C₁₆ isomers, and significantly, a molecular ion peak of 224 is observed for each peak in the GC-MS chromatogram, with very small amounts of 238 molecular ions (C₁₇ alkenes) indicated.

[0046] The mixture of C₁₆-alkene isomers has a measured density of about 0.80 g/mL that is similar to pure linear *n*-hexadecane (0.773 g/mL). One of the unique and useful features for these 1-butene derived fuels is the high degree of branching (100%) yet a good overall retention of fuel density. Although a cetane rating for jet fuels is not specified nor directly related to any performance parameter, there is interest to further evaluate these fuels for their respective cetane and octane ratings. Extensive and regular ethyl branching is not typically found in fuel blends; therefore, an appropriate model for predicting a cetane rating is not presently available. Fuel density is an important parameter that contributes to meeting fuel performance requirements and may ultimately determine if a biojet version of JP-5/JP-8 can indeed meet or exceed mission critical Department of Defense (DoD) requirements.

Scheme 8.



Experimental

[0047] **General Methods.** All organometallic manipulations were carried out using standard Schlenk techniques under an atmosphere of purified nitrogen or in a glovebox. 1-butene (CP grade) was purchased from Specialty Gas Concepts, stirred over CaH₂, and degassed prior to use. MAO (10% in toluene) and PtO₂ were purchased from Aldrich and used as received. Cp₂ZrCl₂ was purchased from Strem and used as received. Butene oligomerization reactions were conducted in a 750 mL stainless steel Parr reactor fitted with a glass insert. ¹H and ¹³C NMR spectra were collected on a Bruker Avance II 300 MHz spectrometer in CDCl₃ and referenced to the residual solvent peaks (¹H, δ 7.27; ¹³C, δ 77.16). Fuel samples were analyzed for viscosity (ASTM D445 at -

20 °C), lubricity (ASTM D6069, HFRR), and flashpoint (ASTM D93) at Southwest Research Institute.

[0048] **GC/MS Analysis Methods.** 0.5 mg of oligomer mixture was dissolved in 1.0 mL of methylene chloride. 1 μ L of sample was injected into an Agilent 6890 gas chromatography (GC) system equipped with a Restek RTX-5MS 30-meter column. The GC inlet temperature was 250 °C, the initial column temperature was 40 °C held at 3 min, and the temperature was increased at 10° C/min up to a final temperature of 350 °C. An Agilent mass selective detector 5973 system was used to identify the sample components.

[0049] Synthesis of Butene Oligomers (Method A). Utilizing Schlenk techniques, Cp_2ZrCl_2 (70 mg, 0.24 mmol) was dissolved in MAO solution (16.5 mL, 25 mmol) to yield a pale yellow solution which was stirred at ambient temperature for 1 h. The resulting golden colored solution was then stripped of solvent under reduced pressure (0.1 mm Hg) to give a yellow solid. The flask was taken into a glovebox and the solid transferred to a bomb. The bomb was then removed from the glovebox and packed in dry ice. 1-butene (375 mL, 4.22 mol) was condensed into the bomb which was sealed, placed on a stir plate, allowed to warm to room temperature, and allowed to react for 16 h with stirring. A port on top of the bomb was opened (with a nitrogen purge) and this released a significant partial vacuum due to the complete conversion of butene to oligomers. The catalyst was quenched with distilled water (1 mL) and the mixture was stirred for 1 h. The top portion of the bomb was completely removed to reveal a white heterogeneous mixture smelling strongly of olefins. This mixture was filtered through a short plug of basic alumina (2 cm) and glass wool to yield 230 g (97%) of butene oligomers.

[0050] Synthesis of Butene Oligomers (Method B). The activated catalyst solution was prepared as above. The solvent was removed under reduced pressure (0.1 mm Hg) and dry 3-methyl heptane (10 mL), was added to the flask with vigorous stirring to form a pale yellow slurry that was then transferred via a syringe into the bomb. The oligomerization reaction was then carried out as above. Yields were similar to Method A.

[0051] **Hydrogenation of Butene Oligomers.** Butene oligomers (400 g) were placed in a 3-neck flask with a gas outlet. The solution was degassed and the atmosphere was replaced with nitrogen. PtO_2 (400 mg, 1.76 mmol) was added and the mixture was placed under a continuous hydrogen

pressure of 2 psig (about 115 kpa). One of ordinary skill in the art will understand that butene oligomers may also readily be hydrogenated under pressure using nickel catalysts. The reaction could be conveniently monitored by NMR spectroscopy, but flocculation of the catalyst occurred upon completion of the reaction and was subsequently used to determine the end point. After 24 h the reaction mixture was filtered through glass wool to give a quantitative yield of colorless liquid.

[0052] **Dimerization of 2-ethyl-1-hexene.** A flask was charged with sulfuric acid (98%, 0.3 mL) and 2-ethyl-1-hexene (4.45 g, 40 mmol) in that order. There was an initial exotherm upon mixing. The heterogeneous mixture was allowed to react with stirring at ambient temperature for a period of 16 h. The colorless organic layer was separated and washed with aqueous Na₂CO₃ solutions (3x3 mL), followed by distilled water (3 mL) and analyzed by GC/MS, ¹H and ¹³C NMR spectroscopy. Most of the peaks observed by GC/MS have molecular ion peaks of 224 and eluted in the range of 15-17 min, suggesting that primarily dimerization had taken place without a significant amount of cracking. The NMR spectra of the mixture were complex due to the formation of several isomers, yet the ratio of aliphatic protons to olefinic protons determined by NMR spectroscopy was consistent with an average formulation of C₁₆H₃₂ based on the assumption that primarily tri-substituted olefins were formed by the acid catalysis.

[0053] By *tuning* the catalyst and then using the dimer produced, it can bring the carbon use to about 95% or greater. This latter point will be particularly important in the future, where the source of raw materials (i.e., biomass/biofeedstock) is limited. Also noteworthy, the batch catalysis approach herein requires a minimal input of energy and hydrogen to make fuels that possess useful flash points, excellent cold flow properties, and high solution density/energy content. This new process affords a saturated hydrocarbon fuel that has a higher solution density and thus possesses a higher calculated power density (per volume) than similar fuels made by the GTL Fischer-Tropsch processes.

[0054] Embodiments of the invention include the conversion of a significant byproduct of 1-butene oligomerization into a hydrocarbon mixture suitable as a stand-alone or component of both turbine and diesel fuel.

[0055] Embodiments include a selective and high yielding (90+%) method for dimerizing 2-ethyl-1-hexene to a complex hydrocarbon mixture, utilizing environmentally favorable solid acid

catalysts. Embodiments described in related applications detailed a method for producing a JP-5 equivalent fuel from 1-butene. As 1-butene can be derived from butanol which can be derived from biomass, this permits an efficient process to convert biomass to full performance jet fuels. The related process converts 98% of the 1-butene into oligomers, with ca. 40% of the product mixture composed of 2-ethyl-1-hexene. The flashpoint of this latter compound is too low to incorporate into JP-5 mixtures (flashpoint: 60°C), although JP-8 mixtures (flashpoint: 38°C) may include up to ca. 15% of this hydrocarbon. To improve the overall yield of jet fuel range hydrocarbons, methods to selectively dimerize 2-ethyl-1-hexene were investigated. This renewable fuel can be used as either a stand-alone fuel or can be blended back in with the butene oligomer (JP-5 equivalent) fuel. In either case, the effective dimerization of 2-ethyl-1-hexene permits for a 1-butene to jet fuel conversion of >90%.

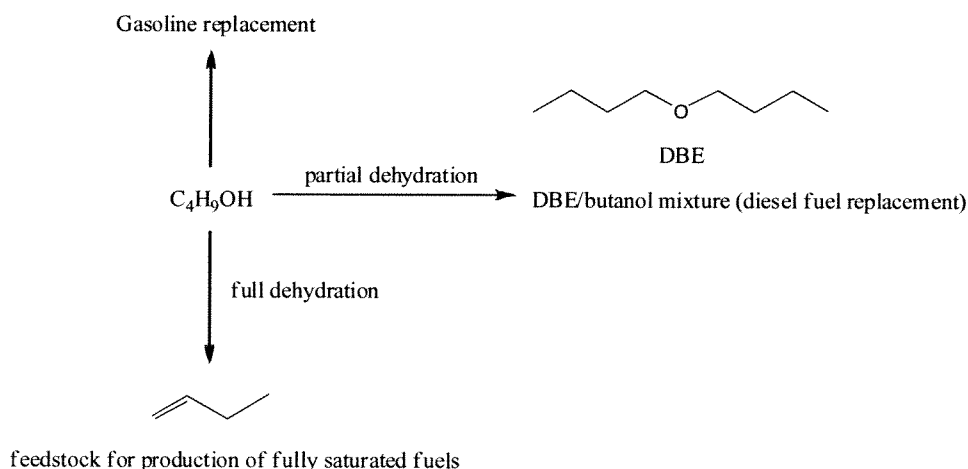
[0056] An efficient method for the selective dimerization of the renewable feedstock, 2-ethyl-1-hexene, to a complex mixture of $C_{16}H_{32}$ hydrocarbons is described below. To optimize the process, the activity of a variety of strongly acidic heterogeneous catalysts was investigated. Montmorillonite K-10 and sulfated zirconia readily isomerized 2-ethyl-1-hexene to a mixture of the cis- and trans- isomers of 3-methyl-2-heptene and 3-methyl-3-heptene, but were inactive for the dimerization of 2-ethyl-1-hexene at temperatures up to 116 °C. In contrast, the cation exchange resins Amberlyst-15 and Nafion readily dimerized 2-ethyl-1-hexene at elevated temperatures. For both sets of catalysts, the degree of hydration strongly affected the rate of isomerization/dimerization. After hydrogenation over PtO_2 and fractional distillation, saturated dimer mixtures could be isolated in up to 90% yield. The dimers have a density of 0.78 g/mL and a freezing point < -60°C, suggesting that they can be blended with renewable or conventional jet fuels, without adversely affecting the overall density and low temperature viscosity of the mixtures.

[0057] Given current concerns about diminishing oil reserves and the potential impact of global warming, research into renewable fuels has been accelerating. Many critics of renewable fuels correctly point out that current fuels such as corn-based ethanol and soybean based biodiesel represent unsustainable approaches to large scale production of alternative fuels. For example, life cycle analysis of corn-based ethanol suggests that its use as a transportation fuel produces more net CO_2 than does gasoline when land use change is included in the calculation (Charles, D. *Science*

2009, 324, 587; Searchinger, T.; Heimlich, R.; Houghton, R. A.; Dong, F.; Elobeid, A.; Fabiosa, J.; Tokgoz, S.; Hayes, D.; Yu, T. *Science* **2008**, 319, 1238-1240). These arguments coupled with impacts on global food prices are driving research into cellulosic biofuels. Ethanol produced from waste or non-food cellulose will result in up to 80% lower CO₂ emissions compared to gasoline. (Durre, P. *Biotech. J.* **2007**, 2, 1525-1534). Despite this, ethanol has several shortcomings as a transportation fuel. Ethanol has only 2/3 the net heat of combustion of gasoline, is volatile, hygroscopic, and much more corrosive than hydrocarbon fuels.

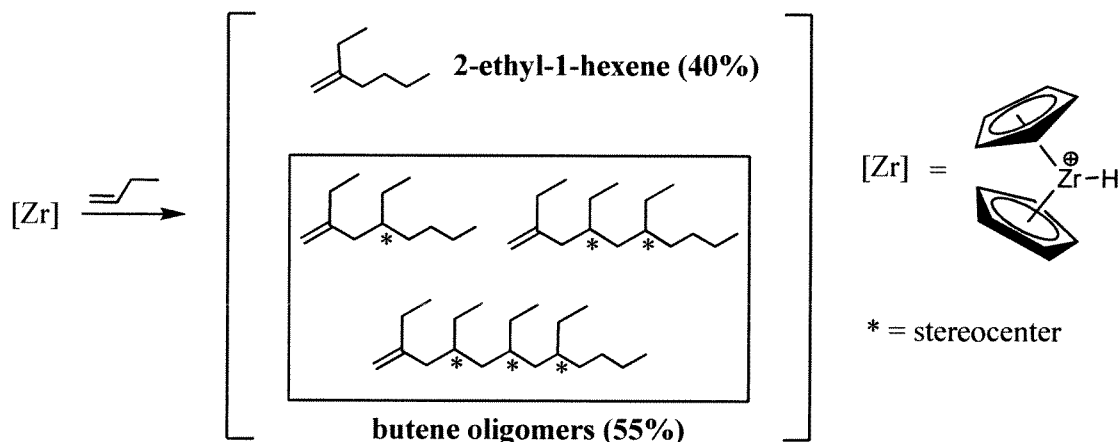
[0058] A higher alcohol including biobutanol has several advantages over ethanol. Butanol has a higher flashpoint, is less corrosive, is easier to separate from water, and can be transported in existing pipelines. (Durre, P. *Biotech. J.* **2007**, 2, 1525-1534). Perhaps most importantly, butanol has roughly 135% the volumetric heating value of ethanol, allowing it to be used as a direct replacement for gasoline in automobiles with virtually no change in gas mileage or performance. Biobutanol can be blended with conventional diesel and biodiesel fuels (Chotwichien, A.; Luengaruemitchai, A.; Jai-In, S. *Fuel* **2009**, 88, 1618-1624; Karabektas, M.; Hosoz, M. *Renew. Energy* **2009**, 34, 1554-1559; Dunn, R. O. *J. Am. Oil Chem. Soc.* **2002**, 79, 709-715) and has been shown to work well in diesel engines when combined with its partial dehydration product dibutyl ether. (Wright, M. E.; Harvey, B. G.; Quintana, R. L. *Prepr. Pap.-Am. Chem. Soc., Fuel Div.* **2008**, 53, 252-253). The versatility of butanol suggests that it has the potential to be an important central feedstock for a variety of fuel products including gasoline, diesel, and saturated fuel precursors (Scheme 9).

Scheme 9. Butanol as a versatile central material for biofuel production

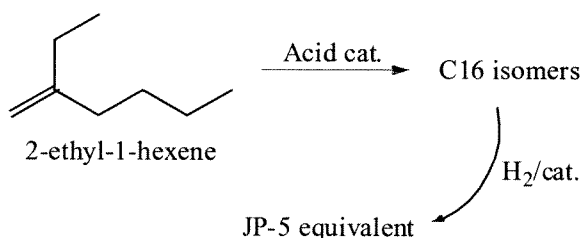


[0059] Although butanol has potential as an automobile fuel, it has limited use as a high performance military fuel due to its relatively low flashpoint and the presence of oxygen which limits its net heat of combustion. Earlier it was shown that a fully saturated fuel mixture can be obtained through the oligomerization of 1-butene, followed by hydrogenation. (Wright, M. E.; Harvey, B. G.; Quintana, R. L. *Energy Fuels* **2008**, 22, 3299-3302). As 1-butene can be derived from biobutanol through dehydration, this process allows for the synthesis of high performance jet and diesel fuels from renewable sources. The oligomerization is carried out with the use of a Ziegler Natta catalyst system and produces primarily 1,2-insertion products (**Scheme 9**). The optimized process for the synthesis of fuel range oligomers (C12, C16) without concomitant production of heavy oligomers can yield up to 40 mass % dimer. To develop an efficient method to incorporate dimer into the overall fuel mixture without adversely affecting the flash point, methods to dimerize 2-ethyl-1-hexene, followed by hydrogenation, to produce C₁₆H₃₄ molecules were investigated (**Scheme 10**).

Scheme 9. Synthesis of butene oligomers with a Ziegler Natta catalyst



Scheme 10. Acid catalyzed dimerization of 2-ethyl-1-hexene for the synthesis of renewable jet fuel.



[0060] Many catalysts promote the dimerization of alpha olefins; however, 1,1-disubstituted and especially unactivated 1,1-disubstituted olefins including 2-ethyl-1-hexene present a challenging target. Strongly acidic catalysts such as H_2SO_4 and HF are used industrially as alkylation and dimerization catalysts to produce high octane fuel additives from isobutylene raffinate. However, sulfuric and hydrofluoric acids are corrosive, dangerous to work with, and require energy intensive recycling processes. (Sheldon, R. A.; Downing, R. S.; *Applied Cat. A.* **1999**, 189, 163-183; Kumar, P.; Vermeiren, W.; Dath, J.; Hoelderich, W. F. *Energy Fuels* **2006**, 20, 481-487). Liquid superacid catalysts, including triflic acid, can also be used for alkylation and addition reactions, yet they can often lead to unproductive cracking reactions (Olah, G. A.; Batamack, P.; Deffieux, D.; Török, B.; Wang, Q.; Molnár, A.; Prakash, G. K. S. *Applied Catalysis A: General* **1996**, 146, 107-117) that may result in lower overall yields of dimers. Solid acid catalysts, including sulfated zirconia, acid treated clays, and cation exchange resins, may offer the ability to selectively dimerize challenging olefins including 2-ethyl-1-hexene while limiting cracking reactions and offering additional benefits such as easy separation and minimal work-up.

[0061] Nafion (5% water alcohol dispersion), Montmorillonite K-10 (MMT-K10), and dry Amberlyst-15 were purchased from Aldrich. Dowex HCR-W2 (hydrated cation exchange resin) was purchased from J. T. Baker. Sulfated zirconia was prepared from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ by a published method. (Song, S. X.; Kydd, R. A. *J. Chem. Soc. Faraday Trans.* **1998**, 94, 1333-1338) Nafion was precipitated from its dispersion by addition of CH_2Cl_2 and ether, followed by filtration and drying under vacuum (1 Torr) at ambient temperature. (Kim, T. K.; Kang, M.; Choi, Y. S.; Kim, H. K.; Lee, W.; Chang, H.; Seung, D. *J. Power Sources* **2007**, 165, 1-8). MMT K-10 was dried under vacuum (1 Torr) at 140°C for 5 h. Dry Amberlyst-15 and Dowex HCR-W2 were used directly from the bottle. 2-Ethyl-1-hexene was prepared from 1-butene and was distilled from CaH_2 prior to use. Its purity was >99% with trace amounts of 3-methylheptane present. All reactions were performed under a nitrogen environment. All NMR data were collected on a Bruker Avance II 300 MHz spectrometer. Product mixtures were analyzed with an Agilent 6890-GC/5973-MS to determine chemical compositions. 2-Ethyl-1-hexene was dimerized with a variety of heterogeneous catalysts and sulfuric acid solutions (**Table 4**). Typical reaction conditions ranged

from ambient temperature up to the reflux temperature of 2-ethyl-1-hexene (typical examples are presented below). Dimer mixtures were upgraded through decantation followed by hydrogenation with 1 wt% PtO₂ under 1-2 psig (about 108-115 kpa) of hydrogen for a period ranging from 12-24 h. Subsequent distillations were carried out under a nitrogen atmosphere at atmospheric pressure.

Table 4. Catalysts for the Selective Dimerization of 2-ethyl-1-hexene.

Catalyst	T (°C)	Time	Products	Dimer Yield (%)	Conversion (%)
H ₂ SO ₄ (98%)	0	0.5	dimer/oligomers	90	100
H ₂ SO ₄ (66%)	0	2	isomers	0	- ^a
H ₂ SO ₄ (66%)	ambient	18	isomers	0	98
MMT-K10 (wet)	ambient	48	isomers	0	14
MMT-K10 (wet)	116	2	isomers	0	90
MMT-K10 (dry)	ambient	24	isomers	0	30
MMT-K10 (dry)	116	2	isomers	0	96
Sulfated ZrO ₂	ambient	24	isomers	0	19
Sulfated ZrO ₂	116	2	isomers	0	96
Amberlyst-15	ambient	24	starting material	0	0
Amberlyst-15	116	2	dimer/oligomers	70	98
Nafion	ambient	24	starting material	0	0
Nafion	116	2	dimer/oligomers	90	100

^anot determined

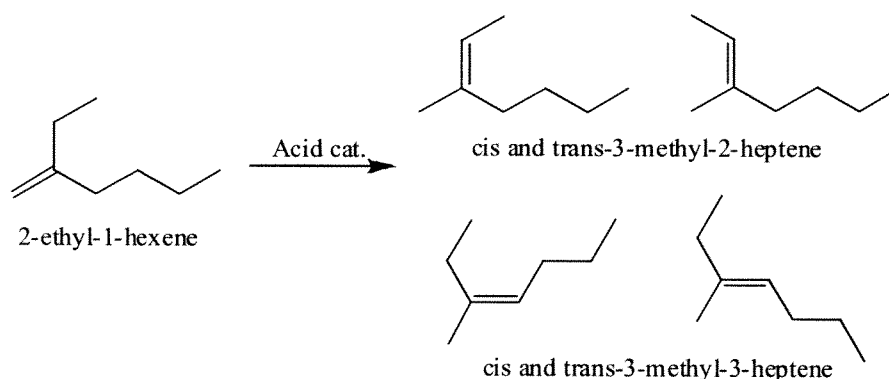
[0062] **2-ethyl-1-hexene dimerization (sulfuric acid).** 2 mL of concentrated sulfuric acid was placed in a 3-necked flask equipped with a Teflon coated stir bar, nitrogen inlet and pressure equalizing addition funnel. The flask was chilled in an ice bath and 10 mL of 2-ethyl-1-hexene was added dropwise. The mixture turned pale yellow and was vigorously stirred at 0°C for an additional 30 min. Upon sitting, the mixture separated into two phases and was transferred to a centrifuge tube. The organic layer was syringed away from the acid layer and was stirred with an aqueous NaHCO₃ solution. The washing process resulted in a thick white emulsion that took several hours to separate. Addition of brine led to a clear organic layer, but subsequent water washes reproduced the emulsion. Attempts to reduce the dimers with Pd/C and PtO₂ under 1-2 psig (about 108-115 kpa) H₂ were unsuccessful.

[0063] **Heterogeneous catalysts (Nafion).** 200 mg of dried, powdered Nafion was placed in a 3-necked flask equipped with a reflux condenser and 10 mL of 2-ethyl-1-hexene was added under nitrogen. The mixture was vigorously stirred and heated to the reflux temperature of 2-ethyl-1-hexene (116 °C) in an oil bath. The reaction was periodically monitored by NMR to determine the conversion to dimer molecules. The reaction was allowed to proceed for 2 h and was then cooled to room temperature. The dimer mixture was then separated by decantation to yield a pale yellow solution containing primarily dimer molecules (ca. 90% by GC/MS). After hydrogenation, fractional distillation gave a colorless dimer fraction.

[0064] Initial results were reported showing that sulfuric acid is an effective catalyst for the facile room temperature conversion of 2-ethyl-1-hexene to a complex mixture of dimers. (Wright, M. E.; Harvey, B. G.; Quintana, R. L. *Energy Fuels* **2008**, 22, 3299-3302). The bulk of the sulfuric acid could be easily removed by decantation, but caustic washes often led to emulsions that were difficult to resolve and the isolated C16 olefins proved difficult to hydrogenate, potentially due to poisoning of the catalyst by sulfonates. The sulfuric acid layer was highly colored suggesting that polar conjugated or polymeric species were being formed as side products. To determine if lower temperatures would allow for a more selective process, the reaction was carried out at 0°C. The acid layer turned pale yellow, suggesting that less side reactions were occurring, but the organic fraction was difficult to work-up as observed before. The use of less concentrated solutions (66%) produced only isomerization products with no dimerization. This result suggested that strongly acidic catalysts were necessary to induce the dimerization reaction. The use of sulfuric acid as a catalyst had several negative aspects, for example, large volumes of sulfuric acid (5/1, v/v, alkene/H₂SO₄) were required for the reaction to go to completion. Additionally, used acid solutions had limited activity and could not be easily recycled.

[0065] To simplify the dimer isolation process, reduce the amount of catalyst, and improve the susceptibility of the olefin mixture to hydrogenation, the use of heterogeneous acid catalysts for the selective dimerization of 2-ethyl-1-hexene were investigated. Several solid acid catalysts, including inorganic and polymer bound systems, were utilized. The solid acids (**Table 5**) included sulfuric acid treated montmorillonite clay (MMT-K10), a cross-linked polystyrene based hydrated cation exchange resin (Dowex HCR-W2), a macroreticular cation exchange resin (Amberlyst -15),

sulfated zirconia, and Nafion (a perfluorinated sulfonic acid resin). MMT-K10 which has been utilized for the dimerization of activated olefins such as 1,1-diphenylethene, (Madhavan, D.; Murugalakshmi, M.; Lalitha, A.; Pitchumani, K. *Catalysis Letters* **2001** 73, 1-4) and more recently, β -pinene and its ring opened isomers, (Harvey, B.G.; Wright, M.E.; Quintana, R.L. *Preprints of Symposia-ACS Div. Fuel Chem.* **2009**, 54, 305-306) was used without modification in a dimerization reaction. At room temperature, no reaction occurred, while at the reflux temperature (116°C) complete isomerization to a mixture of 4 isomers was observed (**Scheme 11**).



Scheme 11. Acid catalyzed isomerization of 2-ethyl-1-hexene.

[0066] The products consisted of the cis- and trans- isomers of 3-methyl-2-heptene and 3-methyl-3-heptene as confirmed through both NMR spectroscopy and GC-MS. The Hammett acidity of MMT-K10 can be drastically affected by the amount of water present, with wet MMT-K10 having $H_0 = (+3.3 \text{ to } +1.5)$ and dry MMT-K10 (5 h 140 °C, in vacuo) having $H_0 = (-5.5 \text{ to } -8.2)$. (Pillai, S. M.; Ravindranathan, M. *J. Chem. Soc. Chem. Commun.* **1994**, 1813-1814) Suitably dried MMT-K10 was utilized as a catalyst and revealed the ability to slowly isomerize 2-ethyl-1-hexene at room temperature but provided similar results to wet MMT-K10 at reflux temperatures and led to no dimerization products. Sulfated zirconia, which is an active catalyst for alkylation reactions and is often considered to have acidity comparable to sulfuric acid (Yadav, G. D.; Nair, J. *J. Microporous Mat.* **1999**, 33, 1-48; Valyon, J.; Onyestyak, G.; Lonyi, F.; Barthos, R. *J. Phys. Chem. B* **2000**, 104, 7311-7319; Umansk, B.; Engelhardt, J.; Hall, W. K. *J. Catal.* **1991**, 127, 128; Busca, G. *Chem. Rev.* **2007**, 107, 5366-5410), was prepared from $ZrOCl_2 \cdot 8H_2O$ and was shown to have similar behavior to MMT-K10 in that it reacted slowly with 2-ethyl-1-hexene at room

temperature and led solely to isomerization at the reflux temperature.

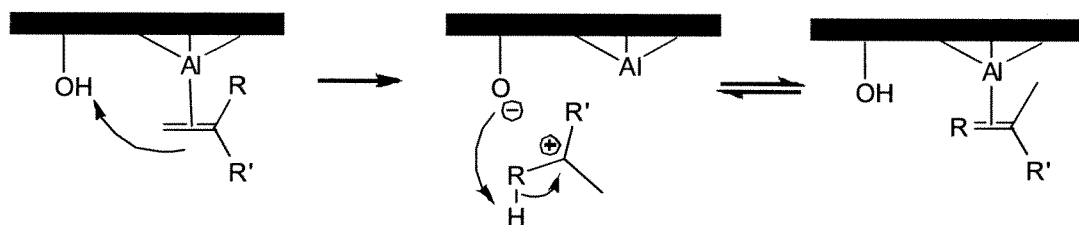
Table 5. Selected Properties of Solid Acid Catalysts.

Catalyst	Surface area (m ² /g)	Hammett acidity function (H ₀)	Acid Type
Montmorillonite K10	273 ^a	Wet (3.3 to 1.5), Dry (-5.6 to -8.2)	Bronsted, Lewis
Sulfated Zirconia	77	-12	Bronsted, Lewis
Amberlyst 15	40 ^a	(-2.2)	Bronsted
Nafion	-	(-11 to -13)	Bronsted

^ameasured by nitrogen desorption.

[0067] In the case of both of these systems, it appears that intermediate carbocations were formed based on the facile isomerization of the olefin at elevated temperatures. However, in order for dimerization to take place, the carbocation must have sufficient stability and charge separation to allow for the reaction with the 1,1-disubstituted primary and tri-substituted internal olefin nucleophiles in solution. MMT-K10 has been shown to be an efficient catalyst for the dimerization of 1,1-disubstituted olefins with intermediate carbocations stabilized by arenes and more recently has been shown to be effective in the dimerization of β -pinene. (Harvey, B.G.; Wright, M.E.; Quintana, R.L. *Preprints of Symposia-ACS Div. Fuel Chem.* **2009**, *54*, 305-306).

[0068] In the case of β -pinene, MMT-K10 reacts exothermically at room temperature, whereas stronger heterogeneous acids including Nafion are unreactive except under reflux conditions. A potential explanation for this behavior is that MMT-K10 (an aluminosilicate clay) has Lewis acid sites that can interact with and bind the incoming olefin. This may aid in bringing the olefin in close proximity to the catalyst surface where the olefin can be protonated by a Bronsted acid site at the clay surface. In contrast to acyclic alkenes, β -pinene undergoes a ring opening reaction to produce mixtures of primarily camphene and limonene; these molecules are then converted to dimers. For alkenes including 2-ethyl-1-hexene, one can propose a mechanism in which the alkene is coordinated by a Lewis acid center and then is readily isomerized by a nearby acid group. The potential interaction of 2-ethyl-1-hexene with MMT-K10 is shown below.

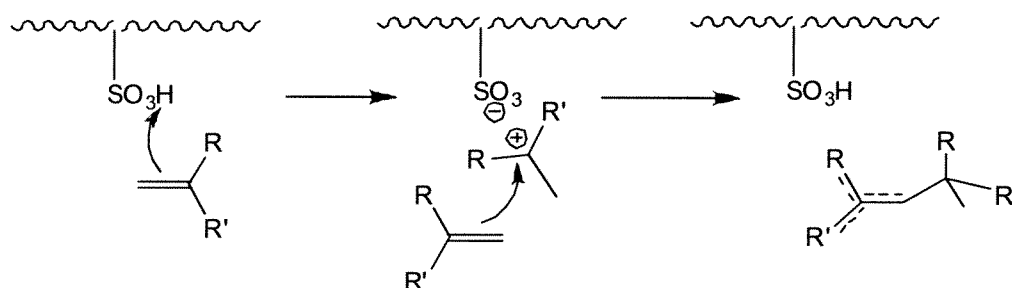


[0069] As isomers are formed, they can then re-coordinate to a metal center, providing a reversible pathway that may limit the lifetime of carbocations. This premise suggests that even when a highly acidic catalyst including sulfated zirconia is used, the carbocations formed are short-lived and therefore unable to interact with olefins in solution, forming only isomers.

[0070] Next, catalysts devoid of Lewis acid sites including Dowex HCR-W2, Amberlyst-15, and Nafion were investigated. Dowex HCR-W2 is a hydrated, gel-type polystyrene-based sulfonic acid resin with no permanent porosity. It was unreactive with the olefin at room temperature and led to slow isomerization at the reflux temperature. Extended periods of reflux led to no observable dimer formation. Amberlyst-15, a low moisture polystyrene-based sulfonic acid resin commonly used for alkylation, dimerization, and oligomerization reactions (Hauge, K.; Bergene, E.; Chen, D.; Fredriksen, G. R.; Holmen, A. *Catalysis Today* **2005**, *100*, 463-466; Alcántara, R.; Alcántara, E.; Canoira, L.; Franco, M. J.; Herrera, M.; Navarro, A. *Reactive and Functional Polymers* **2000**, *45*, 19-27; Cruz, V. J.; Izquierdo, J. F.; Cunill, F.; Tejero, J.; Iberra, M. Fité, C. *Reactive and Functional Polymers* **2005**, *65*, 149-160), did not react at room temperature, but isomerized and dimerized 2-ethyl-1-hexene at the reflux temperature. Increasing the temperature did not improve the yield of dimer and resulted in some trimer formation.

[0071] Nafion, a well-studied superacid catalyst that has applications in alkylation and Friedel-Crafts chemistry, olefin isomerization and dimerization reactions (Molnár, Á. *Curr. Org. Chem.* **2008** *12*, 159-181 Olah, G. A.; Prakash, G. K. S. Molnar, A. Sommer, J. *Superacid Chemistry*, 2nd Edition, Wiley, **2009**; Laufer, MC.; Bonrath, W.; Hoelderich, W. F. *Cat. Lett.* **2005**, *100*, 101-103; Beltrame, P. Zuretti, G. *Applied Cat. A-Gen.* **2005**, *283*, 33-38; Wang, H.; Xu, B. Q. *Applied Cat. A-Gen.* **2004**, *275*, 247-255; Harmer, M. A.; Sun, Q. *Applied Cat. A-Gen.* **2001**, *221*, 45-62; Harmer, M. A.; Sun, Q.; Vega, AJ; Farneth, WE; Heidekun, A.; Hoelderich, W. F. *Green Chem.* **2000**, *2*, 7-14; Sun, Q.; Harmer, M. A.; Farneth, W. E.; *Chem. Commun.* **1996**, 1201-1202; Harmer,

M. A.; Sun, Q.; Michalczyk, M. J.; Yang, Z. *Chem. Commun.* **1997**, 1803-1804; Harmer, M. A.; Sun, Q. *Adv. Mater.* **1998**, *10*, 1255-1257; Fujiwara, M.; Shiokawa, K.; Zhu, YC *J. Mol. Cat. A-Chem.* **2007**, *264*, 153-161; Harmer, M. A.; Farneth, W. E.; Sun, Q. *J. Am. Chem. Soc.* **1996**, *118*, 7708-7715; Sun, Q.; Farneth, W. E.; Harmer, M. A. *J. Catal.* **1996**, *164*, 62-69; Heidekum, A.; Harmer, M.; Hoelderich, W. F. *Catal. Lett.* **1997**, *47*, 243-246; Rác, B.; Mulas, G.; Csongrádi, A.; Lóki, K.; Molnár, Á. *Appl. Catal. A* **2005**, *282*, 255-265; Fritsch, D.; Randjelovic, I.; Keil, F. *Catal. Today* **2004**, *98*, 295-308) was unreactive under ambient conditions, but at reflux temperatures, proved to be an excellent catalyst for dimerization and produced a complex array of C₁₆H₃₄ molecules in greater than 90% yield (as shown below).



[0072] As shown above, a potential dimerization reaction of 2-ethyl-1-hexene on a Nafion or Amberlyst-15 surface.

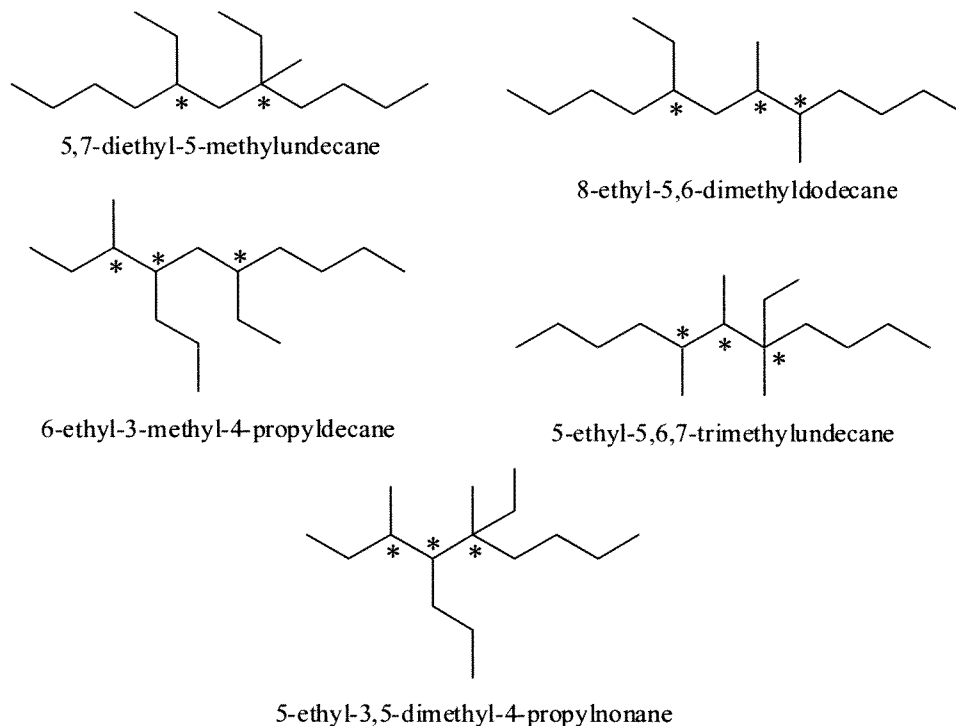
[0073] Interestingly, neither Amberlyst-15, nor Nafion produced isomers or dimers at ambient temperature, providing further evidence for a mechanism in which Lewis acid sites in the previously discussed inorganic catalysts are important in promoting the isomerization of 2-ethyl-1-hexene at room temperature through initial olefin coordination. As expected, the presence of excess water (wet MMT-K10, Dowex HCR-W2) diminished the capacity of both inorganic and polystyrene supported catalysts to isomerize and dimerize 2-ethyl-1-hexene.

[0074] It's important to note that although H_0 is often used to describe the acidity of solid acid catalysts, a simple comparison of this value across different catalyst types and in different environments with different substrates is ineffective for the prediction of behavior. In the current study, dry Montmorillonite-K10, with H_0 as low as -8.2, efficiently promotes the room temperature isomerization of 2-ethyl-1-hexene, but is completely inactive for the dimerization of the olefin. In a similar manner, sulfated zirconia, which has been characterized as having a Hammet acidity of ~ 12

is also ineffective for dimerization. In contrast, Amberlyst-15 with a much less acidic H_0 (-2.2) was effective at both isomerization and dimerization, while Nafion (H_0 = -11 to -13) was exceptionally active, particularly when considering the extremely low surface area of the native resin (0.02 m²/g). The results suggest that both Lewis and Bronsted acid sites promote the isomerization of 2-ethyl-1-hexene, but that Lewis acid sites have an inhibitory effect for the dimerization reaction.

[0075] The crude product was separated from the catalysts by simple decantation and analyzed by both GC/MS and NMR spectroscopy. A GC/MS chromatogram (**Figure 9**) revealed a complex distribution of compounds that eluted over the course of ca. 2 min on the GC column. A parent ion with m/z 224 was observed for these peaks. This crude mixture was then upgraded through hydrogenation under mild conditions (1-2 psig H₂(about 108-115 kpa), PtO₂ cat.) and subsequent distillation afforded a colorless product. The GC-MS chromatogram was similar to that for the unsaturated solution with the exception that a low intensity parent ion peak with m/z 226 could be detected for some of the compounds. The parent ion peak was unobservable for many of the peaks in the chromatogram, but the saturation of the products and a molecular mass of 226 could be inferred from the splitting pattern (**Figure 10**). The saturation of the products was further confirmed through NMR spectroscopy.

[0076] An attempt was made to identify individual components of the hydrogenated mixture, but was largely unsuccessful. Based on the structure of 2-ethyl-1-hexene and its subsequent isomers, some inferences can be made in regard to the structures of the products. Potential hydrogenated structures of 2-ethyl-1-hexene dimers (shown below).



[0077] The proposed product structures each include at least two stereocenters, resulting in a total of 18 GC resolvable isomers, not including more complicated alternative mechanisms including cracking, rearrangements, methyl shifts, and cyclization. Based on the GC chromatograms, the product distribution is very complex; however, the presence of a variety of isomers in solution is beneficial for a potential fuel mixture as it often prevents crystallization and improves the low temperature fluidity of the fuel. Evidence for this effect is provided by the observation that the mixture did not freeze even after being submerged in a -78°C bath for 2 hours. In addition to having an exceptionally low freezing point, the density of the $\text{C}_{16}\text{H}_{34}$ mixture was 0.78 g/mL. These physical properties should allow for the use of these mixtures in diesel and high flashpoint jet fuels.

[0078] An efficient process for the conversion of 2-ethyl-1-hexene to a complex mixture of $\text{C}_{16}\text{H}_{34}$ hydrocarbons has been developed. This process allows for the conversion of 1-butene to jet fuel range hydrocarbons in greater than 90% yield. Inorganic catalysts such as sulfated zirconia and MMT-K10 efficiently isomerize 2-ethyl-1-hexene, but do not promote dimerization. Dry cationic

exchange resins including Nafion and Amberlyst-15 produce primarily dimers and small amounts of trimers. The results with native Nafion suggest that Nafion nanocomposites would be ideal catalysts for the dimerization reaction. The difference in reactivity between the inorganic catalysts and the cation exchange resins is attributed to interactions between alkenes and Lewis acid centers that inhibit the dimerization reaction. Further work to determine key fuel properties for hydrocarbon mixtures composed exclusively of 2-ethyl-1-hexene dimers as well as mixed systems with hydrogenated butene oligomer mixtures is also being examined.

[0079] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither, or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

[0080] Embodiments of the invention clearly have military and commercial applications including oil and biofuel companies which may invest in butanol fermentation, refiners, as well as companies that produce polyolefins for polymer applications.

CLAIMS

What is Claimed is:

1. A process for making fuels, comprising:
providing at least one branched olefin;
adding at least one active heterogeneous acid catalyst to said at least one branched olefin to produce a mixture;
heating said mixture of catalyst and branched olefin to a temperature greater than 80°C for a sufficient amount of time to produce a mixture comprising the catalyst and dimers of the branched olefin;
removing said catalysts from said dimers and catalyst mixture; and
after removal of the catalyst, adding at least one hydrogenation catalyst to said dimers under a hydrogen atmosphere to produce a mixture of stable fuels.
2. The process according to claim 1, further characterized by said providing at least one branched olefin further comprising providing a mixture of branched olefins.
3. The process according to claim 1, further characterized by said step of adding active heterogeneous acid catalyst to said branched olefin being performed under a N₂ atmosphere.
4. The process according to claim 1, further characterized by said at least one branched olefin comprising a C₆-C₁₅ branched olefin.
5. The process according to claim 4, further characterized by said at least one branched olefin comprising a C₇-C₁₀ branched olefin.

6. The process according to claim 5, further characterized by said at least one branched olefin comprising a C₈ branched olefin.

7. The process according to claim 6, further characterized by said at least one branched olefin comprising 2-ethyl-1-hexene.

8. The process according to claim 7, further characterized by said at least one branched olefin comprising 2-ethyl-1-hexene.

9. The process according to claim 1, further characterized by said at least one catalyst comprising a catalyst selected from the group consisting of supported and unsupported cation exchange resins, acid clays, zeolites, polyoxometallates, and sulfated metal oxides.

10. The process according to claim 1, further characterized by said fuels are unsaturated hydrocarbons.

11. The process according to claim 1, further characterized by said fuels being selected from the group consisting of 5,7-diethyl-5-methylundecane, 8-ethyl-5,6-dimethyldodecane, 6-ethyl-3-methyl-4-propyldecane, 5-ethyl-5,6,7-trimethylundecane, 5-ethyl-3,5-dimethyl-4-propylnonane, and molecules produced from the coupling of any two structural isomers of 2-ethyl-1-hexene.

12. The process according to claim 1, further characterized by said heating step being performed at a temperature of at least 100°C.

13. The process according to claim 1, further characterized by said heating step being performed at a temperature of up to 120°C.

14. The process according to claim 1, further characterized by said heating step being performed at a temperature of 110°C to 120°C.

15. The process according to claim 1, further comprising the step of purifying said stable fuels in removing short chain branched olefins remaining in said stable fuels.

16. The process according to claim 15, further characterized by said purifying step including at least one of filtration and distillation.

17. The process according to claim 1, further characterized by said catalyst including a Ziegler-Natta catalyst.

18. The process according to claim 2, further characterized by said catalyst further including a co-catalyst.

19. The process according to claim 1, further characterized by said mixture of catalyst and branched olefin being solvent free.

20. The process according to claim 1, further characterized by said mixture of catalyst and branched olefin including dimer formed in a prior iteration of the process.

21. The process according to claim 1, further characterized by the branched olefin comprising a mixture of branched olefins produced by the dimerization of 1-butene.

22. Fuels formed in accordance with the process of any one of claims 1-21.

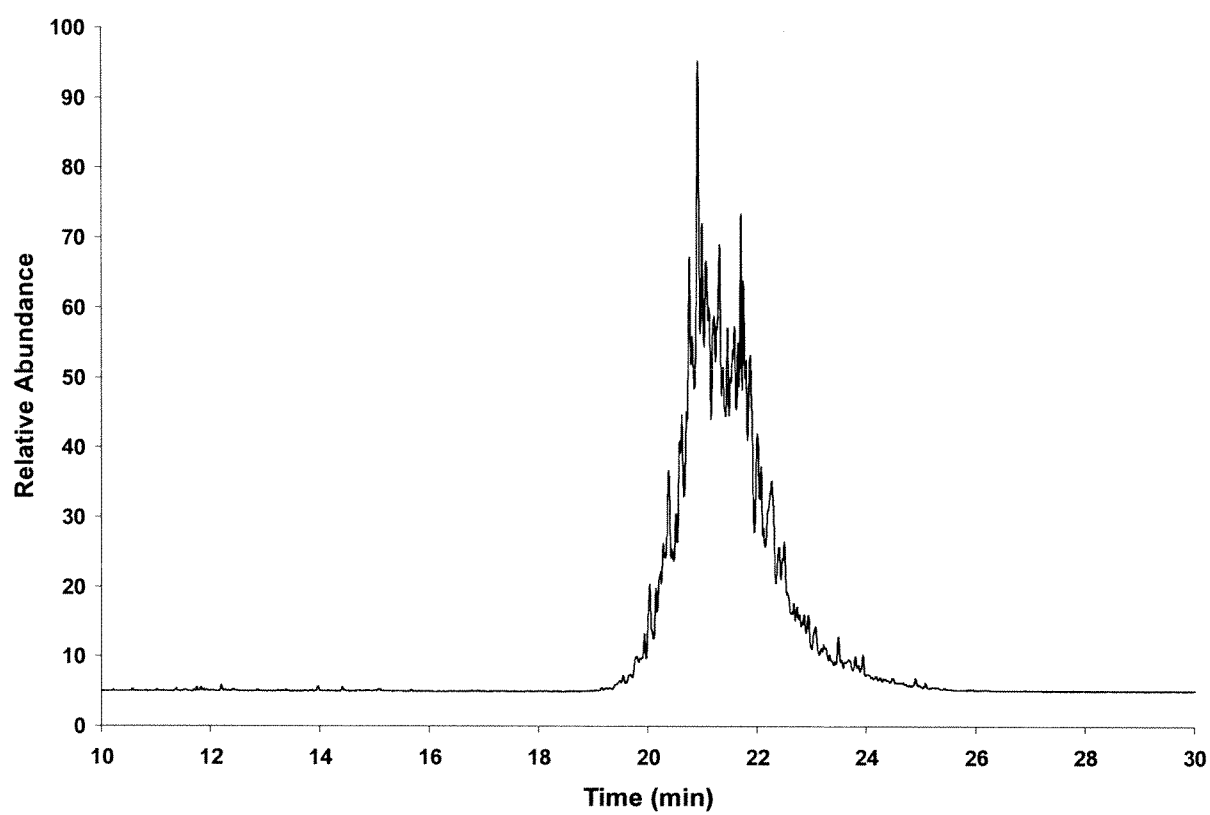
23. Butene oligomer fuels formed in accordance with the process of any one of claims 1-21.

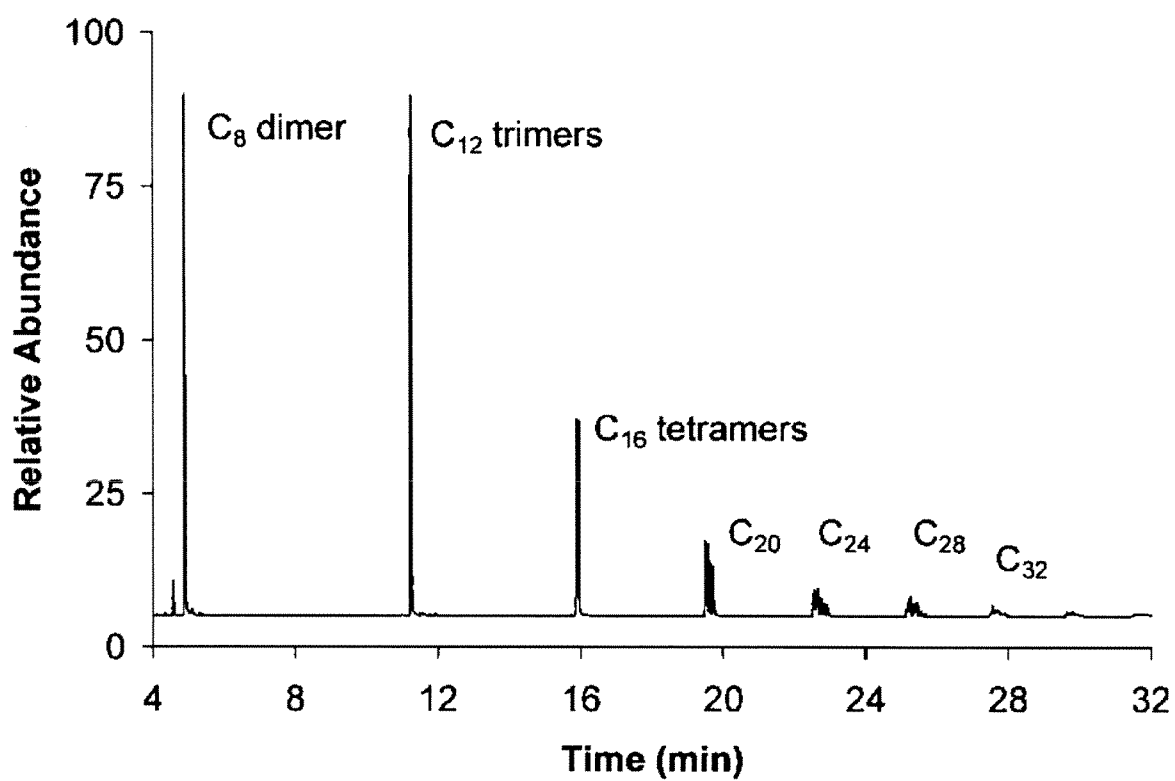
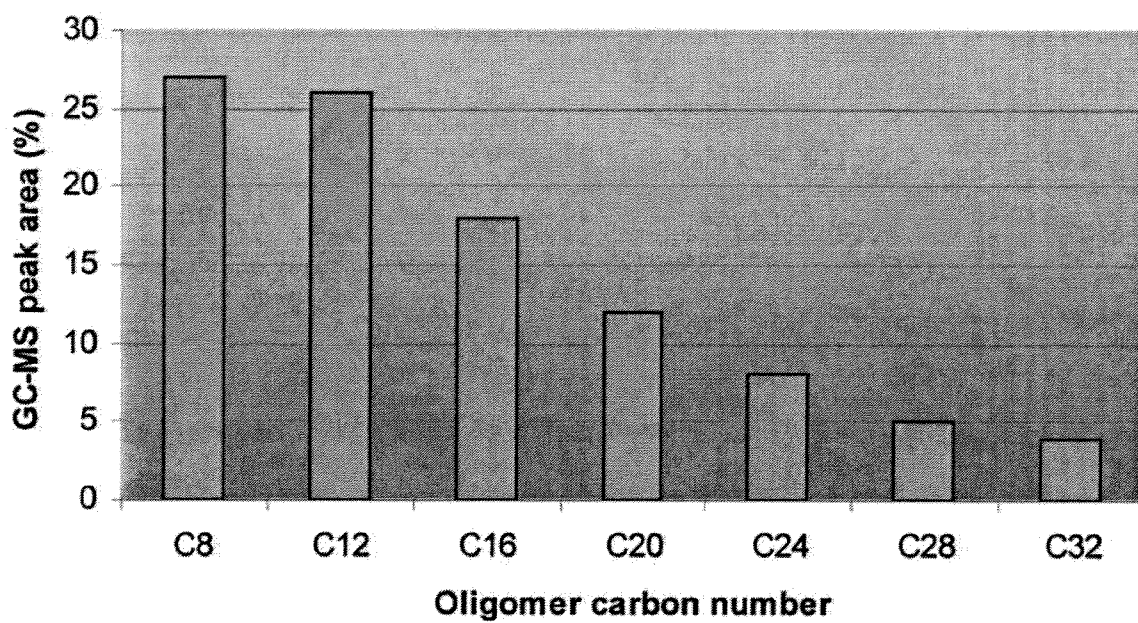
24. A process for making fuels, comprising:
providing an amount of at least one branched olefin, the branched olefin including 2-ethyl-1-hexene;
adding active heterogeneous acid catalyst to said at least one branched olefin to produce a solvent-free mixture;

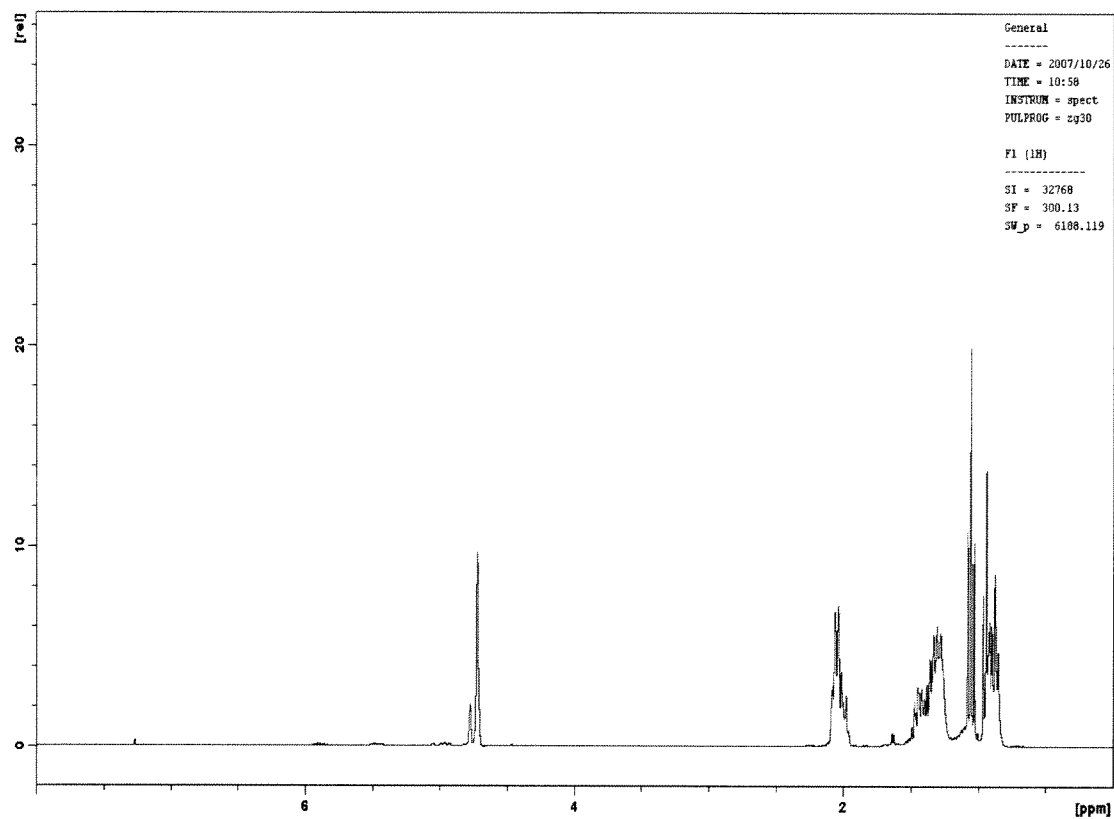
heating said solvent-free mixture to a temperature greater than 80°C to produce a C₁₆ dimers/catalyst mixture;
removing said catalyst from said dimers/catalyst mixture; and
adding hydrogenation catalyst to said dimers under a hydrogen atmosphere to produce a mixture of stable fuels.

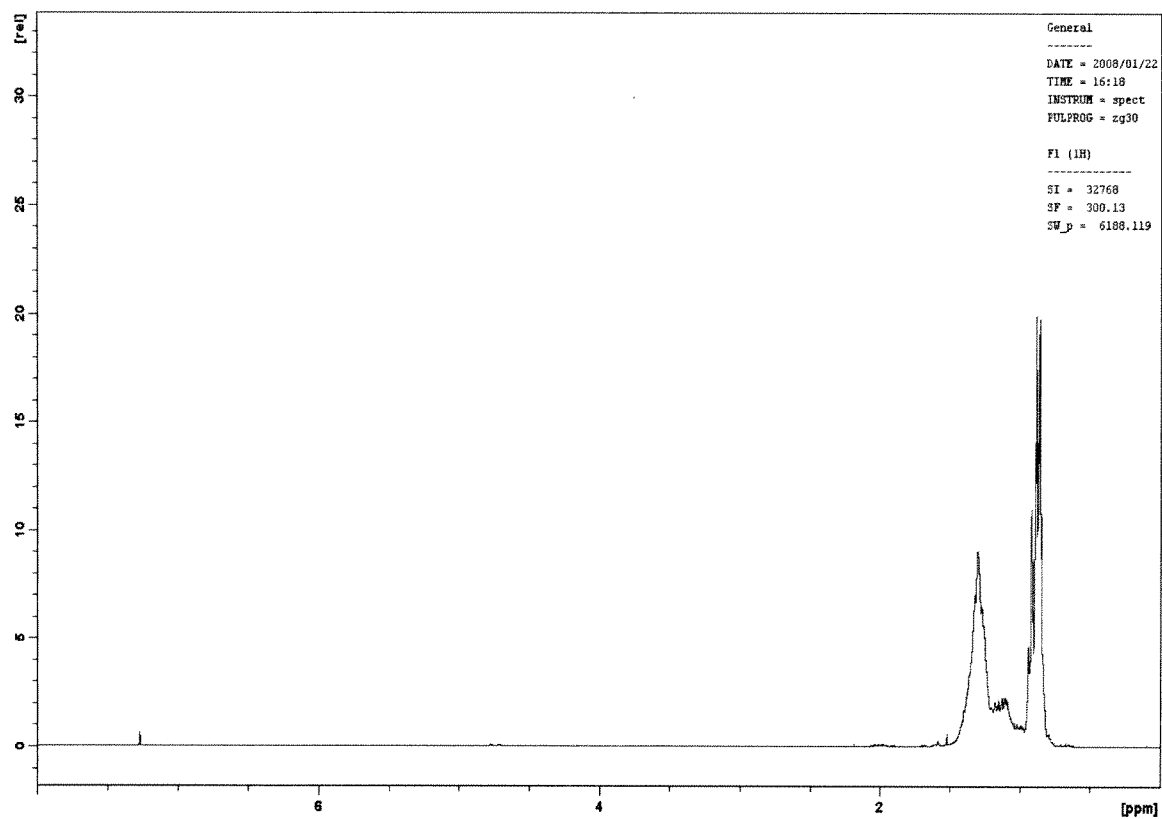
25. The process according to claim 24, further characterized by said catalysts being selected from the group consisting of supported or unsupported cation exchange resins, acid clays, zeolites, polyoxometallates, sulfated metal oxides, and other heterogeneous acids.

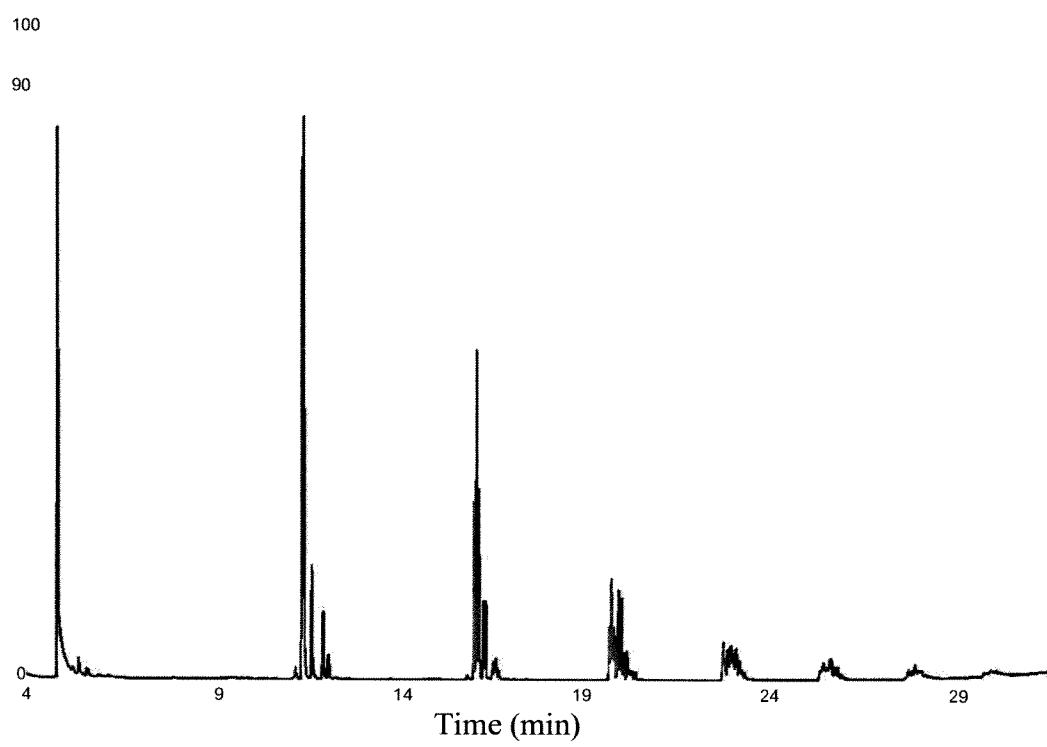
26. The process according to claim 24, further characterized by said fuels being selected from the group consisting of 5,7-diethyl-5-methylundecane, 8-ethyl-5,6-dimethyldodecane, 6-ethyl-3-methyl-4-propyldecane, 5-ethyl-5,6,7-trimethylundecane, and 5-ethyl-3,5-dimethyl-4-propylnonane and similar molecules, or molecules produced from the coupling of any two structural isomers of 2-ethyl-1-hexene.

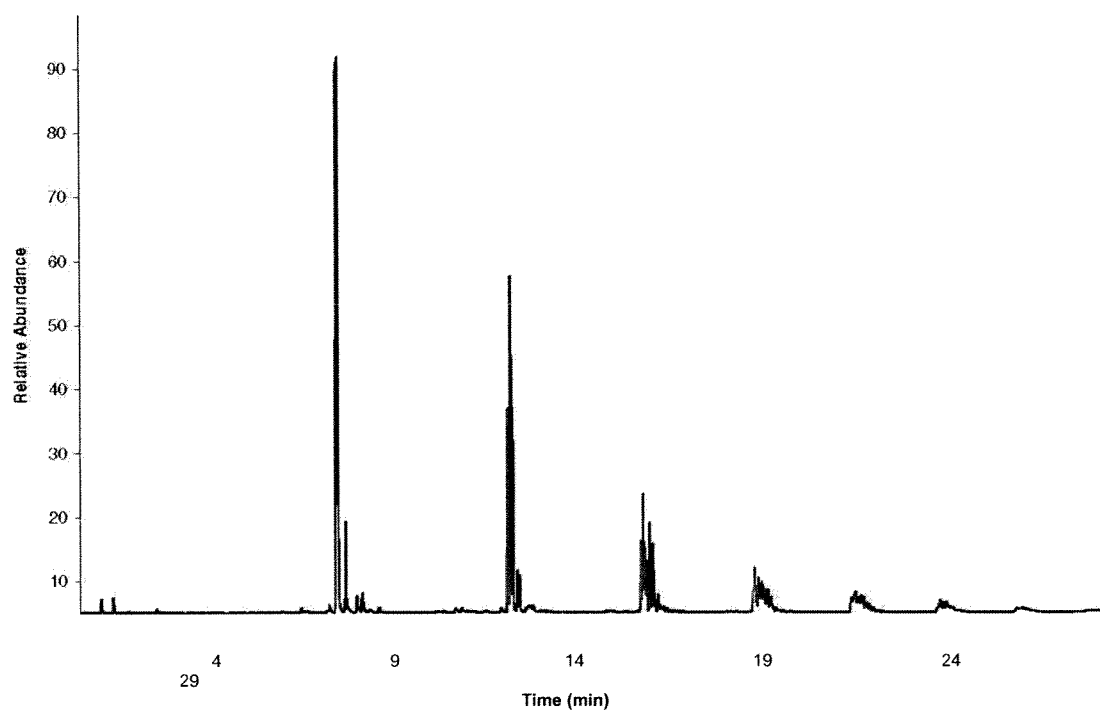
**FIG. 1**

**FIG. 2****FIG. 3**

**FIG. 4**

**FIG. 5**

**FIG. 6**

**FIG. 7**

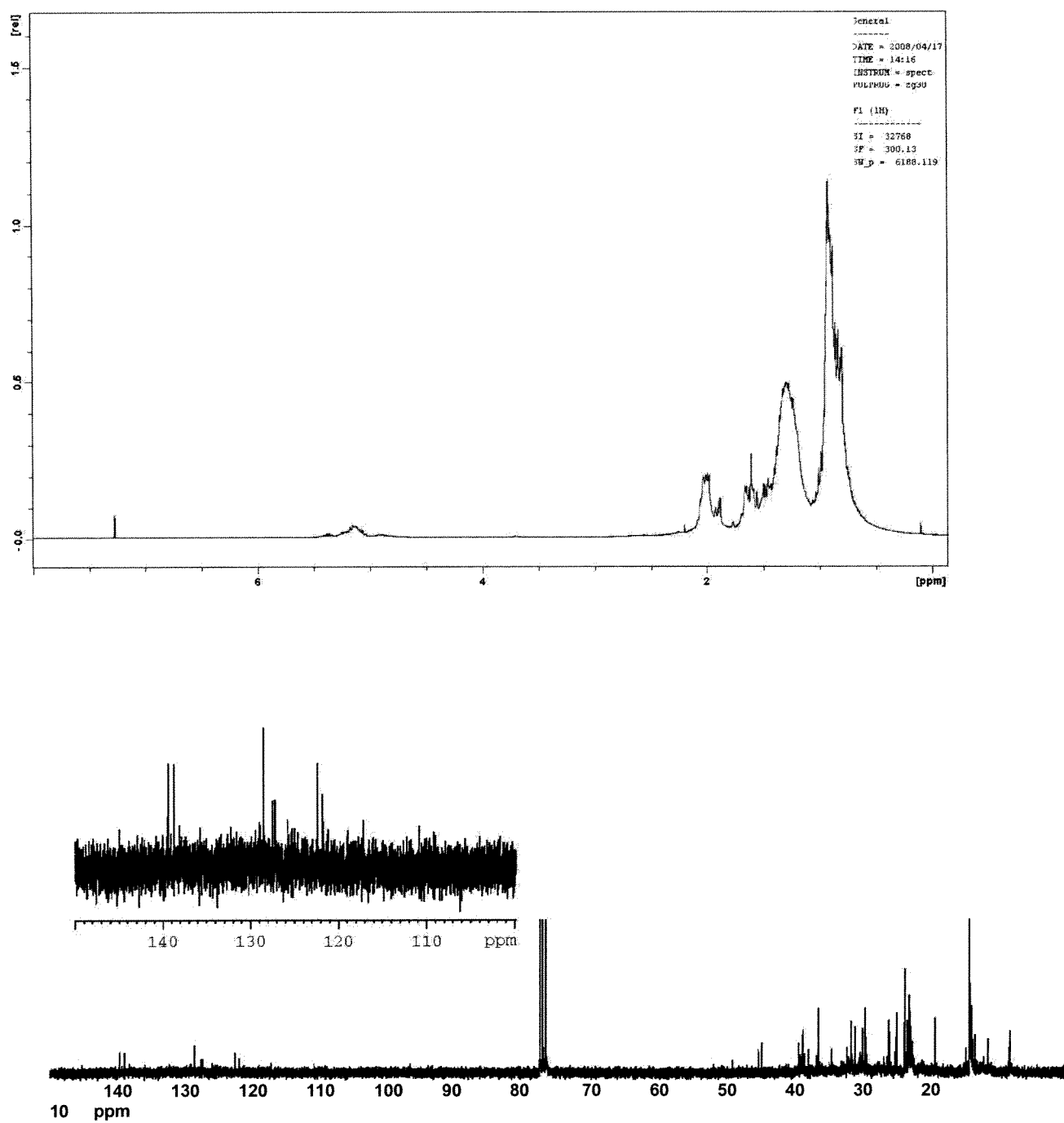
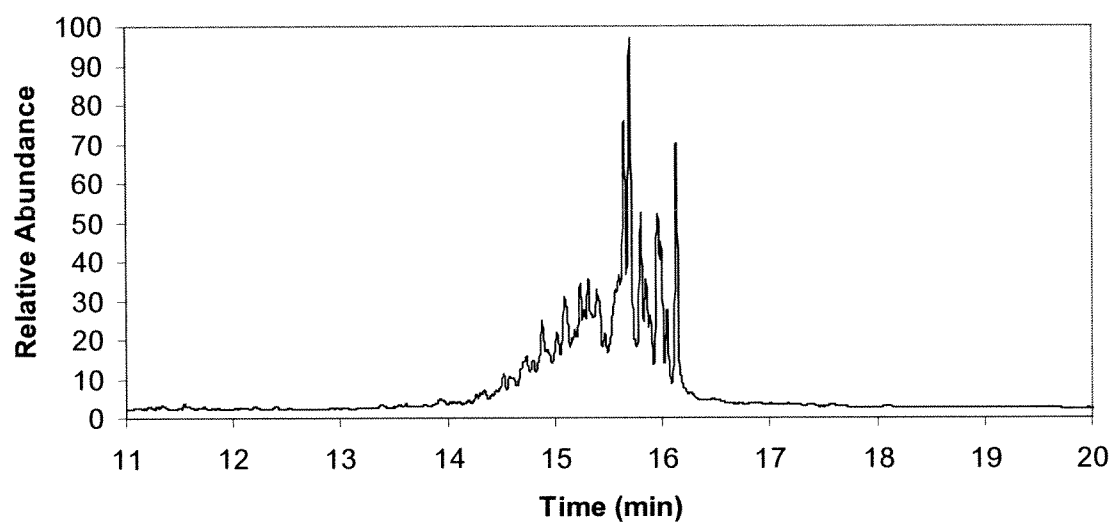
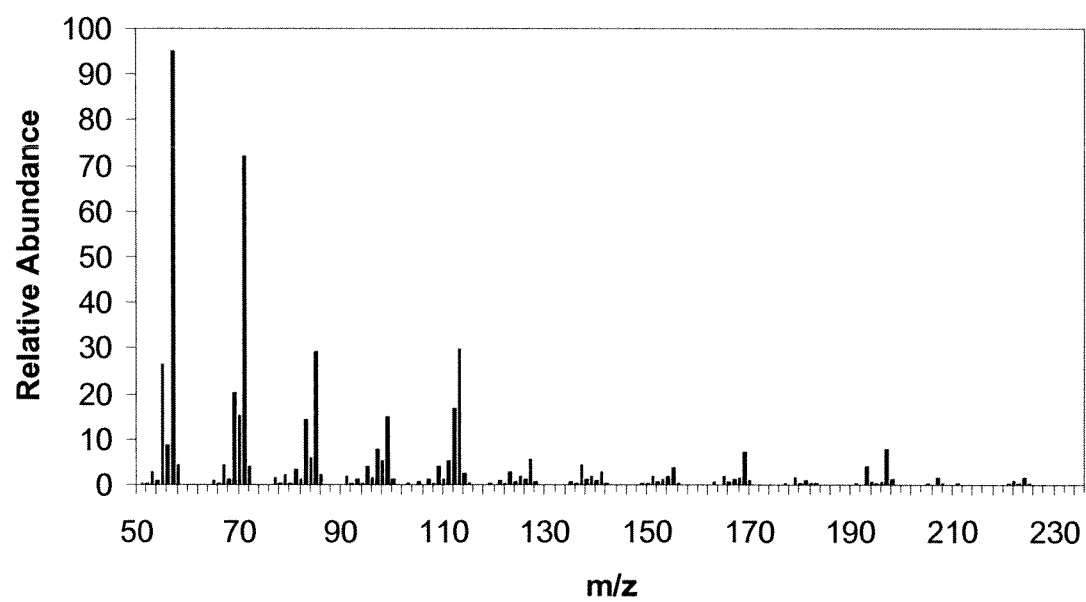


FIG. 8

**FIG. 9**

**FIG. 10**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/35190

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 5/00; C07C 5/22 (2012.01)

USPC - 585/510; 585/500

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC - 585/510; 585/500

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

USPC - all classes; NPL (keyword limited)

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

PatBase; Google Scholar

Search terms - Branched, olefin, fuel, dimer, heating, "heterogeneous acid catalyst", 2-ethyl-1-hexene, Harvey, Quintana, acid clay, zeolite, hydrogenation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Harvey et al., 'Synthesis of renewable jet and diesel fuels from 2-ethyl-1-hexene', Energy Environ. Sci., 2010, 3, 352-357; abstract	1, 3-17, 20-23
Y		2, 18, 19, 24-26
Y	US 6,291,733 B1 (Small et al.) 18 September 2001 (18.09.2001); col 1, ln 10-14	2, 18, 19, 24-26
Y	Wright et al. 'Highly Efficient Zirconium-Catalyzed Batch Conversion of 1-Butene: A New Route to Jet Fuels' Energy Fuels, 2008, 22 (5), pp 3299-3302; abstract	1-26
X, E	US 2012/0209040 A1 (Wright) 16 August 2012 (16.08.2012); entire document	1-26
X, E	US 2012/0209036 A1 (Harvey et al.) 16 August 2012 (16.08.2012); entire document	1-26

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:

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

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

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

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

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

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Date of the actual completion of the international search

08 January 2013 (08.01.2013)

Date of mailing of the international search report

28 JAN 2013

Name and mailing address of the ISA/US

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