

## HETERODIMERS OF TERPENES AND LINEAR OR BRANCHED ALKENES

## CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/425,959, filed on November 16, 2022, which is incorporated by reference herein in its entirety.

## TECHNICAL FIELD

[0002] This invention relates to catalyst-assisted heterodimerization of terpenes with linear or branched alkenes, as well hydrogenation of the resulting dimers.

## BACKGROUND

[0003] Bio-renewable homodimers of terpenes, including pinenes, camphenes, and limonenes have high density (up to 0.94 g/cm<sup>3</sup>) and high volumetric net heat of combustions (137,000 to 142,000 Btu/gallon). However, said homodimers of terpenes have high viscosities (e.g., 20-35 mPa•s at 40°C) that limit their ability for use in ultra-performance capacities.

## SUMMARY

[0004] This disclosure describes catalyst-assisted heterodimerization of monomers (e.g., terpenes and non-cyclic alkenes) that can be commercial bio-sourced monomers. The dimerizations disclosed herein can be carried out under mild reaction conditions in the presence of a dimerization catalyst (e.g., BF<sub>3</sub> or a natural mineral, such as Montmorillonite). Once the terpene-alkene heterodimers are hydrogenated to yield hydrogenated terpene-alkene heterodimers, the hydrogenated terpene-alkene heterodimers disclosed herein can be characterized by one or more of the following properties: high density (e.g., at least about 0.85 g/cm<sup>3</sup> at 15°C), high volumetric net heat of combustion (e.g., at least about 130,000 Btu/gallon), low to moderate viscosity (e.g., less than about 850 mPa•s at -35°C), and low freezing point (e.g., less than about 70°C). In some embodiments, the hydrogenated terpene-alkene heterodimers disclosed herein can be characterized by a high density (e.g., at least about 0.85 g/cm<sup>3</sup>). In some embodiments, the hydrogenated terpene-alkene heterodimers disclosed herein can be characterized by a high volumetric net heat of combustions (e.g., at least about 130,000 Btu/gallon). In some embodiments, the hydrogenated terpene-alkene heterodimers disclosed herein can be characterized by low viscosities (e.g., less than about

850 mPa•s at -35°C). In some embodiments, the hydrogenated terpene-alkene heterodimers disclosed herein can be characterized by a low freezing point (e.g., less than 70°C). This disclosure describes a high yielding and selective hydrogenation of the terpene/alkene heterodimers, as well as the by-products of the heterodimerization reaction (e.g., terpene and alkene homodimers).

[0005] Provided herein are methods for synthesizing a terpene-alkene heterodimer, the methods comprising: contacting a terpene with a linear or branched alkene in the presence of a dimerization catalyst to yield a product mixture comprising the terpene-alkene heterodimer. Further methods can include hydrogenating the product mixture.

[0006] Also provided herein are fuel components comprising a hydrogenated terpene-alkene heterodimer of the disclosure.

[0007] Also provided herein are fuels comprising a hydrogenated terpene-alkene heterodimer of the disclosure and a C<sub>5</sub>-C<sub>20</sub> alkyl.

[0008] The details of one or more embodiments of the subject matter of this disclosure are set forth in the accompanying drawings and the description. Other features, aspects, and advantages of the subject matter will become apparent from the description, the drawings, and the claims.

[0009] Traditional homodimers of terpenes have had potential applications as ultra-performance components for jet and tactical fuels due to their high density and high volumetric net heat of combustions. However, the main limitation of homodimers of terpenes is their high viscosity resulting in poor low temperature performance. There is a need for fuels with high density and high volumetric net heat of combustions that have low viscosity (e.g., less than about 850 mPa•s at -35°C), such that the fuels are better equipped for low temperature performance.

#### BRIEF DESCRIPTION OF DRAWINGS

[0010] FIG. 1A depicts a step in a scheme for synthesizing a terpene-alkene heterodimer of the disclosure.

[0011] FIG. 1B depicts a step in a scheme for hydrogenating a product mixture including terpene-alkene heterodimers, terpene homodimers, and alkene homodimers of the disclosure.

[0012] FIG. 2 is a gas chromatography (GC) plot of the product mixture from the synthesis of a  $\beta$ -pinene/1-hexene heterodimer using a BF<sub>3</sub> catalyst.

[0013] FIG. 3 is a GC plot of the product mixture from the synthesis of a limonene/2,4,4-trimethylpent-1-ene (TMP) heterodimer using a Montmorillonite catalyst.

[0014] FIG. 4 is a GC plot of the product mixture from the synthesis of a  $\beta$ -pinene/TMP heterodimer using a Montmorillonite catalyst.

[0015] FIG. 5 is a GC plot of the hydrogenation product mixture from the hydrogenation of the product mixture of FIG. 3.

[0016] FIG. 6 is two GC plots of two fractions of the distillation of the hydrogenation product mixture of FIG. 5.

#### DETAILED DESCRIPTION

[0017] This disclosure describes catalyst-assisted heterodimerization of terpenes with non-cyclic (e.g., linear or branched) alkenes, as well as the hydrogenation of the resulting heterodimers. The heterodimerization can be carried out under mild reaction conditions in the presence of a dimerization catalyst. The disclosure describes a high yielding conversion of the terpenes and linear or branched alkenes into homo- and heterodimers.

[0018] Provided herein are methods of synthesizing a terpene-alkene heterodimer, wherein the methods include contacting a terpene with a linear or branched alkene in the presence of a dimerization catalyst to yield a product mixture comprising the terpene-alkene heterodimer. The method of the disclosure can further include hydrogenating the product mixture to yield a hydrogenated product mixture including a hydrogenated terpene-alkene heterodimer. The methods of the disclosure can further include separating the hydrogenated terpene-alkene heterodimer. For example, FIG. 1A and FIG. 1B depict steps in a scheme for synthesizing a terpene-alkene heterodimer and a hydrogenated terpene-alkene heterodimer. As used herein, the term “terpene-alkene heterodimer” refers to a compound resulting from a carbon-carbon bond forming between a terpene and a linear or branched alkene. As used herein, the term “terpene homodimer” refers to a compound resulting from a carbon-carbon bond forming between two terpene molecules. As used herein, the term “linear or branched alkene homodimer” (e.g., alkene homodimer) refers to a compound resulting from a carbon-carbon bond forming between two linear or branched alkene molecules.

[0019] This disclosure describes an approach of chemically blending (e.g., reacting) terpenes with linear or branched alkenes to form terpene-alkene heterodimers and after hydrogenation, forming hydrogenated terpene-alkene heterodimers. The hydrogenated terpene-alkene heterodimers, such as those shown in FIG. 1B, can include one or more properties of the group of high density (e.g., at least about 0.85 g/cm<sup>3</sup> or other density values described herein), high volumetric net heat of combustion (e.g., at least about 135,000

Btu/gallon or other volumetric net heat of combustion values described herein), and low viscosity (e.g., less than about 20 mPa•s at 40°C or other viscosity values described herein).

[0020] The method of synthesizing a terpene-alkene heterodimer can include contacting a terpene with a linear or branched alkene in the presence of a dimerization catalyst to yield a product mixture comprising the terpene-alkene heterodimer. The terpene can include any monoterpene or derivative thereof (e.g., a monocyclic monoterpene or a bicyclic monoterpene). As used herein, the term “monoterpene” refers to a cyclic compound composed of two isoprene units. In some embodiments, the terpene can include one or more of limonene, pinene, camphene, thujene, and sabinene. In some embodiments, the terpene can include limonene or pinene (e.g.,  $\beta$ -pinene). The terpenes may be present in any stereoisomeric form or present as a mixture of stereoisomeric forms. For example, if the terpene is pinene, the pinene can be present as  $\alpha$ -pinene,  $\beta$ -pinene, or a mixture of  $\alpha$ -pinene and  $\beta$ -pinene.

[0021] The linear or branched alkene can include a C<sub>3</sub>-C<sub>20</sub> alkene. The term “C<sub>3</sub>-C<sub>20</sub> alkene” as used herein, refers to an unsaturated, branched- or straight-chain alkene containing from 3 to 20 carbon atoms, such as, but not limited to, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 2-ethyl-1-hexene, and 4-methylpent-1-ene. In some embodiments, the linear or branched alkene included one or more of 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-pent-1-ene, and 2,4,4-trimethylpent-2-ene. In some embodiments, the linear or branched alkene is 1-hexene or 2,4,4-trimethylpent-2-ene.

[0022] The terpene and branched linear alkene can be present in a molar ratio in a range of about 0.8:1 to about 1:20, respectively. For example, the terpene and linear or branched alkene are present in a molar ratio in a range of about 1:1 to about 1:10, about 1:1 to about 1:7.5, about 1:1 to about 1:5, or about 1:1 to about 1:3, respectively.

[0023] The dimerization catalyst can include a homogenous catalyst or a heterogeneous catalyst. In some embodiments, the dimerization catalyst (e.g., homogenous catalyst) includes one or more of aluminum, antimony, boron, silicon, tin, titanium, zirconium, iron, copper or zinc. In some embodiments, the dimerization catalyst includes TiCl<sub>4</sub>, BF<sub>3</sub>, FeCl<sub>3</sub>, ZnCl<sub>2</sub>, SbF<sub>5</sub>, SnCl<sub>4</sub>, or AlCl<sub>3</sub>, or a Lewis acid-base adduct thereof. In some embodiments, the dimerization catalyst is BF<sub>3</sub>. In some embodiments, the dimerization catalyst can be a Lewis acid-base adduct (e.g., BF<sub>3</sub> can be complexed with diethyl ether (Et<sub>2</sub>O) to form BF<sub>3</sub>-(OEt<sub>2</sub>), a Lewis-base adduct). The dimerization catalyst can be a Brønsted acid catalyst. In some embodiments, the dimerization catalyst is a heterogeneous catalyst. In some embodiments,

the dimerization catalyst is a polymer supported catalyst (e.g., Nafion<sup>TM</sup>, a perfluorosulfonic acid-based polymer; or AmberLyst<sup>TM</sup>, a sulfonic acid-containing, polystyrene-based ion exchange resin). In some embodiments, the dimerization catalyst comprises Nafion<sup>TM</sup> NR-50, Amberlyst<sup>TM</sup>-15, or a zeolite. In some embodiments, the dimerization catalyst is a natural mineral. In some embodiments, the dimerization catalyst can be a natural mineral belonging to the smectite group (e.g., saponite, nontronite, beidellite, montmorillonite, or hectorite). The dimerization catalyst can include montmorillonite (e.g., Montmorillonite K10). In some embodiments, the dimerization catalyst is montmorillonite.

[0024] The dimerization catalyst can be present in an amount in a range of about 0.001 mol% to about 50 mol%. For example, the dimerization catalyst can be present in an amount in a range of about 0.01 mol% to about 25 mol%, or about 0.1 mol% to about 20 mol%, or about 1 mol% to about 15 mol%, based on the total amount of mols of the terpene. In some embodiments, the dimerization catalyst is present in an amount in a range of about 0.1 mol% to about 5 mol%. In some embodiments, the dimerization catalyst is present in an amount in a range of about 5 mol% to about 15 mol%.

[0025] In some embodiments, contacting a terpene with a linear or branched alkene in the presence of a dimerization catalyst can further include a solvent. The solvent can include any suitable aprotic or protic organic solvent, such as, acetone, acetonitrile, diethylether, pentanes, hexanes, toluene, xylenes, dichloromethane, ethyl acetate, tetrahydrofuran, methanol, ethanol, propanol, butanol, or the like.

[0026] The step of contacting of a terpene with a linear or branched alkene in the presence of a dimerization catalyst can occur under an inert atmosphere (e.g., N<sub>2</sub> or Ar). In some embodiments, the contacting can occur under an N<sub>2</sub> atmosphere.

[0027] The step of contacting of a terpene with a linear or branched alkene in the presence of a dimerization catalyst can occur at a temperature in a range of about 0°C to about 200°C. For example, the temperature can be in a range of about 15°C to about 150°C, or about 22°C to about 115°C, or about 25°C to about 100°C, or about 35°C to about 100°C, or 15°C to about 60°C, or about 15°C to about 45°C, or about 60°C to about 120°C, or about 75°C to about 110°C. In some embodiments, the temperature is in a range of about 15°C to about 45°C. In some embodiments, the temperature is in a range of about 75°C to about 110°C.

[0028] The step of contacting of a terpene with a linear or branched alkene in the presence of a dimerization catalyst can occur for about 10 minutes to about 2 days. For example, contacting of a terpene with a linear or branched alkene in the presence of a

dimerization catalyst can occur for about 30 minutes to about 12 hours, or about 30 minutes to about 8 hours, or about 30 minutes to about 4 hours, or about 30 minutes to about 2 hours. In some embodiments, the contacting can occur for about 30 minutes to about 2 hours.

[0029] The product mixture of the disclosure can further include terpene homodimers, linear or branched alkene homodimers, or both terpene homodimers and linear or branched alkene homodimers.

[0030] The methods of the disclosure further include hydrogenating the product mixture to yield a hydrogenated product mixture comprising a hydrogenate terpene-alkene heterodimer. The step of hydrogenating can include contacting the product mixture with H<sub>2</sub> in the presence of a hydrogenation catalyst.

[0031] The hydrogenation catalyst can include a heterogeneous hydrogenation catalyst or a homogeneous hydrogenation catalyst. In some embodiments, the hydrogenation catalyst can include a metal, a metal oxide, or both. The hydrogenation catalyst can be one or more of NiO, Ni, Pd/C, Ru, Ru/C, Ru<sub>2</sub>O<sub>3</sub>, Ru/alumina, PdO, Pd, Pt, Ir, or PtO<sub>2</sub>. In some embodiments, the catalyst is PtO<sub>2</sub>. In some embodiments, the hydrogenation catalyst includes Ni (e.g., a NiSat® catalyst). In some embodiments, the catalyst can be any suitable single-site hydrogenation catalyst to one of ordinary skill in the art, for example, chloridotris(triphenylphosphine)rhodium(I) or (cycloocta-1,5-diene)(pyridine) (tricyclohexylphosphane)iridium(I) hexafluoridophosphate. As used herein, the term “single-site hydrogenation catalyst” refers to a hydrogenation catalyst including a metal atom, ion, or small cluster of atoms (e.g., about 2 to about 10 atoms), held by surface ligands to a rigid framework.

[0032] The hydrogenation catalyst can be provided in any suitable amount to an ordinary skilled artisan (e.g., about 0.0001 wt% to about 50 wt%). For example, the hydrogenation catalyst is present in an amount in a range of about 0.01 wt% to about 25 wt%, or about 0.1 wt% to about 20 wt%, or about 0.1 wt% to about 15 wt%, or about 1 wt% to about 10 wt%, or about 1 wt% to about 5 wt%, based on the total weight of the product mixture. In some embodiments, the hydrogenation catalyst is present in an amount in a range of about 1 wt% to about 5 wt%.

[0033] The step of hydrogenating can occur at a temperature in a range of about 25°C to about 500°C. For example, the temperature can be in a range of about 50°C to about 400°C, or about 100°C to about 350°C, or about 150°C to about 300°C, or about 200°C to about 260°C. In some embodiments, the temperature is in a range of about 150°C to about 300°C. In some embodiments, the temperature is in a range of about 200°C to about 260°C.

[0034] The step of hydrogenating can include H<sub>2</sub> as a gas, and the H<sub>2</sub> can be provided at a pressure of at least 25 psi. For example, the H<sub>2</sub> can be provided at a pressure of about 50 psi to about 1000 psi, or about 100 psi to about 750 psi, or about 250 psi to about 750 psi, or about 500 psi to about 750 psi. In some embodiments, the H<sub>2</sub> is provided at a pressure of about 600 psi to about 700 psi.

[0035] The step of hydrogenating can occur for about 10 minutes to about 1 day. For example, the step of hydrogenating can occur for about 30 minutes to about 12 hours, or about 1 hour to about 6 hours, about 1 hour to about 4 hours, or about 1 hour to about 3 hours.

[0036] The hydrogenated product mixture can include one or more of terpene monomers, linear or branched alkene monomers, terpene homodimers, linear or branched alkene homodimers, and the hydrogenated terpene-alkene heterodimer.

[0037] The methods of the disclosure can further include separating the hydrogenated terpene-alkene heterodimer from the hydrogenated product mixture. In some embodiments, the hydrogenated product mixture includes the hydrogenated terpene-alkene heterodimer in an amount of at least 20 wt%, at least 25 wt%, at least 30 wt%, at least 35 wt%, or at least 40 wt%.

[0038] Separating the hydrogenated terpene-alkene heterodimer from the hydrogenated product mixture can include any suitable separation process or their combination to one of ordinary skill in the art, e.g., filtration, distillation, crystallization, chromatography, or the like. In some embodiments, separating the hydrogenated terpene-alkene heterodimer from the hydrogenated product mixture includes distilling the hydrogenated product mixture.

[0039] Distilling the hydrogenated product mixture can occur at a temperature in a range of about 50°C to about 200°C, or about 75°C to about 175°C, or about 100°C to about 150°C, or about 110°C to about 130°C. In some embodiments, distilling the hydrogenated product mixture can occur at a temperature of about 115°C to about 130°C (e.g., about 120°C to about 130°C). In some embodiments, distilling the hydrogenated product mixture occurs under reduced pressure. In some embodiments, distilling the hydrogenated product mixture can occur at a pressure in a range of about 0.1 mTorr to about 760 Torr (e.g., about 1 mTorr to about 500 Torr, or about 0.1 Torr to about 250 Torr, or about 1 Torr to about 25 Torr).

[0040] The methods of the disclosure demonstrate a high yielding and highly selective synthesis of terpene-alkene heterodimers. In some embodiments, methods of the disclosure demonstrate a high yielding and highly selective synthesis of hydrogenated terpene-alkene heterodimers and hydrogenated homodimers. In some embodiments, the methods including

contacting, hydrogenation, and separation steps of the disclosure provide an overall conversion of terpenes into hydrogenated homodimers and hydrogenated terpene-alkene heterodimers of at least about 40%, or at least about 50%, or at least about 60% or more; or from about 40% to 99% (e.g., from about 40% to 95%, 40% to 90%, 40% to 80%, 40% to 70%, 50% to 99%, 50% to 95%, 50% to 90%, 50% to 80%, 50% to 70%, 60% to 99%, 60% to 95%, 60% to 90%, 60% to 80%, or 60% to 70%). In some embodiments, the methods including contacting, hydrogenation, and separation steps of the disclosure provide a synthesis of a hydrogenated terpene-alkene heterodimer having a terpene-alkene heterodimer selectivity of at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%; or from about 55% to 99% (e.g., from about 55% to 95%, 55% to 90%, 55% to 80%, 60% to 99%, 60% to 95%, 60% to 90%, 60% to 80%, 65% to 99%, 65% to 95%, 65% to 90%, 65% to 80%, 70% to 99%, 70% to 95%, 70% to 90%, or 70% to 80%).

[0041] The overall conversion of terpenes into homo- and heterodimers over 3 steps (dimerization, hydrogenated, separation) demonstrated at the lab scale is about 62% with the selectivity of the heterodimer formation of about 75%.

[0042] Also provided herein is a fuel component including a hydrogenated terpene-alkene heterodimer of the disclosure.

[0043] Also provided herein is a fuel including a hydrogenated terpene-alkene heterodimer of the disclosure and a C<sub>5</sub>-C<sub>20</sub> alkyl. The term "C<sub>5</sub>-C<sub>20</sub> alkyl" as used herein, refers to a saturated, cyclic, branched- or straight-chain alkyl group containing from 5 to 20 carbon atoms, such as, but not limited to, *n*-pentyl, isopentyl, neopentyl, cyclopentyl, *n*-hexyl, heptyl, octyl, decyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, cycloheptyl, methylcyclohexyl, methylcyclopentyl, and the like.

## EXAMPLES

### Example 1: Heterodimerization of $\beta$ -pinene and 1-hexene in the presence of BF<sub>3</sub>.

[0044] The catalyst, BF<sub>3</sub>, was used as a complex with Et<sub>2</sub>O (48 wt% BF<sub>3</sub>, Sigma-Aldrich®).  $\beta$ -Pinene (Sigma-Aldrich®) and 1-hexene were dried over activated AZ300 (UOP Adsorbent AZ-300, A Honeywell Company), purged with N<sub>2</sub> gas, and stored above molecular sieves (3 Å) for about 12 hours. The reaction was done in the N<sub>2</sub>-purged glove box. 1-Hexene (61 g, 0.734 mol) and BF<sub>3</sub>/Et<sub>2</sub>O (22 mmol BF<sub>3</sub>, 2.80 mL) were combined together in a 0.5 L flask. The catalyst was activated by adding 1 mL of BF<sub>3</sub>/BuOH (1.3 M, Sigma-Aldrich®) solution, and then dropwise addition of  $\beta$ -pinene (100 g, 0.734 mol) was initiated

at ambient temperature. After 1 hour, all the  $\beta$ -pinene was added. The residual  $\text{BF}_3$  was reacted with aqueous NaOH solution (10 wt%, 200 mL), the resulting organic phase was separated, washed subsequently with water (100 mL) and brine (100 mL), and dried above anhydrous  $\text{MgSO}_4$ . The filtration of the resulting organic liquid through alumina/silica plug gave 87 g of a product mixture. Gas chromatography (GC) analysis of the product mixture showed the product mixture included about 11 wt% of terpene-alkene heterodimers, 70 wt% of terpene homodimers, and 19 wt% of pinene and its isomerized forms (FIG. 2).

[0045] Characterization of reaction mixture by GC-MS: To obtain a qualitative measurement by relative peak area % of the contents of the reaction mixture the method as described in Table 1 was used.

Table 1

|                             |                                                       |
|-----------------------------|-------------------------------------------------------|
| <b>Instrument</b>           | Agilent 7890 GC with 5977B Inert Plus MSD Turbo EI/CI |
| <b>Inlet Temperature</b>    | 280°C                                                 |
| <b>Detector Temperature</b> | 280°C                                                 |
| <b>Sample Temp. Program</b> | Initial 50°C, hold for 2 min                          |
|                             | Ramp @15°C/min to 250°C, hold for 5 min               |
| <b>Column Flow</b>          | 2 mL/min                                              |
| <b>Split</b>                | Split mode; 200:1                                     |
| <b>Injector</b>             | Autosampler (0.1 $\mu\text{L}$ )                      |
| <b>Column Composition</b>   | Agilent 19091S-433 HP-5Ms                             |
| <b>Detection Method</b>     | MSD                                                   |
| <b>Timed Event</b>          | MSD shut off 1.25-1.45 min                            |

[0046] Samples were prepared by diluting 50  $\mu\text{L}$  of nonane into 500  $\mu\text{L}$  of reaction sample and 500  $\mu\text{L}$  of isohexane. Mixtures of homodimers and heterodimers were observed. Peaks of the products were identified by mass, and then the amount of unreacted and isomerized monomers, homodimers and heterodimers were determined by the area in relation to the total area of all the peaks to get a qualitative wt% of the sample, calculated using the following formula:

$$\text{peak area \%} = \frac{\text{area of component}}{\text{Sum of all Areas} - \text{Nonane Area}} \times 100$$

In examples where nonane (C9) was not added to the sample, the following formula was used:

$$\text{peak area \%} = \frac{\text{area of component}}{\text{Sum of all Areas}} \times 100$$

Example 2. Heterodimerization of  $\beta$ -pinene and 2,4,4-trimethylpent-1-ene in the presence of Montmorillonite.

[0047] A mixture of  $\beta$ -pinene (2.12 g, 15.6 mmol) and 2,4,4-trimethylpent-1-ene (4.37 g, 38.9 mmol) was added dropwise over 10 minutes to a slurry of Montmorillonite (MMT-K10, 0.75 g) in heptane (6.5 mL) at 100 °C in a 25 mL flask. After stirring for 2.5 h at 100°C, the mixture was filtered through a short silica plug. The low boiling point components in the resulting mixture were removed by distillation at 105°C and ambient pressure to provide a product mixture. GC analysis of the product mixture showed the product mixture included terpene monomers (5 wt%), TMP homodimers (35 wt%), TMP-terpene heterodimers (37 wt%), terpene homodimers (14 wt%), and terpene-TMP trimers (10 wt%) (FIG. 4). The method of GC analysis performed was the same as in Example 1.

Example 3. Dimerization of limonene and 2,4,4-trimethylpent-1-ene in the presence of Montmorillonite.

[0048] 2,4,4-trimethylpent-1-ene (TMP) and limonene were purged with nitrogen and stored above molecular sieves (3 Å) for about 12 h. The Montmorillonite (MMT-K10) was dried *in vacuo* for 24 hours. Limonene was purchased from Sigma-Aldrich® and passed through a column with activated basic alumina. The reaction was done in an N<sub>2</sub>-purged glove box. A slurry of MMT-K10 (5 g) in heptane (20 mL) was added to the mixture of TMP (135 g, 187 mL, 1.2 mol) and limonene (65.5 g, 77.6 mL, 0.481 mol) at 85°C in a 0.5 L flask and stirred for 90 minutes at 85°C. The reaction mixture was then filtered through activated basic alumina to give around 200 g of a liquid product mixture. Heptane and TMP were partially distilled off from this mixture at 120°C and ambient pressure leaving 124 g of the final product mixture. GC analysis of the product mixture showed the product mixture included 5 wt% heptane, 30 wt% of TMP (including isomers), 10 wt% terpenes, 7 wt% of TMP homodimers, 32 wt% terpene-alkene heterodimers, and 16 wt% of terpenes homodimers, along with a trace amount of trimers (FIG. 3). The method of GC analysis performed was the same as in Example 1.

Example 4. Hydrogenation of terpene-TMP heterodimers.

[0049] The product mixture generated in Example 3 (124 g) was added to a 0.5 L Parr reactor containing commercial NiSat hydrogenation catalyst (2.5 g, 2 wt%). The reactor was sealed, purged with N<sub>2</sub>, and then heated to 232°C before being pressured by hydrogen gas (650 psi). The reaction mixture was then agitated (400 rpm) for 2.5 h. The reactor was cooled to ambient temperature, depressurized, and opened. The catalyst was removed from the reaction mixture by filtration through the celite plug under anaerobic conditions to give a fully saturated liquid, a hydrogenated product mixture, according to <sup>1</sup>H NMR spectroscopy (>99% saturation). GC analysis of the product mixture showed the following composition of fully hydrogenated compounds: TMP (15 wt%), terpenes (11 wt%), TMP homodimers (12 wt%), heterodimer (40 wt%), and terpene homodimers (21 wt%) in addition to trace amounts of heptane and oligomers (FIG. 5). The method of GC analysis performed was the same as in Example 1.

Example 5. Distillation of terpene-TMP heterodimers.

[0050] The hydrogenated product mixture obtained in Example 4 was distilled at reduced pressure with the collection of following high boiling point (bp) fractions after removal low bp components: 1) Fraction 1 collected at 123°C (7 Torr), 22.0 g; and 2) Fraction 2 collected at 124-128°C (4 Torr), 57.0 g. GC analysis for both fractions are summarized in Table 2 below (FIG. 6). The overall conversion of limonene into hydrogenated and distilled terpene-derived homo- and heterodimers over three steps (Examples 3-5) is 62% ( $100 \times (2 \times m_{\text{terpene-homodimers}} + m_{\text{terpene-heterodimers}}) / m_{\text{limonene}}$ ) with the selectivity of forming heterodimers at 75% ( $100 \times (m_{\text{terpene-heterodimers}} / (2 \times m_{\text{terpene-homodimers}} + m_{\text{terpene-heterodimers}}))$ ).

Table 2. GC composition for high boiling point fractions 1 and 2 (wt%).

|            | Hydro-terpenes<br>(hydro-limonenes)<br>wt% | Hydro-TMP<br>homodimer<br>wt% | Hydro-<br>heterodimers wt% | Hydro-terpene<br>homodimers<br>wt% |
|------------|--------------------------------------------|-------------------------------|----------------------------|------------------------------------|
| Fraction 1 | 16                                         | 33                            | 48                         | 3                                  |
| Fraction 2 | 0                                          | 5                             | 78                         | 17                                 |

[0051] Various embodiments of the features of this disclosure are described herein. However, it should be understood that such embodiments are provided merely by way of example, and numerous variations, changes, and substitutions can occur to those skilled in the

art without departing from the scope of this disclosure. It should also be understood that various alternatives to the specific embodiments described herein are also within the scope of this disclosure.

[0052] Embodiment 1 is a method of method for synthesizing a terpene-alkene heterodimer, the method comprising:

contacting a terpene with a linear or branched alkene in the presence of a dimerization catalyst to yield a product mixture comprising the terpene-alkene heterodimer.

[0053] Embodiment 2 is the method of embodiment 1, wherein the dimerization catalyst is a natural mineral or a polymer supported catalyst.

[0054] Embodiment 3 is the method of embodiment 1 or 2, wherein the dimerization catalyst comprises saponite, nontronite, beidellite, montmorillonite, or hectorite.

[0055] Embodiment 4 is the method of any one of embodiments 1-3, wherein the dimerization catalyst comprises one or more of aluminum, antimony, boron, silicon, tin, titanium, zirconium, iron, copper, and zinc.

[0056] Embodiment 5 is the method of embodiment 1 or 4, wherein the dimerization catalyst is  $\text{TiCl}_4$ ,  $\text{BF}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{SbF}_5$ ,  $\text{SnCl}_4$ , or  $\text{AlCl}_3$ , or a Lewis acid-base adduct thereof.

[0057] Embodiment 6 is the method of embodiment 5, wherein the dimerization catalyst is  $\text{BF}_3$ .

[0058] Embodiment 7 is the method of any one of embodiments 1-6, wherein the dimerization catalyst is present in an amount in a range of about 0.01 mol% to about 25 mol%, or about 0.1 mol% to about 20 mol%, or about 1 mol% to about 15 mol%, based on the total amount of mols of the terpene.

[0059] Embodiment 8 is the method of any one of embodiments 1-7, wherein the terpene comprises one or more of limonene, pinene, camphene, thujene, and sabinene.

[0060] Embodiment 9 is the method of any one of embodiments 1-8, wherein the terpene comprises limonene or pinene.

[0061] Embodiment 10 the method of any one of embodiments 1-9, wherein the linear or branched alkene is a  $\text{C}_3$ - $\text{C}_{20}$  alkene.

[0062] Embodiment 11 is the method of any one of embodiments 1-10, wherein the linear or branched alkene comprises one or more of 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-pent-1-ene, and 2,4,4-trimethylpent-2-ene.

- [0063] Embodiment 12 is the method of any one of embodiments 1-11, wherein the terpene and the linear or branched alkene are present in a molar ratio in a range of about 1:1 to about 1:10, or about 1:1 to about 1:5, or about 1:1 to about 1:3, respectively.
- [0064] Embodiment 13 is the method of any one of embodiments 1-12, wherein the product mixture further comprises terpene homodimers, linear or branched alkene homodimers, or both.
- [0065] Embodiment 14 is the method of any one of embodiments 1-13, wherein the contacting occurs at a temperature of about 10°C to about 200°C, or about 15°C to about 150°C, or about 25°C to about 100°C, or about 35°C to about 100°C.
- [0066] Embodiment 15 is the method of any one of embodiments 1-14, further comprising hydrogenating the product mixture to yield a hydrogenated product mixture comprising a hydrogenated terpene-alkene heterodimer.
- [0067] Embodiment 16 is the method of embodiment 15, wherein the hydrogenating comprises contacting the product mixture with H<sub>2</sub> in the presence of a hydrogenation catalyst.
- [0068] Embodiment 17 is the method of embodiment 16, wherein the hydrogenation catalyst is a heterogeneous catalyst.
- [0069] Embodiment 18 is the method of embodiment 16, wherein the hydrogenation catalyst is a homogenous catalyst.
- [0070] Embodiment 19 is the method of embodiment 16, wherein the hydrogenation catalyst comprises a metal, a metal oxide, or both.
- [0071] Embodiment 20 the method of embodiment 19, wherein the hydrogenation catalyst comprises NiO, Ni, Pd/C, Ru, Ru/C, Ru<sub>2</sub>O<sub>3</sub>, Ru/alumina, PdO, Pd, Pt, Ir, or PtO<sub>2</sub>.
- [0072] Embodiment 21 is the method of any one of embodiments 16-20, wherein the hydrogenation catalyst is present in an amount in a range of about 0.01 wt% to about 25 wt%, or about 0.1 wt% to about 20 wt%, or about 1 wt% to about 10 wt%, based on the total weight of the product mixture.
- [0073] Embodiment 22 is the method of any one of embodiments 16-21, wherein the hydrogenating occurs at a temperature of about 50°C to about 400°C, or about 100°C to about 350°C, or about 150°C to about 300°C, or about 200°C to about 260°C.
- [0074] Embodiment 23 is the method of any one of embodiments 16-22, further comprising separating the hydrogenated terpene-alkene heterodimer from the hydrogenated product mixture.

- [0075] Embodiment 24 is the method of embodiment 23, wherein the separating comprises distilling the hydrogenated product mixture to separate the hydrogenated terpene-alkene heterodimer from the hydrogenated product mixture.
- [0076] Embodiment 25 is the method of embodiment 23 or 24, wherein the overall conversion of terpenes into homodimers and heterodimers is at least about 50%.
- [0077] Embodiment 26 is the method of any one of claims 23-25, wherein the overall conversion of terpenes into homodimers and heterodimers is at least about 60%.
- [0078] Embodiment 27 is the method of any one of embodiments 23-26, wherein the selectivity of the hydrogenated terpene-alkene heterodimer formation is at least about 60%.
- [0079] Embodiment 28 is the method of any one of embodiments 23-27, wherein the selectivity of the hydrogenated terpene-alkene heterodimer formation is at least about 70%.
- [0080] Embodiment 29 is a fuel component comprising a hydrogenated terpene-alkene heterodimer.
- [0081] Embodiment 30 is a fuel comprising a hydrogenated terpene-alkene heterodimer and a C<sub>5</sub>-C<sub>20</sub> alkyl.
- [0082] Although this disclosure contains many specific embodiment details, these should not be construed as limitations on the scope of the subject matter or on the scope of what may be claimed, but rather as descriptions of features that may be specific to particular embodiments. Certain features that are described in this disclosure in the context of separate embodiments can also be implemented, in combination, in a single embodiment. Conversely, various features that are described in the context of a single embodiment can also be implemented in multiple embodiments, separately, or in any suitable sub-combination. Moreover, although previously described features may be described as acting in certain combinations and even initially claimed as such, one or more features from a claimed combination can, in some cases, be excised from the combination, and the claimed combination may be directed to a sub-combination or variation of a sub-combination.
- [0083] Particular embodiments of the subject matter have been described. Other embodiments, alterations, and permutations of the described embodiments are within the scope of the following claims as will be apparent to those skilled in the art. While operations are depicted in the drawings or claims in a particular order, this should not be understood as requiring that such operations be performed in the particular order shown or in sequential

order, or that all illustrated operations be performed (some operations may be considered optional), to achieve desirable results.

[0084] Accordingly, the previously described example embodiments do not define or constrain this disclosure. Other changes, substitutions, and alterations are also possible without departing from the spirit and scope of this disclosure.

## WHAT IS CLAIMED IS:

1. A method for synthesizing a terpene-alkene heterodimer, the method comprising:  
contacting a terpene with a linear or branched alkene in the presence of a dimerization catalyst to yield a product mixture comprising the terpene-alkene heterodimer.
2. The method of claim 1, wherein the dimerization catalyst is a natural mineral or a polymer supported catalyst.
3. The method of claim 1 or 2, wherein the dimerization catalyst comprises saponite, nontronite, beidellite, montmorillonite, or hectorite.
4. The method of any one of claims 1-3, wherein the dimerization catalyst comprises one or more of aluminum, antimony, boron, silicon, tin, titanium, zirconium, iron, copper, and zinc.
5. The method of claim 1 or 4, wherein the dimerization catalyst is  $\text{TiCl}_4$ ,  $\text{BF}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{SbF}_5$ ,  $\text{SnCl}_4$ , or  $\text{AlCl}_3$ , or a Lewis acid-base adduct thereof.
6. The method of claim 5, wherein the dimerization catalyst is  $\text{BF}_3$ .
7. The method of any one of claims 1-6, wherein the dimerization catalyst is present in an amount in a range of about 0.01 mol% to about 25 mol%, or about 0.1 mol% to about 20 mol%, or about 1 mol% to about 15 mol%, based on the total amount of mols of the terpene.
8. The method of any one of claims 1-7, wherein the terpene comprises one or more of limonene, pinene, camphene, thujene, and sabinene.
9. The method of any one of claims 1-8, wherein the terpene comprises limonene or pinene.
10. The method of any one of claims 1-9, wherein the linear or branched alkene is a  $\text{C}_3$ - $\text{C}_{20}$  alkene.
11. The method of any one of claims 1-10, wherein the linear or branched alkene comprises one or more of 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-pent-1-ene, and 2,4,4-trimethylpent-2-ene.
12. The method of any one of claims 1-11, wherein the terpene and the linear or branched alkene are present in a molar ratio in a range of about 1:1 to about 1:10, or about 1:1 to about 1:5, or about 1:1 to about 1:3, respectively.
13. The method of any one of claims 1-12, wherein the product mixture further comprises terpene homodimers, linear or branched alkene homodimers, or both.

14. The method of any one of claims 1-13, wherein the contacting occurs at a temperature of about 10°C to about 200°C, or about 15°C to about 150°C, or about 25°C to about 100°C, or about 35°C to about 100°C.
15. The method of any one of claims 1-14, further comprising hydrogenating the product mixture to yield a hydrogenated product mixture comprising a hydrogenated terpene-alkene heterodimer.
16. The method of claim 15, wherein the hydrogenating comprises contacting the product mixture with H<sub>2</sub> in the presence of a hydrogenation catalyst.
17. The method of claim 16, wherein the hydrogenation catalyst is a heterogeneous catalyst.
18. The method of claim 16, wherein the hydrogenation catalyst is a homogenous catalyst.
19. The method of claim 16, wherein the hydrogenation catalyst comprises a metal, a metal oxide, or both.
20. The method of claim 19, wherein the hydrogenation catalyst comprises NiO, Ni, Pd/C, Ru, Ru/C, Ru<sub>2</sub>O<sub>3</sub>, Ru/alumina, PdO, Pd, Pt, Ir, or PtO<sub>2</sub>.
21. The method of any one of claims 16-20, wherein the hydrogenation catalyst is present in an amount in a range of about 0.01 wt% to about 25 wt%, or about 0.1 wt% to about 20 wt%, or about 1 wt% to about 10 wt%, based on the total weight of the product mixture.
22. The method of any one of claims 16-21, wherein the hydrogenating occurs at a temperature of about 50°C to about 400°C, or about 100°C to about 350°C, or about 150°C to about 300°C, or about 200°C to about 260°C.
23. The method of any one of claims 16-22, further comprising separating the hydrogenated terpene-alkene heterodimer from the hydrogenated product mixture.
24. The method of claim 23, wherein the separating comprises distilling the hydrogenated product mixture to separate the hydrogenated terpene-alkene heterodimer from the hydrogenated product mixture.
25. The method of claim 23 or 24, wherein the overall conversion of terpenes into homodimers and heterodimers is at least about 50%.
26. The method of any one of claims 23-25, wherein the overall conversion of terpenes into homodimers and heterodimers is at least about 60%.
27. The method of any one of claims 23-26, wherein the selectivity of the hydrogenated terpene-alkene heterodimer formation is at least about 60%.

28. The method of any one of claims 23-27, wherein the selectivity of the hydrogenated terpene-alkene heterodimer formation is at least about 70%.
29. A fuel component comprising a hydrogenated terpene-alkene heterodimer.
30. A fuel comprising a hydrogenated terpene-alkene heterodimer and a C<sub>5</sub>-C<sub>20</sub> alkyl.