Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.


*Supporting Information*

# Low-Temperature Thermal Oxidation of Biomass Jet Fuel Pinane

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**Table S1.** Physicochemical properties of pinane and typical hydrocarbon fuels

| Properties | | pinane | JP-10 [a] | RP-3 [b] |
|---|---|---|---|---|
| Molecular formula | | $C_{10}H_{18}$ | $C_{10}H_{16}$ | - |
| Molecular weight | | 138 | 136 | - |
| Appearance | | clear colorless liquid | clear colorless liquid | clear colorless liquid |
| Color / Saybolt number | | >+30 | +25 | +25 |
| Index of refraction at 298 K | | 1.4605 [c] | - | - |
| Dissolved oxygen at 298 K / ppm | | 7.5 | 10 [f] | - |
| Solubility in water at 298 K / $mg \cdot L^{-1}$ | | 6.01 [c] | - | - |
| Density / $g \cdot cm^{-3}$ | at 293 K | 0.8576 | 0.9359 [f] | 0.775 ~ 0.830 |
| | at 333 K | 0.8261 | 0.9045 [f] | - |
| Viscosity / mPa·s | at 298 K | 2.02 | 2.99 [f] | 0.97 ~ 1.04 |
| | at 333 K | 1.13 | 1.52 [f] | - |
| Kinematic viscosity / $mm^2 \cdot s^{-1}$ | at 253K | 7.15 | 10 (255 K) | 8.0 |
| | at 233K | 14.48 | 40 (219 K) | - |
| Heat conductivity coefficient at 295K / $W \cdot m^{-1} \cdot K^{-1}$ | | 0.1429 | 0.1483 | - |
| Boiling point / K | | 440 [d] | 458 | <478 ~ <573 |
| Vapor Pressure at 298K / mm Hg | | 2.19 [c] | - | - |
| Melting point / K | | 220 | 194 [f] | 226 |
| Flash point / K | | 314 | 327 | 311 |
| Autoignition temperature / K | | 546 [e] | - | - |
| Ignition delay time / s | at 848 K | 1.53 | 2.20 | - |
| | at 873 K | 0.33 | 1.07 | - |
| Evaporation rate constant | at 773 K | 0.45 | 0.39 | - |
| | at 789 K | 0.62 | - | - |
| | at 823 K | 0.85 | - | - |
| Enthalpy of combustion / $MJ \cdot kg^{-1}$ | | 41.5 | 42.1 | 42.8 |

[a] Data is obtained from MIL-DTL-87107E.

[b] Data is obtained from GB 6537-2018.

[c] Data is obtained from Hazardous Substances Data Bank.

[d] Data is obtained from NIST Standard Reference Database.

[e] Data is obtained from CAMEO Chemicals.

[f] Data is determined by DSC.

**Table S2-1.** Typical composition of oxidized pinane samples (90 ºC, 1 MPa $O_2$)[a]

| No. | Most Possible Match | RT | Relative Contents (mol%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Reaction time (min) | | | | | | |
| | | | 0 | 15 | 30 | 45 | 60 | 75 | 90 |
| 2 | 1-methyl-4-(prop-1-en-2-yl)cyclohexane | 8.43 | 0.61 | 0.62 | 0.63 | 0.62 | 0.63 | 0.63 | 0.63 |
| 3 | 1-methyl-4-(prop-1-2-ylidene)cyclohexane | 8.51 | 0.26 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 |
| 4 | *cis*-pinane-2-ene | 8.60 | 0.75 | 0.76 | 0.75 | 0.74 | 0.73 | 0.73 | 0.71 |
| 5 | 1-isopropyl-4-lethylcyclohex-1-ene | 8.83 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 |
| 6 | *trans*-pinane | 9.17 | 11.89 | 12.18 | 12.16 | 12.10 | 12.14 | 12.16 | 12.07 |
| 7 | *cis*-pinane | 9.35 | 86.22 | 85.66 | 85.04 | 84.64 | 84.05 | 83.51 | 82.95 |
| 19 | *trans*-pinane-2-ol | 13.98 | | | 0.17 | 0.25 | 0.33 | 0.42 | 0.52 |
| 20 | *cis*-pinane-2-ol | 14.45 | 0.08 | 0.31 | 0.79 | 1.18 | 1.57 | 1.98 | 2.52 |
| 21 | *cis*-pinane-3-one | 14.62 | | | | | 0.08 | 0.10 | 0.13 |

[a] blank indicates the product is not detected.

**Table S2-2.** Typical composition of oxidized pinane samples (100 ºC, 1 MPa $O_2$)

| No. | Most Possible Match | RT | Relative Contents (mol%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Reaction time (min) | | | | | | |
| | | | 0 | 15 | 30 | 45 | 60 | 75 | 90 |
| 2 | 1-methyl-4-(prop-1-en-2-yl)cyclohexane | 8.43 | 0.63 | 0.63 | 0.62 | 0.61 | 0.61 | 0.60 | 0.58 |
| 3 | 1-methyl-4-(prop-1-2-ylidene)cyclohexane | 8.51 | 0.27 | 0.27 | 0.26 | 0.25 | 0.25 | 0.24 | 0.23 |
| 4 | *cis*-pinane-2-ene | 8.60 | 0.76 | 0.75 | 0.73 | 0.68 | 0.66 | 0.61 | 0.57 |
| 5 | 1-isopropyl-4-lethylcyclohex-1-ene | 8.83 | 0.19 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.17 |
| 6 | *trans*-pinane | 9.17 | 12.05 | 12.07 | 11.87 | 11.58 | 11.57 | 11.24 | 11.03 |
| 7 | *cis*-pinane | 9.35 | 86.00 | 84.65 | 82.42 | 81.13 | 78.96 | 77.26 | 74.39 |
| 14 | 3-hydroxy-4,6,6-trimethylbicyclo[3.1.1]heptane-2-one | 11.91 | | | | | 0.13 | 0.17 | 0.26 |
| 15 | 2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one | 12.43 | | | | | 0.07 | 0.10 | 0.14 |
| 19 | *trans*-pinane-2-ol | 13.98 | | 0.25 | 0.63 | 0.90 | 1.26 | 1.62 | 2.17 |
| 20 | *cis*-pinane-2-ol | 14.45 | 0.10 | 1.19 | 3.00 | 4.28 | 5.77 | 7.34 | 9.58 |
| 21 | *cis*-pinane-3-one | 14.62 | | | 0.21 | 0.30 | 0.41 | 0.48 | 0.67 |
| 22 | 6-(hydroxymethyl)-2,6-dimethylbicyclo[3.1.1]heptane-2-ol | 14.93 | | | 0.07 | 0.10 | 0.13 | 0.16 | 0.21 |

**Table S2-3.** Typical composition of oxidized pinane samples (110 ºC, 1 MPa $O_2$)

| No. | Most Possible Match | RT | Relative Contents (mol%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Reaction time (min) | | | | | | |
| | | | 0 | 15 | 30 | 45 | 60 | 75 | 90 |
| 1 | acetone | 4.32 | | | | | | | 0.45 |
| 2 | 1-methyl-4-(prop-1-en-2-yl)cyclohexane | 8.43 | 0.58 | 0.58 | 0.58 | 0.56 | 0.55 | 0.51 | 0.48 |
| 3 | 1-methyl-4-(prop-1-2-ylidene)cyclohexane | 8.51 | 0.25 | 0.25 | 0.24 | 0.23 | 0.22 | 0.19 | 0.17 |
| 4 | *cis*-pinane-2-ene | 8.60 | 0.71 | 0.69 | 0.63 | 0.57 | 0.50 | 0.44 | 0.50 |
| 5 | 1-isopropyl-4-lethylcyclohex-1-ene | 8.83 | 0.17 | 0.17 | 0.17 | 0.16 | 0.15 | 0.16 | 0.16 |
| 6 | *trans*-pinane | 9.17 | 11.42 | 11.26 | 11.00 | 10.71 | 10.19 | 9.44 | 9.01 |
| 7 | *cis*-pinane | 9.35 | 86.66 | 83.79 | 78.70 | 73.86 | 68.94 | 62.78 | 56.96 |
| 8 | 4-isopropyl-1-methylcyclohex-1-ene | 9.95 | | | | | | | 0.14 |
| 10 | 4-isopropyl-1-methylcyclohex-2-ene-1-ol | 10.97 | | | | | | | 0.10 |
| 12 | 4-methyl-3-(prop-1-en-2-yl)cyclohexan-1-one | 11.59 | | | | | | | 0.21 |
| 14 | 3-hydroxy-4,6,6-trimethylbicyclo[3.1.1]heptane-2-one | 11.92 | | | 0.16 | 0.29 | 0.48 | 0.83 | 1.48 |
| 15 | 2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one | 12.43 | | | | 0.13 | 0.21 | 0.33 | 0.50 |
| 16 | 6-isopropyl-3-methylcyclohex-2-en-1-one | 12.57 | | | | | | | 0.07 |
| 17 | 5-methyl-2-(prop-1-en-2-yl)cyclohexan-1-one | 12.92 | | | | 0.08 | 0.14 | 0.24 | 0.41 |
| 19 | *trans*-pinane-2-ol | 13.98 | | 0.53 | 1.39 | 2.27 | 3.17 | 4.35 | 5.30 |
| 20 | *cis*-pinane-2-ol | 14.45 | 0.21 | 2.54 | 6.46 | 10.09 | 13.88 | 18.20 | 21.41 |
| 21 | *cis*-pinane-3-one | 14.62 | | 0.19 | 0.50 | 0.77 | 1.08 | 1.40 | 1.67 |
| 22 | 6-(hydroxymethyl)-2,6-dimethylbicyclo[3.1.1]heptane-2-ol | 14.93 | | | 0.17 | 0.27 | 0.42 | 0.53 | 0.67 |
| 23 | unidentified | 15.84 | | | | | | 0.49 | 0.11 |
| 24 | unidentified | 17.38 | | | | | 0.06 | 0.11 | 0.22 |

**Table S2-4.** Typical composition of oxidized pinane samples (120 ºC, 1 MPa $O_2$)

| No. | Most Possible Match | RT | Relative Contents (mol%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Reaction time (min) | | | | | | |
| | | | 0 | 15 | 30 | 45 | 60 | 75 | 90 |
| 1 | acetone | 4.32 | | | 0.25 | 0.97 | 1.84 | 2.83 | 3.76 |
| 2 | 1-methyl-4-(prop-1-en-2-yl)cyclohexane | 8.43 | 0.61 | 0.57 | 0.56 | 0.56 | 0.57 | 0.59 | 0.61 |
| 3 | 1-methyl-4-(prop-1-2-ylidene)cyclohexane | 8.51 | 0.26 | 0.23 | 0.22 | 0.19 | 0.18 | 0.17 | 0.17 |
| 4 | *cis*-pinane-2-ene | 8.60 | 0.75 | 0.70 | 0.85 | 1.24 | 2.00 | 2.15 | 2.17 |
| 5 | 1-isopropyl-4-lethylcyclohex-1-ene | 8.83 | 0.19 | 0.17 | 0.20 | 0.31 | 0.55 | 0.71 | 0.86 |
| 6 | *trans*-pinane | 9.17 | 11.88 | 10.97 | 10.49 | 9.94 | 9.85 | 9.86 | 10.11 |
| 7 | *cis*-pinane | 9.35 | 85.73 | 78.60 | 67.45 | 59.84 | 55.15 | 53.52 | 54.03 |
| 8 | 4-isopropyl-1-methylcyclohex-1-ene | 9.95 | | | 0.64 | 1.53 | 2.32 | 2.05 | 1.83 |
| 9 | 3-isopropyl-6-methylcyclohex-1-ene | 10.05 | | | | 0.16 | 0.42 | 0.53 | 0.70 |
| 10 | 4-isopropyl-1-methylcyclohex-2-ene-1-ol | 10.97 | | | 0.37 | 2.27 | 6.38 | 7.98 | 8.80 |
| 11 | *trans*-pinane-3-ol | 11.37 | | | | 0.29 | 0.83 | 1.05 | 1.18 |
| 12 | 4-methyl-3-(prop-1-en-2-yl)cyclohexan-1-one | 11.59 | | | 0.15 | 0.60 | 1.22 | 1.47 | 1.34 |
| 13 | 4-methyl-3-(propan-2-ylidene)cyclohexan-1-one | 11.86 | | | 0.12 | 0.57 | 1.36 | 1.59 | 1.58 |
| 14 | 3-hydroxy-4,6,6-trimethylbicyclo[3.1.1]heptane-2-one | 11.92 | | 0.20 | 1.05 | 2.97 | 3.55 | 2.72 | 1.30 |
| 15 | 2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one | 12.43 | | | 0.36 | 0.93 | 1.34 | 1.66 | 1.65 |
| 16 | 6-isopropyl-3-methylcyclohex-2-en-1-one | 12.57 | | | 0.34 | 1.09 | 1.88 | 2.10 | 2.26 |
| 17 | 5-methyl-2-(prop-1-en-2-yl)cyclohexan-1-one | 12.92 | | | 0.24 | 0.62 | 1.02 | 1.29 | 1.46 |
| 18 | unidentified | 13.05 | | | | | | 0.01 | 0.02 |
| 19 | *trans*-pinane-2-ol | 13.98 | 0.11 | 1.36 | 2.71 | 2.78 | 1.44 | 1.03 | 0.83 |
| 20 | *cis*-pinane-2-ol | 14.45 | 0.48 | 6.45 | 11.92 | 10.88 | 5.51 | 3.66 | 2.25 |
| 21 | *cis*-pinane-3-one | 14.62 | | 0.55 | 1.27 | 1.06 | 0.65 | 0.60 | 0.45 |
| 22 | 6-(hydroxymethyl)-2,6-dimethylbicyclo[3.1.1]heptane-2-ol | 14.93 | | 0.20 | 0.63 | 0.77 | 1.16 | 1.47 | 1.61 |
| 23 | unidentified | 15.84 | | | 0.11 | 0.25 | 0.38 | 0.48 | 0.48 |
| 24 | unidentified | 17.38 | | | 0.05 | 0.19 | 0.39 | 0.50 | 0.56 |

**Table S3.** C-H BDEs of trans-pinane using different basis sets (kJ/mol)

| | M06 | | | B3LYP w/DFT-D3 | | |
|---|---|---|---|---|---|---|
| | **6-31G(d,p)** | **6-311G(d,p)** | **def2-TZVPP** | **6-31G(d,p)** | **6-311G(d,p)** | **def2-TZVPP** |
| 1 | 437.8 | 422.9 | 422.3 | 429.9 | 424.8 | 424.7 |
| 2 | 385.0 | 381.7 | 378.8 | 387.0 | 381.4 | 381.1 |
| 3 | 392.0 | 379.9 | 380.8 | 389.5 | 383.9 | 383.8 |
| 4 | 408.1 | 391.8 | 390.5 | 399.8 | 393.6 | 393.1 |
| 5 | 437.6 | 422.0 | 421.3 | 429.6 | 424.7 | 424.4 |
| 7 | 430.5 | 412.6 | 412.1 | 426.0 | 418.4 | 418.8 |
| 8 | 428.9 | 420.3 | 419.3 | 426.4 | 419.6 | 418.9 |
| 9 | 432.7 | 415.3 | 440.8 | 421.9 | 416.8 | 416.7 |
| 10 | 419.8 | 401.2 | 415.6 | 418.4 | 411.5 | 411.1 |

**Table S4.** C-C BDEs of *trans*-pinane using different basis sets (kJ/mol)

| | M06 | | | B3LYPw/DFT-D3 | | |
|---|---|---|---|---|---|---|
| | **6-31G(d,p)** | **6-311G(d,p)** | **def2-TZVPP** | **6-31G(d,p)** | **6-311G(d,p)** | **def2-TZVPP** |
| 1-2 | 318.2 | 312.5 | 307.1 | 306.5 | 301.5 | 296.4 |
| 2-3 | 306.0 | 300.0 | 294.6 | 297.2 | 290.6 | 285.6 |
| 3-4 | 323.4 | 316.4 | 312.4 | 316.3 | 310.1 | 306.8 |
| 4-5 | 340.0 | 330.3 | 329.7 | 329.0 | 325.1 | 321.2 |
| 5-6 | 204.1 | 197.4 | 193.0 | 193.5 | 185.4 | 181.4 |
| 1-6 | 212.5 | 207.7 | 204.2 | 203.2 | 198.2 | 196.0 |
| 1-7 | 235.7 | 228.6 | 225.8 | 225.1 | 218.7 | 216.3 |
| 5-7 | 229.6 | 219.6 | 218.8 | 222.8 | 215.4 | 213.7 |
| 2-8 | 362.3 | 354.7 | 347.0 | 352.0 | 341.9 | 353.8 |
| 6-9 | 373.4 | 360.8 | 353.5 | 362.9 | 345.5 | 358.7 |
| 6-10 | 377.0 | 370.8 | 363.5 | 362.9 | 357.8 | 359.4 |

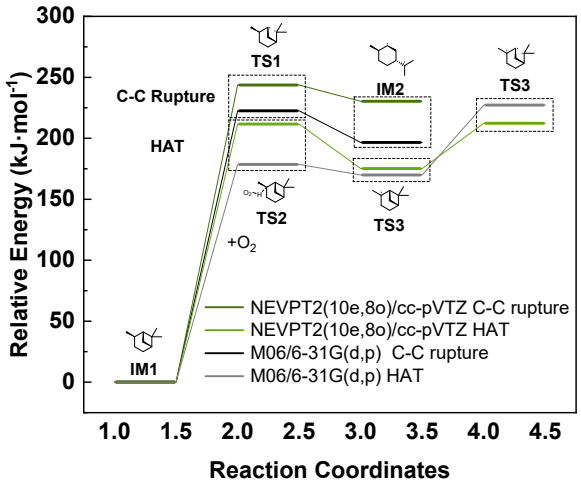


**Fig. S1.** The energy profiles of pinane to form terpane skeleton products