Supplementary Information (SI) for Sustainable Energy & Fuels.

Cycloalkane-Rich Sustainable Aviation Fuel Production via Hydrotreating Lignocellulosic Biomass-derived Catalytic Fast Pyrolysis Oils

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Supporting Information

Product characterization methods

^{13}C-NMR analysis was conducted a 500 MHz Varian Unity Plus spectrometer with samples in deuterated dimethyl sulfoxide (d_6-DMSO) and a relaxation agent, chromium(II) acetylacetonate. Spectra were processed using Mestre-Nova software and categorized be carbon type group.[1–3]

GC-MS-FID analysis was performed on an Agilent G1530A GC equipped with an Agilent 5973 mass-selective detector. 1 μl sample diluted 1:10 in acetone was injected into the GC, which contained a 30 m x 0.25 mm x 0.25 μm Restek Rtx-50 (50%-phenyl-methylpolysiloxane phase) column. The GC oven temperature was held at 40 °C for 2min, ramped to 140 °C with a ramping rate of 7 °C min^{-1}, then to 290 °C with 12 °C min^{-1} and held for 5 min. The inlet temperature was 250 °C, transfer line temperature 300 °C, and there was a helium carrier gas flow of 1ml min^{-1} with a split ratio of 10:1. Semi-quantitative analysis was performed based on 18 calibration compounds typical of those observed in CFP-oils, which were acetaldehyde, benzene, 2,5-dimethylfuran, toluene, ethylbenzene, p-xylene, 2-furaldehyde, 2-cyclopentenone, phenol, 1,2,3-trimethylbenzene, 2,3-benzofuran, indene, o-cresol, o-methoxyphenol, 1-naphthol, naphthalene, 2-methylnaphthalene, phenanthrene.[1]

GPC analysis was performed on an Agilent HPLC with three GPC columns (Polymer Laboratories, 300 × 7.5 mm) packed with polystyrene-divinylbenzene copolymer gel (10 μm beads) having nominal pore diameters of 10^4,10^3, and 10^2 Å, respectively. The eluent was THF and the flow rate 1.0 mL/min. The sample concentration was 1-2 mg/mL and an injection volume of 25 μL was used. The HPLC was attached to a diode-array detector measuring absorbance at 260 nm (bandwidth 40 nm). Retention time was converted into molecular weight by applying a calibration curve established using 18 polystyrene standards of known molecular weight in the range from 1 × 10^6 to 580 Da plus toluene (92). The molecular weights calculated are not absolute molecular weights but are an approximation based on the polystyrene calibration standards.[4]

GC×GC-TOFMS-FID analysis was conducted on a LECO Pegasus IV system equipped with a liquid nitrogen cooled thermal modulator and a flame ionization detector (FID) and post column flow splitter for simultaneous MS-FID analysis to provide both qualitative and quantitative analyses. Samples were diluted in acetone using a mass ratio of 1:10. The injection volume was 1.0 μL and the split ratio was 1:100. The inlet temperature was 300 °C. Two columns were used

for compound separation including a primary column as a semi-polar phase (Rtx-17Sil, 20 m x 180 μm, x 0.18 μm, Restek) and a secondary column as a non-polar phase (ZB-5HT Inferno, 1.5 m, 180 μm, 0.10 μm, Phenomenex) for a better speciation of oxygenates. There are two ovens: the primary oven was held at 35 °C for 5 minutes, then ramped to 125 °C at a rate of 3 °C/min and continuously ramped to 350 °C at 10 °C/min and held for 1 min; the secondary oven was set to an offset of 30 °C above then primary oven. The modulator was set 15 °C higher than the secondary oven. The temperatures of TOF MS and FID were both 350 °C. A standard mixture of 36 compounds were calibrated. The response factors of other compounds were estimated according to their effective carbon numbers.[5]

GC-VUV analysis was performed using an extended version of ASTM D8701. PIONA data was detected by a VGA-101 VUV detector (VUV Analytics, Inc., Cedar Park, TX) coupled with an Agilent 7890A gas chromatography (Agilent Technologies, Inc., Santa Clara, CA). Samples were run undiluted with a syringe rinse of dichloromethane from VWR (Radnor, PA) or carbon disulfide from Sigma Aldrich (St. Louis, MO). For VUV detector, the wavelength range was 125-430nm and the acquisition frequency was 5.00 Hz. The temperature of flow cell and transfer line was 275 °C. The helium makeup gas pressure was 0.40 psi. VUVision 3.4.0 was used for VUV instrument control and data analysis. Gas chromatography was used for analyzing samples controlled by an Agilent MSD ChemStation E.02.02.1431. Like GC-MS analysis, a 30 m x 0.25 mm x 0.25 μm Restek Rxi-1ms column was used. The inlet temperature was 250 °C. The carrier gas was Helium with a flow rate of 1mL/min. The injection volume was 0.1μL and the split ratio was 50:1. The oven temperature was held at 35 °C for 10 minutes, then ramped to 200 °C at a heating rate of 7 °C/min and continuously ramped to 200 °C holding for 5 min.[5]

Table S1. Range of biomass feed elemental compositions

C, wt%	50.4-50.8
H, wt%	6.2-6.3
N, wt%	0.1
S, wt%	<0.1
Ash, wt%	0.7-1.1
Moisture, wt%	1.5-1.6
Oxygen, by difference, wt%	41.8-42.5

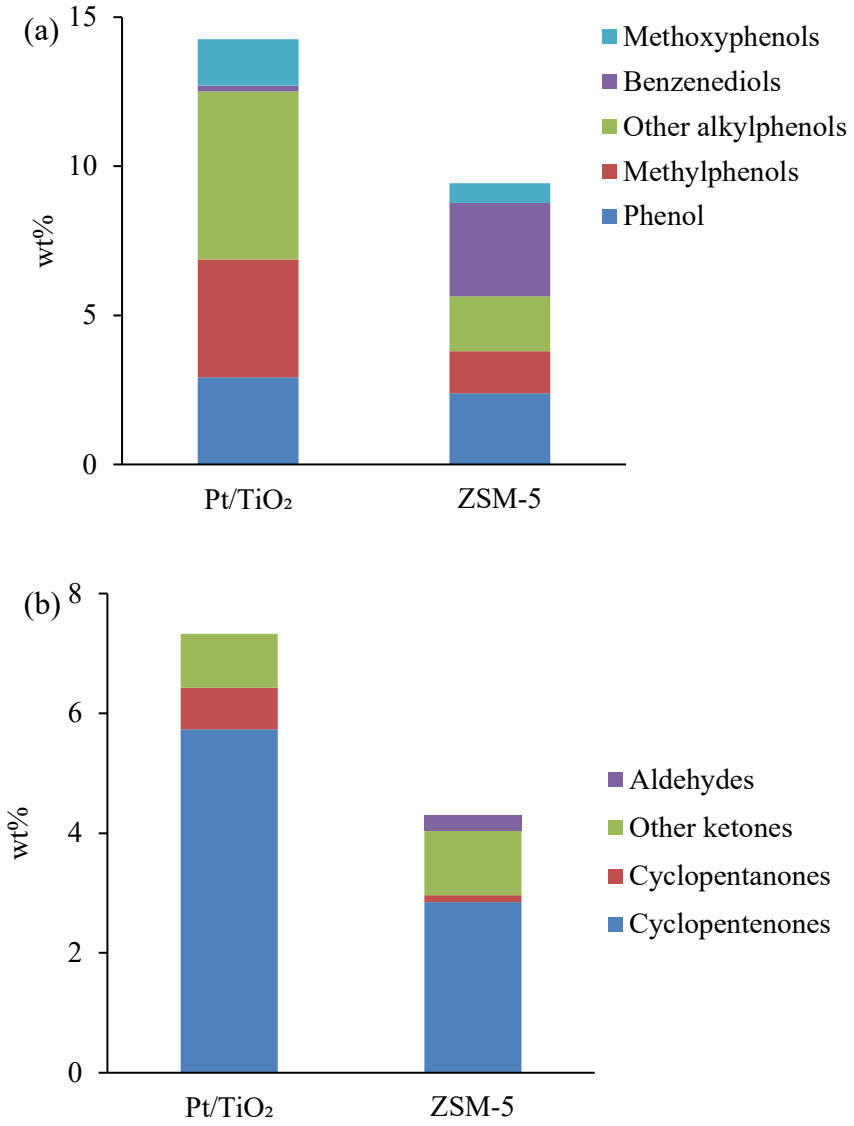

Figure S1. a) Phenols speciation, and b) carbonyls speciation by GC-MS analysis for CFP oils.

Table S2. Compounds detected by GC-MS analysis in CFP oils

Compounds	Retention Time	Pt/TiO_2 Mass %	ZSM-5 Mass %
Acetaldehyde	2.64	-	0.05
Acetic acid	3.68	0.44	0.40
2,3-Butanedione	4.01	-	0.13
2-Butanone	4.08	0.16	0.15
Propanoic acid	5.54	0.34	-

2-Pentanone	5.84	0.05	-
3-Pentanone	4.33	0.04	0.02
Acetaldehyde, hydroxy-	4.39	-	0.20
2-Butenal	5.75	-	0.01
2-Propanone, 1-hydroxy-	6.69	-	0.10
Toluene	7.92	0.02	0.05
Butanoic acid	8.49	0.17	-
3-Penten-2-one, (E)-	8.69	0.17	-
Cyclopentanone	12.39	0.69	-
Cyclopentanone	12.42	0.13	0.06
p-Xylene	12.66	-	0.04
Cyclopentanone, 3-methyl-	14.98	0.09	
Furfural	16.26	0.16	0.03
2-Cyclopenten-1-one	17.00	2.65	0.90
Furan, 2-ethyl-	17.81	0.15	-
2-Cyclopenten-1-one, 3-methyl-	18.55	0.07	-
2(3H)-Furanone, 5-methyl-	18.68	0.12	-
Cyclopentanone, 3-methyl-	18.99	0.09	-
2-Vinylfuran	19.02	-	0.11
2-Cyclopenten-1-one, 2-methyl-	20.67	1.19	0.22
Cyclopent-4-ene-1,3-dione	21.13	-	0.07
Ethanone, 1-(2-furanyl)-	21.24	0.23	-
1,2-Cyclopentanedione	22.62	-	0.05
Phenol	24.84	2.92	2.38
2-Furancarboxaldehyde, 5-methyl-	26.45	0.50	-
2-Cyclopenten-1-one, 3-methyl-	27.67	1.70	-
2,4-Dimethylfuran	27.69	-	0.24
2(5H)-Furanone, 5-methyl-	28.22	0.59	-
Dodecane	28.46	-	0.89
Phenol, 2-methyl-	32.71	1.06	3.08
2(5H)-Furanone, 3-methyl-	33.44	0.27	-
p-Cresol	35.11	2.89	-
Phenol, 2-methoxy-	37.39	0.31	0.25
Phenol, 2-ethyl-	39.02	0.19	0.13
Phenol, 2,6-dimethyl-	39.64	0.25	0.23
Phenol, 2,4-dimethyl-	39.73	0.40	0.53
4-Methyl-5H-furan-2-one	40.12	0.37	
Phenol, 3-ethyl-	40.89	0.94	0.35
Phenol, 4-ethyl-	41.01	1.22	0.28
Phenol, 2-ethyl-4-methyl-	41.59	0.03	-
Phenol, 3,5-dimethyl-	41.67	0.21	-
Naphthalene	42.06	-	0.08
Creosol	42.50	-	0.29

Phenol, 4-methoxy-3-methyl-	42.51	0.42	-
Catechol	43.27	-	1.38
Phenol, 2-ethyl-4-methyl-	43.28	0.14	0.23
Benzofuran, 2,3-dihydro-	43.64	0.23	-
Phenol, 2-ethyl-4-methyl-	43.83	0.37	-
Benzaldehyde, 4-methyl-	44.06	0.10	-
Phenol, 4-propyl-	44.56	1.29	0.09
Phenol, 2-ethyl-4-methyl-	44.77	0.11	-
1H-Inden-5-ol, 2,3-dihydro-	44.99	0.34	-
2,2'-Bifuran	45.44	-	0.20
Phenol, 2,3,5-trimethyl-	45.25	0.06	-
Phenol, 4-ethyl-2-methoxy-	45.62	0.13	0.05
1,2-Benzenediol, 3-methyl-	45.72	-	0.26
Naphthalene, 2-methyl-	46.20	0.04	0.07
Phenol, 2-methyl-5-(1-methylethyl)-	46.28	0.07	-
Thymol	46.57	0.08	-
1,2-Benzenediol, 4-methyl-	46.73	-	0.89
Benzene, 1-methoxy-4-propyl-	46.80	0.14	-
Benzene, 1-methyl-3-propyl-	46.86	0.18	-
Ethanone, 1-(2-hydroxy-5-methylphenyl)-	47.60	0.21	-
Hydroquinone	47.93	-	0.14
1H-Inden-5-ol, 2,3-dihydro-	48.08	0.46	-
1H-Inden-1-one, 2,3-dihydro-	48.29	-	0.16
Benzofuran, 2,3-dihydro-2-methyl-	48.31	1.11	-
1H-Inden-5-ol, 2,3-dihydro-	48.48	1.38	0.29
Benzofuran, 2-methyl-	49.01	0.19	0.09
Cinnamaldehyde, (E)-	49.34	0.21	-
4-Ethylcatechol	49.67	-	0.40
Cinnamaldehyde, (E)-	49.82	-	0.52
Benzofuran, 2-methyl-	49.83	0.68	-
1,3-Benzenediol, 4-ethyl-	50.03	-	0.07
Orcinol	50.04	0.19	-
trans-Isoeugenol	50.30	0.13	-
2-Allyl-4-methylphenol	50.48	0.10	-
2-Allyl-4-methylphenol	50.71	0.18	-
6-Methyl-4-indanol	51.38	0.06	-
trans-Isoeugenol	51.56	0.56	-
Phenol, 2-methoxy-6-(1-propenyl)-	51.56	-	0.05
Vanillin	52.11	-	0.26
Benzene, 2-ethenyl-1,3,5-trimethyl-	52.60	0.13	-
Benzene, hexamethyl-	52.79	0.03	-
Apocynin	54.29	-	0.03
1-Naphthalenol	54.64	0.08	-

2-Naphthalenol	54.99	0.13	0.18
beta-D-Glucopyranose, 1,6-anhydro-	55.62	-	0.27
1-Naphthalenol, 2-methyl-	57.06	0.05	-
1-Naphthalenol, 4-methyl-	57.35	0.09	0.05
1-Naphthalenol, 2-methyl-	57.48	0.03	-
Coniferyl aldehyde	60.61	-	0.06
Methyl dehydroabietate	62.71	0.15	-
Methyl biphenyl-4-carboxylate	65.02	-	0.05
Retene	68.70	0.09	-

Table S3. Gas product yields during hydrotreating

Gas	Pt/TiO_2	ZSM-5
CH_4	1.3%	1.1%
C_2	0.9%	1.0%
C_3	1.4%	1.3%
C_4	2.0%	1.9%
C_5	1.6%	1.1%

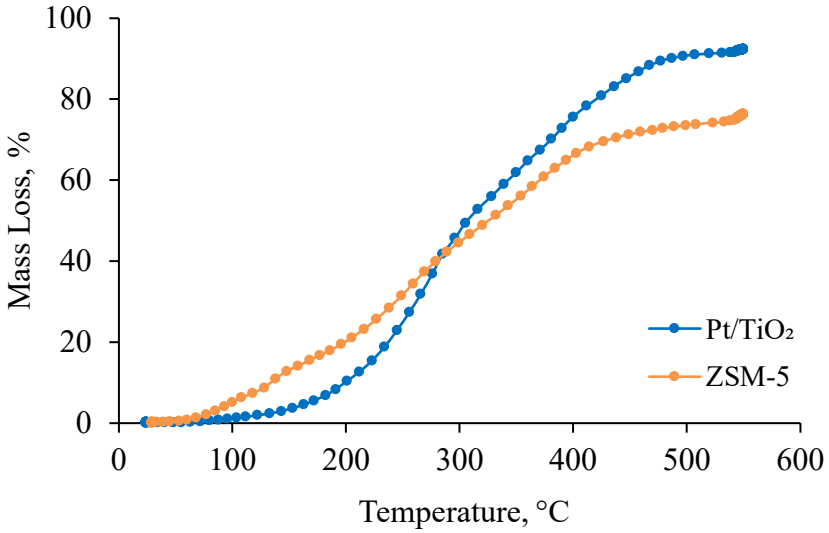

Figure S2. TGA-SimDist results of CFP oils.

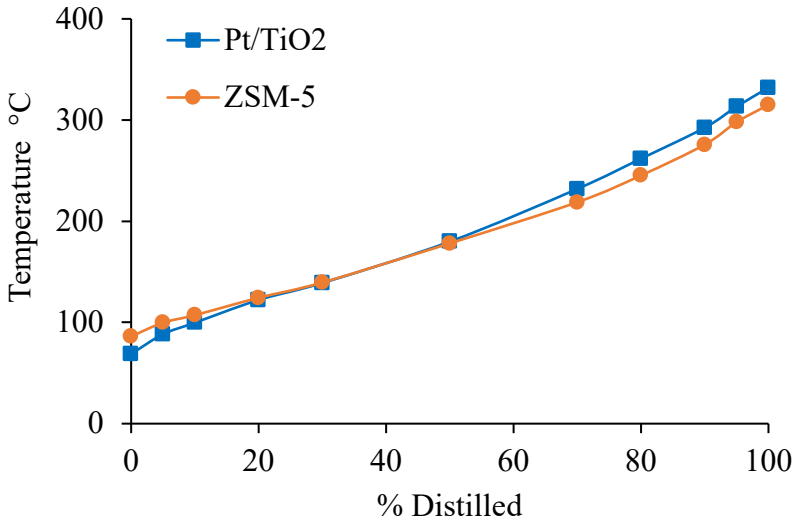

Figure S3. Simulated distillation results of hydrotreated oils.

Table S4. GC-MS-FID analysis of the gasoline-range fractions.

Compound	Group	Group 2	Pt/TiO_2 FID Area%	Pt/TiO_2 FID Area%
Butane, 2-methyl-	Isoalkane		0.51	0.17
Pentane	n-Alkane		1.76	0.50
Cyclopentane	Cycloalkane	Cyclopentane	4.74	1.63
Pentane, 2-methyl-	Isoalkane		0.92	0.42
Pentane, 3-methyl-	Isoalkane		0.74	0.32
n-Hexane	n-Alkane		3.28	1.05
Cyclopentane, methyl-	Cycloalkane	Cyclopentane	8.33	3.83
Benzene	Aromatic		0.40	0.34
Cyclohexane	Cycloalkane	Cyclohexane	11.73	12.43
Hexane, 2-methyl-	Isoalkane		0.57	0.52
Hexane, 3-methyl-	Isoalkane		0.53	0.43
Cyclopentane, 1,3-dimethyl-, trans-	Cycloalkane	Cyclopentane	0.80	0.77
Cyclopentane, 1,3-dimethyl-, cis-	Cycloalkane	Cyclopentane	0.59	0.59
Cyclopentane, 1,2-dimethyl-, trans-	Cycloalkane	Cyclopentane	0.63	0.90
Heptane	n-Alkane		1.06	0.66
Cyclohexane, methyl-	Cycloalkane	Cyclohexane	17.92	22.61
Cyclopentane, ethyl-	Cycloalkane	Cyclopentane	2.92	2.65
Cyclopentane, 1,2,4-trimethyl-	Cycloalkane	Cyclopentane	0.18	0.35
Cyclopentane, 1,1,2-trimethyl-	Cycloalkane	Cyclopentane	0.11	0.21
Toluene	Aromatic		1.18	1.26
Heptane, 2-methyl-	Isoalkane		0.11	0.25
Cyclohexane, 1,3-dimethyl-, cis-	Cycloalkane	Cyclohexane	2.59	4.32
Cyclohexane, 1,4-dimethyl-	Cycloalkane	Cyclohexane	1.39	2.11

Cyclohexane, 1,1-dimethyl-	Cycloalkane	Cyclohexane	0.14	0.27
Cyclopentane, 1-ethyl-3-methyl-, trans-	Cycloalkane	Cyclopentane	0.89	1.09
Cyclopentane, 1-ethyl-3-methyl-, cis-	Cycloalkane	Cyclopentane	0.78	0.97
Cyclopentane, 1-ethyl-2-methyl-	Cycloalkane	Cyclopentane	0.60	0.93
Cyclopentane, 1-ethyl-1-methyl-	Cycloalkane	Cyclopentane	0.09	0.15
Cyclohexane, 1,2-dimethyl-, trans-	Cycloalkane	Cyclohexane	1.37	2.13
Cyclohexane, 1,4-dimethyl-, cis-	Cycloalkane	Cyclohexane	2.27	3.63
Octane	n-Alkane		0.84	0.56
Cyclopentane, butyl-	Cycloalkane	Cyclopentane	0.25	0.26
Cyclopentane, 1-ethyl-3-methyl-	Cycloalkane	Cyclopentane	0.21	0.29
Cyclohexane, 1,2-dimethyl-, cis-	Cycloalkane	Cyclohexane	0.65	0.98
Cyclohexane, ethyl-	Cycloalkane	Cyclohexane	15.17	13.14
Cyclohexane, 1,1,3-trimethyl-	Cycloalkane	Cyclohexane	0.01	1.55
Ethylbenzene	Aromatic		0.20	0.55
Cyclohexane, 1,3,5-trimethyl-	Cycloalkane	Cyclohexane	0.74	0.53
p-Xylene	Aromatic		0.31	0.49
Cyclohexane, 1-ethyl-4-methyl-, trans-	Cycloalkane	Cyclohexane	0.42	1.79
Cyclohexane, 1-ethyl-4-methyl-, cis-	Cycloalkane	Cyclohexane	1.10	0.88
Cyclohexane, propyl-	Cycloalkane	Cyclohexane	0.57	1.57
1H-Indene, octahydro-, trans-	Cycloalkane	Octahydroindene	0.39	0.48
1H-Indene, octahydro-, cis-	Cycloalkane	Octahydroindene	0.37	0.38

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