Electronic Supplementary Material (ESI) for Energy Advances.

Diesel Production via Standalone and Co-Hydrotreating of Catalytic Fast Pyrolysis Oil

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Supporting Information

Table S1. Biomass feed ultimate analysis

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

Safety precautions for hydrotreating experiments

Before each hydrotreating experiment and after each maintenance event, a leak test was conducted for each section of the system at a pressure equal to 110% of the experiment operating pressure with a criterion of no measured pressure loss for 30 minutes. The hydrotreating system was placed in a room with approximately forty air exchanges an hour, and the room was equipped with H_2, CO, and H_2S monitors and fire eyes. The system was controlled by OPTO 22, and the operators could be alerted, feeds stopped, an automatic safety shutdown initiated, and/or power shut off to the entire room if the system was outside its operating window or gases detected in the room.

Product characterization methods

GC-MS-FID analysis was performed on an Agilent 8890 Gas Chromatograph with 8977B mass selective detector (MSD) with a PolyArc FID. The GC was equipped with a post column flow splitter for simultaneous MS-FID analysis. A PolyArc detector was placed in line with the FID for quantitation and the response was verified with a mixture of representative compounds. The PolyArc system acts as a methanizer, converting all organic components to methane and generating detector response relative to carbon number. Samples were diluted 1:10 gravimetrically in acetone. The injection volume was 1 µl and the split ratio was 1:100. The inlet temperature was 275 °C. The column used for compound separation was a 30 m x 0.25 mm x 0.25 µm Restek Rtx-50 (50%-phenyl-methylpolysiloxane phase). The oven temperature was held at 35 °C for 2 min, then increased to 300 °C at a heating rate of 5 °C/min and then held at 300 °C for 10 min. The MSD was operated in continuous scan mode from m/z 29 to 300. Both FID and MSD transfer lines were set to 350 °C.

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.

GC x GC analysis was conducted by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC x GC-TOF MS) 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 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.

Table S2. Hydrotreating operating conditions

Feed	SRD (36 h); SRD & CFP oil (24 h)	SRD (36 h); SRD & CFP oil (24 h)	CFP oil	CFP oil
Isothermal temperature, °C	325	325	325	385
Pressure, bar	56	56	56	125
Feed rate, mL/h	10	10	4	2
Catalyst	$NiMo/Al_2O_3$	$CoMo/Al_2O_3$	$NiMo/Al_2O_3$	$NiMo/Al_2O_3$
Heating fluid flow	Counter-current	Counter-current	Counter-current	Co-current
Catalyst in isothermal zone, g	10	10	10	12.5
Catalyst in transition zone, g	~2		~2	7.5
SiC in transition zone, g	-	-	-	30
H_2, smL/min	100	100	100	125
WHSV, g/(gh)	1.0	1.0	0.4	0.16
Time-on-stream, h	36 + 24	36 + 24	72	76
Sulfiding liquid flow rate, mL/min	0.05	0.05	0.05	0.045
H_2 during sulfidation, smL/min	100	100	100	125

Table S3. Major compounds from GC-MS analysis of CFP oil. In total, 65 compounds were identified and quantified. Only the compounds present with mass% ≥ 0.10 are included.

Compounds	RT, min	Mass %
2-Butanone	9.406	0.17
Acetic acid	13.749	0.81
2-Propanone, 1-hydroxy-	15.81	0.18
Propanoic acid	20.052	0.29
Cyclopentanone	21.813	0.60
Butanoic acid	25.718	0.26
2-Cyclopenten-1-one	26.173	2.18
2-Cyclopenten-1-one, 2-methyl-	29.623	1.02
Ethanone, 1-(2-furanyl)-	30.572	0.18
2-Furancarboxaldehyde, 5-methyl-	34.800	0.14
2-Cyclopenten-1-one, 3-methyl-	35.255	1.03

Butyrolactone	35.679	0.58
2(5H)-Furanone	36.226	0.38
2(5H)-Furanone, 3-methyl-	38.580	0.27
2-Furanone, 2,5-dihydro-3,5-dimethyl	39.153	0.10
Phenol	40.009	2.5
Phenol, 2-methyl-	42.362	0.74
Phenol, 2,6-dimethyl-	43.068	0.10
p-Cresol	44.098	0.81
Phenol, 3-methyl-	44.208	1.51
Creosol	45.782	0.36
Phenol, 2-ethyl-	45.987	0.19
Phenol, 2,5-dimethyl-	46.300	0.59
Phenol, 3,5-dimethyl-	47.988	0.16
Phenol, 4-ethyl-	48.195	0.65
Phenol, 3-ethyl-	48.313	1.16
Phenol, 3,4-dimethyl-	49.391	0.11
Phenol, 3-ethyl-5-methyl-	50.133	0.22
Benzene, (ethenyloxy)-	51.438	0.18
Phenol, 2,4,5-trimethyl-	51.827	0.10
Phenol, 2-propyl-	52.065	1.12
2-Methoxy-4-vinylphenol	52.237	0.15
Phenol, 4-(2-propenyl)-	52.438	0.20
Phenol, 2-methoxy-3-(2-propenyl)-	53.261	0.28
Eugenol	53.363	0.12
Benzaldehyde, 2-ethyl-	54.693	0.30
Phenol, 2-methoxy-4-(1-propenyl)-	55.630	0.13
1H-Inden-5-ol, 2,3-dihydro-	56.018	0.69
2-Allylphenol	56.581	0.53
Cinnamaldehyde, (E)-	56.734	0.18
Benzofuran, 2-methyl-	57.611	0.36
trans-Isoeugenol	57.844	0.62
Hydroquinone	59.048	0.21
Apocynin	62.143	0.11
.beta.-D-Glucopyranose, 1,6-anhydro-	67.705	0.70

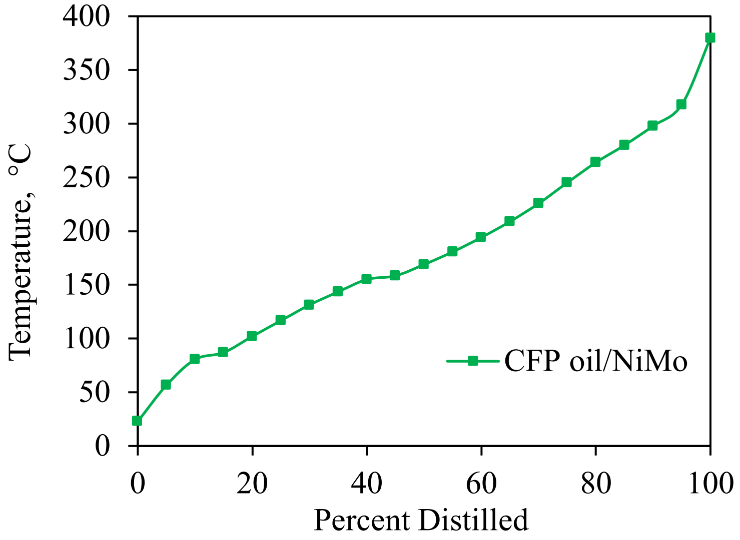

Figure S1. Simulated distillation of the product from two-zone standalone CFP oil hydrotreating at 385 °C, 125 bar over sulfided NiMo.

Table S4. Major compounds determined by GC x GC analysis. In total, 144 compounds were identified and quantified, and the compounds with mass% > 0.9 are given.

Compound	1D RT, min	2D RT, min	Mass % (> 0.9)
Cyclohexane, propyl-	342	4.855	1.77
Cyclohexane, 1-methyl-2-propyl-	462	5.665	1.84
Cyclohexane, 1-ethyl-1-methyl-	510	5.670	1.07
1H-Indene, octahydro-, cis-	582	4.600	1.22
Cyclohexane, butyl-	614	5.680	1.4
Cyclohexane, 2-ethyl-1,3-dimethyl-	630	6.295	1.11
1H-Indene, octahydro-5-methyl-	694	5.145	1.31
Bicyclo[4.1.0]heptane,3,7,7-trimethyl-,[1S-(1α,3α,6α)]-	750	5.860	1.23
Naphthalene, decahydro-, trans-	758	5.160	2.19
(2-Methylbutyl)cyclohexane	782	6.115	1.05
cis-Decalin, 2-syn-methyl-	814	5.640	0.92
C12 Cycloalkane	870	5.55	0.95
Naphthalene, decahydro-2-methyl-	886	5.59	2.16
C12 Cycloalkane	894	6.55	0.97
Cyclohexane, pentyl-	910	5.94	1.17
1-Methyldecahydronaphthalene	950	5.44	1.38
Cyclopentane, 1-methyl-3-(2-methylpropyl)-	1030	6.33	1.23

Cyclohexane, (2-methylpropyl)-	1078	6.23	0.91
Cyclopentane, 1-methyl-3-(2-methylpropyl)-	1310	6.45	1.25
C13 Cycloalkane	1486	5.745	1.11
Cyclohexane, (3-cyclopentylpropyl)-	1758	5.81	1.16
Cyclohexane, 1,1'-(1,2-ethanediyl)bis-	1942	5.525	1.24
Cyclohexane, 1-(cyclohexylmethyl)-3-methyl-, trans-	2030	5.855	1.55
Heptadecane	2222	3.900	1.13
1,1'-Bicyclohexyl, 2-methyl-, trans-	2230	3.415	1.26
C18 Isoalkane	2254	3.335	2
C18 Isoalkane	2278	3.310	1.97
C18 Cycloalkane	2302	3.025	1.61
Octadecane	2326	2.995	0.91
C19 Cycloalkane	2390	2.525	1.36
C19 Cycloalkane	2414	2.440	1.11

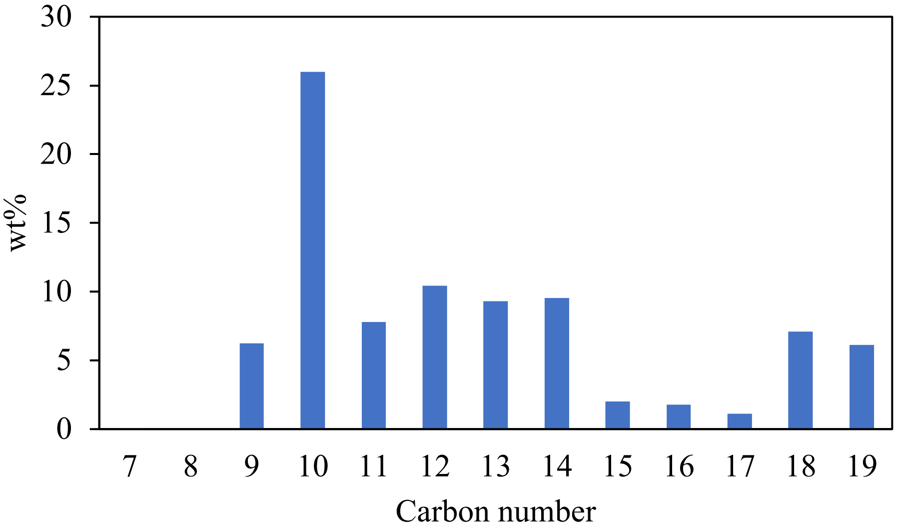

Figure S2. Carbon distribution by GC x GC analysis for the diesel fraction from two-zone hydrotreating of CFP oil.