Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Oxygen removal from intact biomass to produce liquid fuel range hydrocarbons via fast-hydropyrolysis and vapor-phase catalytic hydrodeoxygenation

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Materials

The microcrystalline cellulose (50μm) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The poplar feedstock (termed BESC standard poplar) was a genotype of *Populus trichocarpa* grown at Oak Ridge National Laboratory.[1] The poplar feedstock, which was dried and milled to less than 80 mesh (< 0.177 mm), was obtained from National Renewable Energy Laboratory (NREL). The poplar feedstock was then sieved to pass through a 270 mesh screen for a particle size of <53 μm, comparable to the microcrystalline cellulose, for the experiments reported in this manuscript. Ultra high purity (99.999%) hydrogen and high purity (99.995%) nitrogen purchased from Indiana Oxygen Company (Indianapolis, IN, USA) were used for the experiments.

Table S.1: Ultimate and proximate analysis of cellulose and poplar feedstocks

Ultimate Analysis		
	Cellulose	Poplar
Carbon / %wt (dry)	44.70	50.72
Hydrogen / %wt (dry)	6.31	5.88
Nitrogen / %wt (dry)	0.19	0.14
Sulfur / %wt (dry)	<0.01	<0.01
Ash / %wt (dry)	0.04	1.89
Oxygen / %wt (dry), by difference	48.76	41.37
Proximate Analysis		
Moisture / % wt as used	0.94	3.32
Volatile Matter / %wt (dry)	98.24	88.63
Fixed Carbon / %wt (dry)	1.72	9.48
HHV / BTU lb^{-1}	6963	8153

Table S.2: Compositional analysis of the poplar feedstock, % wt (dry)

	Poplar
Cellulose	44.5
Xylan	14.0
Arabinan	0.2
Galactan	1.1
Mannan	2.6
Hemicellulose (total)	17.9
Lignin	26.3
Extractives	3.1
Acetate	3.6

Table S.3: Overall product distribution from cellulose and poplar on % carbon in feed basis (data as shown in Figure 2) and estimated hydrogen consumption

	Cellulose	Poplar
CO / % carbon in feed	15.6	9.6
CO_2 / % carbon in feed	2.0	2.7
Char / % carbon in feed	3.4	28.5
Aqueous phase / % carbon in feed	0.9	0.4
Product Hydrocarbons Yield / % carbon in feed		
Methane (C_1)	5.3	9.8
Ethane (C_2)	6.1	6.9
Propane (C_3)	6.2	5.0
Total (C_1 - C_3) range	***17.6***	***21.7***
i-butane	0.3	0.4
n-butane	7.9	5.3
Total C_4	***8.2***	***5.7***
2-methyl butane	0.8	0.5
n-pentane	10.9	3.0
cyclopentane	4.5	3.0
Total C_5	***16.2***	***6.5***
n-hexane	17.6	1.1
cyclohexane	1.6	2.6
Other C_6 branched and cyclic isomers	4.0	1.2
Total C_6	***23.2***	***4.9***
(Mixture of n-heptane, methylcyclohexane, other branched and cyclic isomers) ***Total C_7***	***1.9***	***2.8***
(Mixture of n-octane, ethylcyclohexane, n-nonane, propylcyclohexane, other branched and cyclic isomers) ***Total C_{8+}***	***5.5***	***12.2***
Total C_{4+} range	***55.0***	***32.1***
Total hydrocarbons (C_1 - C_{8+})	***72.6***	***53.8***
Overall carbon balance	94.5	95.0
Unaccounted carbon	5.5	5.0
Estimated hydrogen consumption / $g_{H2}\ g_{feed}^{-1}$	~0.05	~0.05

Table S.4: Carbon and hydrogen contents of char from cellulose and poplar experiments

	Cellulose	Poplar
Carbon / wt%	80.9	76.3
Hydrogen / wt%	3.6	3.7

Table S.5: Carbon, hydrogen and water contents of aqueous phase products from cellulose and poplar experiments

	Cellulose	Poplar
Carbon / wt%	2.2	1.1
Hydrogen / wt%	11.3	11.8
Water / wt%	91.2	97.2

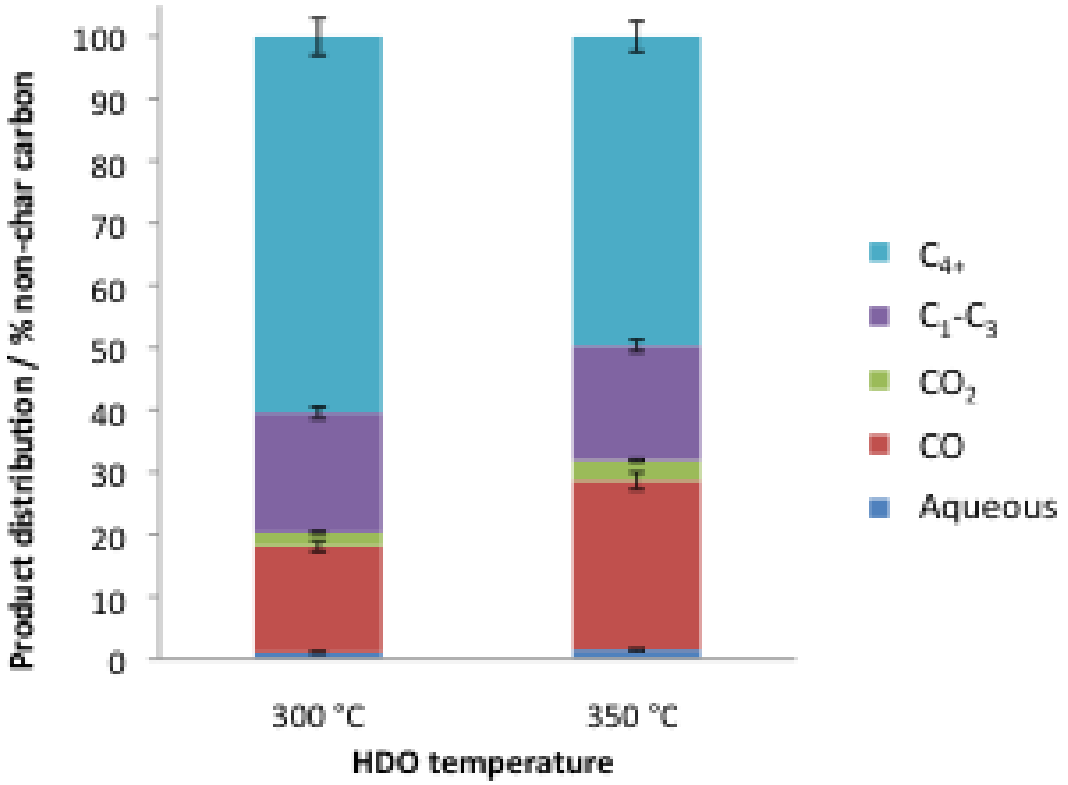

Figure S.1: Comparison of product distribution (% non-char carbon basis) from HDO of cellulose fast-hydropyrolysis vapors as a function of HDO temperature. Process conditions: P_{H_2}=25 bar, P_{N_2}= 2 bar, P_{total}=27 bar, fast-hydropyrolysis=480°C

Catalyst Characterization

CO chemisorption was performed to quantify CO uptake for the 5wt%Pt-2.5wt%Mo/MWCNT catalyst. ~124 mg of the fresh, as-prepared and reduced, catalyst was loaded into a Micromeritics ASAP 2020 instrument. The catalyst was degassed and reduced *in situ*, in H_2 flow, with a temperature ramp to 450 °C in 2 hours and held at 450 °C for 2 hours, similar to the *in situ* catalyst reduction procedure used in the HDO reactor before the start of the experiments. The catalyst was then evacuated at 450°C for 2 hours and a leak test was performed at 35°C, to ensure that the pressure increase rate, due to sample outgassing, was less than 10 μmHg min^{-1}. The CO uptake analysis was performed at 35°C and in a pressure range of 200 mmHg to 400 mmHg.

The CO uptake value for the 5wt%Pt-2.5wt%Mo/MWCNT catalyst was ~67 μmol g^{-1} and the corresponding isotherm is shown in Figure S.2.

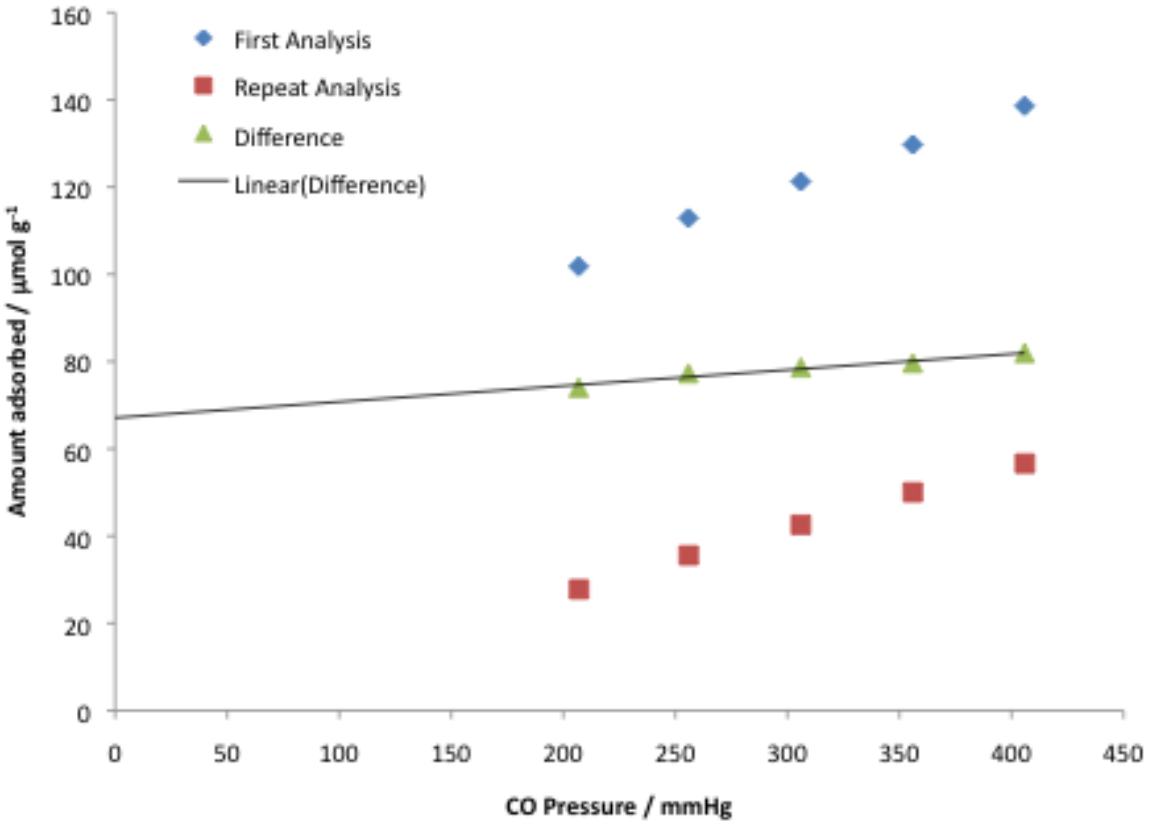

Figure S.2: CO chemisorption isotherm

References

1. M. H. Studer, S. Brethauer, J. D. DeMartini, H. L. McKenzie and C. E. Wyman, *Biotechnol. Biofuels*, 2011, 4, 19.