

ELECTRONIC SUPPLEMENTARY INFORMATION

Ex situ Hydrodeoxygenation in Biomass Pyrolysis using Molybdenum Oxide and Low Pressure Hydrogen

Michael W. Nolte, Jing Zhang and Brent H. Shanks

Department of Chemical and Biological Engineering, Iowa State University,
Ames, IA, 50011, United States

Center for Biorenewable Chemicals, Iowa State University, Ames, IA, 50011,
United States

S1 Experimental Methods

S1.1 Materials

Cellulose (Sigmacell 50) and molybdenum(VI) oxide ($\geq 99.5\%$) were purchased from Sigma Aldrich. The cellulose was used as received. The received molybdenum oxide catalyst was pelletized and sieved to 140-400 mesh particle sizes. Prior to use in a reaction, the catalyst was calcined in air at 600 °C for 3 hours. Lignin was provided by Archer Daniels Midland (ADM) and had been isolated from corn stover using the Organosolv process. Prior to use, the lignin was purified by washing with dilute acid. Approximately 10 g of lignin sample was washed with 100 mL of 0.1 N HCl for 15 minutes, followed by two subsequent washes with deionized water. Corn stover was received from the BioCentury Research Farm at Iowa State University and was dried and milled to $\sim 200 \mu\text{m}$ particle size. No demineralization or acid washing treatment was performed.

S1.2 Micropyrolyzer

As was mentioned in the main article, the tandem micropyrolyzer is a series of two reactors. In the first reactor, the biomass is pyrolyzed in an inert atmosphere. The generated pyrolysis vapors are quickly swept into the second reactor containing the catalyst bed and then are swept into the gas chromatograph (GC) for analysis. To perform an experiment, a small mass of sample (200-300 μg) was loaded into a deactivated stainless steel cup. The cups were dropped by gravity into the preheated first reactor. The helium carrier gas (UHP300, Airgas) at 30 mL/min quickly swept the vapors into the second reactor. A reaction gas inlet which allows for a second gas to flow over the catalyst was located at the interface between the two reactors (i.e., with He as a carrier, H_2 can be added to reduce the catalyst, or air can be added to oxidize the catalyst or burn off coke). During an experiment, hydrogen (UHP300, Airgas) was added as the secondary gas at 30 mL/min.

After the second reactor, the vapors were swept into the GC-MS/TCD/FID (Agilent 7890B GC, Agilent 5977A Mass Selective Detector, Thermal Conductivity Detector, Flame Ionization Detector) for identification and quantification. The GC parameters included an injection temperature of 270 °C and an oven program of a hold at 25 °C for 7 minutes, followed by a ramp of 10 °C/min to 300 °C. The MS was operated in electron ionization

mode with a scan between 20-500 m/z. The FID and TCD were held at 260 °C. Separation and quantification of non condensible gases and C₁-C₇ hydrocarbons was achieved with a GS-GASPRO column (Agilent) and quantified by TCD. Condensible volatile compounds were separated using a medium polarity DB-1701 column (Agilent) and identified and quantified using the MS and FID, respectively. Pure standards and standard gas mixtures were used to identify and calibrate for all possible products.

Quartz tubes (3 mm I.D.) were loaded with 200 mg MoO₃ with quartz wool placed above and below the catalyst bed to secure it in place. The typical length of a catalyst bed was 12 mm.

Product yields are reported as C% of the feed. The char yields from cellulose, lignin, and corn stover were measured to be 10.1 C%, 55.5 C%, and 43.0 C%, respectively.

S1.3 Coke Measurement

Coke yields were measured through an oxidative treatment of the catalyst bed *in situ* using 1.6 vol% air in He at 61 mL/min. The catalyst bed temperature was initially held at reaction temperature, 400 °C, for 15 min, followed by a ramp at 5 °C/min to 550 °C. The temperature was held at 550 °C for 2 hr. The CO₂ that evolved off the catalyst was detected and quantified using the MS by tracking the ion count at a m/z of 44.

S1.4 H₂ Consumption

The hydrogen consumption was calculated using the stoichiometric equation for the overall HDO reaction (equation 1).



By completing an atom balance for C, H, and O using values of l , m , and n as determined by elemental analysis for each of the feedstocks (2)

$$Cellulose = CH_{1.67}O_{0.83} \quad (2)$$

$$Lignin = CH_{0.977}O_{0.4} \quad (3)$$

$$Cornstover = CH_{1.51}O_{0.68} \quad (4)$$

$$(5)$$

and values of x and y for each individual hydrocarbon product, the coefficient for H₂, b , can be determined.

S2 Pyrolysis Product Identification and Quantification

The compounds listed in Table S1 include the compounds that were identified and quantified from the HDO using MoO₃. The products from cellulose pyrolysis have been previously reported and are not included here [1]. The TCD was used to separate and quantify the CO, CO₂, olefins and paraffins. Benzene and toluene could be identified and quantified using both the FID and TCD. Very similar yields for these two products were reported when comparing both detectors. All other aromatics were quantified using only the FID.

Table S1: Identified products from fast pyrolysis of cellulose and after catalysis with MoO₃.

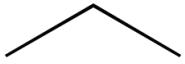
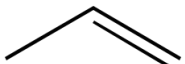
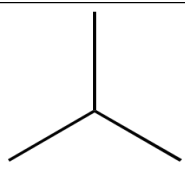
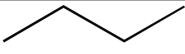
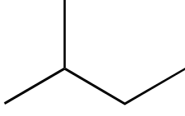
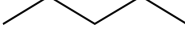

Compound	Structure	Molecular Weight (Da)	Retention Time (min)	Major Ion Fragments [m/z (rel. height)]
Light Gases and Hydrocarbons (Detected and Quantified using TCD)				
Carbon Monoxide (CO)	$\text{C} \equiv \text{O}$	28	3.2	–
Methane	CH_4	16	3.3	–
Ethane	$\text{H}_3\text{C} - \text{CH}_3$	30	4.95	–
Carbon Dioxide (CO ₂)	$\text{O} = \text{C} = \text{O}$	44	5.0	–
Ethylene	$\text{H}_2\text{C} = \text{CH}_2$	28	6.2	–
Propane		44	11.1	–
Propylene		42	13.9	–
i-Butane		58	15.3	–
n-Butane		58	15.8	–
i-Pentane		72	18.7	–
n-Pentane		72	19	–
n-Hexane		86	21.8	–

Table S1 – Identified pyrolysis products continued

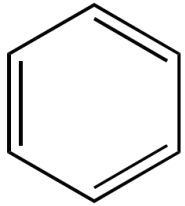
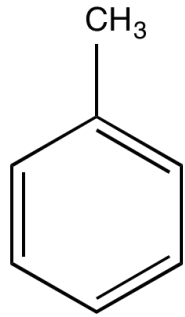
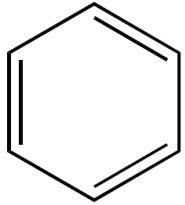
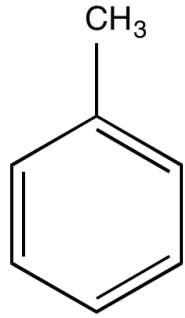
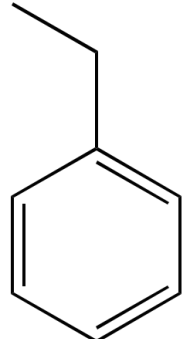
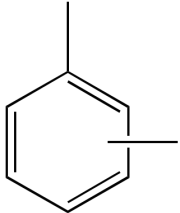
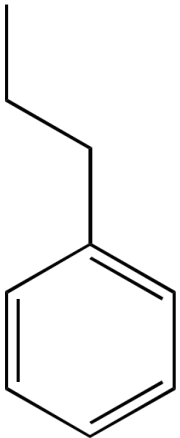
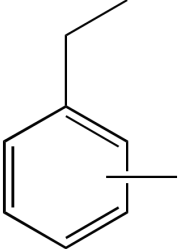
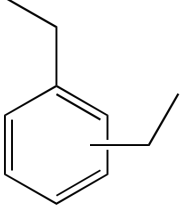
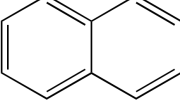
Compound	Structure	Molecular Weight (Da)	Retention Time (min)	Major Ion Fragments [m/z(rel. height)]
Benzene		78	24.6	–
Toluene		92	27.3	–
Condensable Hydrocarbons (Detected by MS and Quantified by FID)				
Benzene		78	10.4	78(999) 77(236) 52(180)
Toluene		92	13.5	91(999) 92(638) 65(147)
Ethyl Benzene		106	15.7	91(999) 106(986) 51(368) 65(363) 77(328)

Table S1 – Identified pyrolysis products continued

Compound	Structure	Molecular Weight (Da)	Retention Time (min)	Major Ion Fragments [m/z(rel. height)]
Xylenes		106	<i>p/m</i> -15.9, <i>o</i> -16.4	91(999) 106(451) 105(187)
Propyl Benzene		120	17.4	91(999) 120(267)
Methyl Ethyl Benzenes		120	17.6-18.0	105(999) 120(465) 91(216)
Diethyl Benzenes		134	19.1-19.3	105(999) 119(935) 134(476)
Naphthalene		128	22	128(999) 127(129)

S3 Hydrodeoxygenation at 300 °C

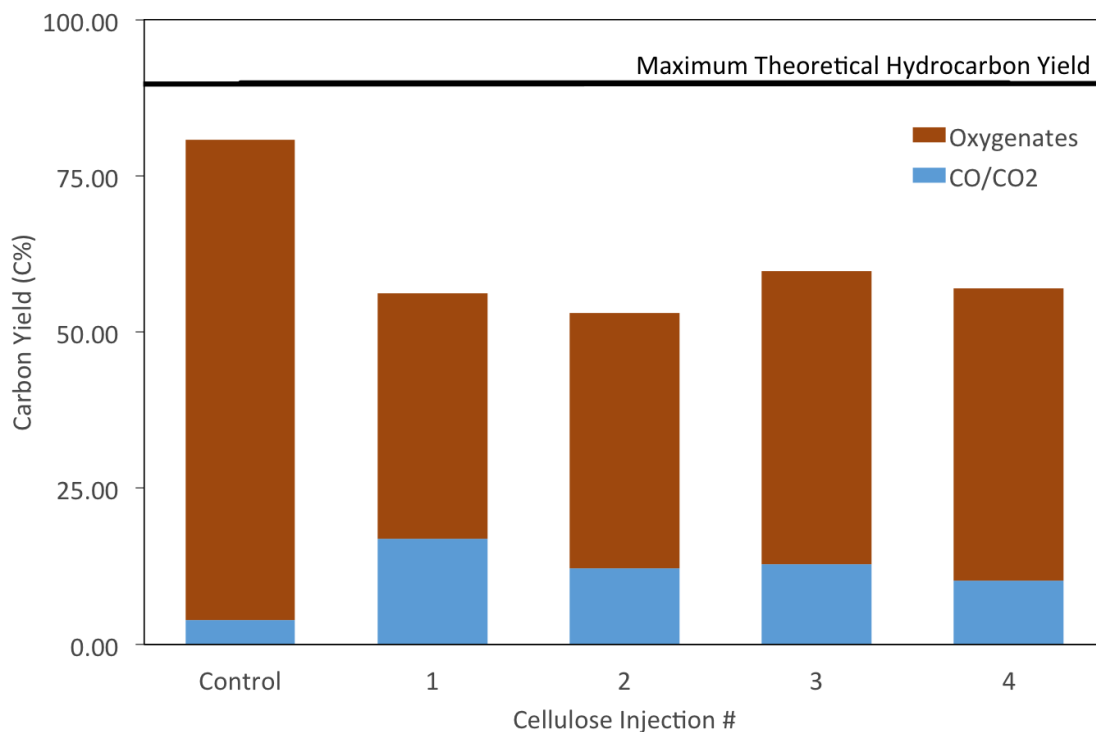


Figure S1: The hydrodeoxygenation of cellulose at 300 °C using MoO₃.

The HDO of cellulose was performed at a catalyst bed temperature of 300 °C (Figure S1). No catalyst pre-reduction was performed. The detected products included CO, CO₂, and the oxygenated products that are typical of cellulose pyrolysis. However, there was a change in the relative product distribution in that the use of catalyst resulted in a decreased levoglucosan yield and increases in levoglucosan dehydration products (*e.g.*, levoglucosenone). Importantly, there was no measured hydrocarbon production. The unaccounted fraction is likely to be mainly coke as well as some detected but unquantified products.

S4 Catalyst Characterization

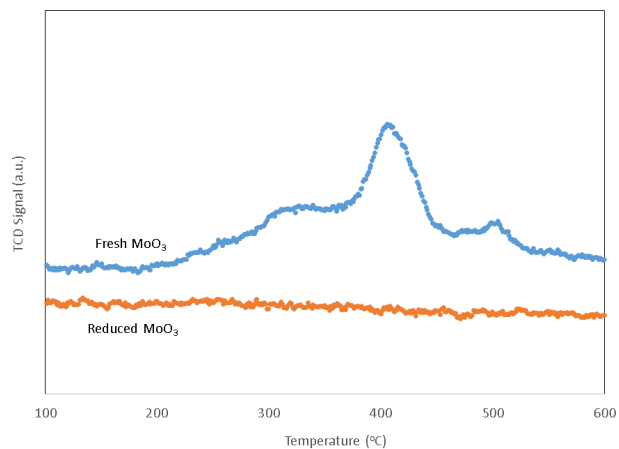


Figure S2: NH₃-TPD of fresh and reduced MoO₃.

The number and strength of the acid sites of fresh and reduced MoO₃ was measured using ammonia-temperature programmed desorption (NH₃-TPD) (Figure S2). The MoO₃ was reduced *in situ* at 350 °C using 125 mL/min of 1:10 v/v H₂:Ar. It can be seen there was some amount of acidity in the fresh catalyst. After reducing for 1 hr, the acidity noticeably decreased.

S5 Detailed Product Distributions

Table S2: Product distribution for multiple injections at a 200 mg MoO₃ catalyst loading in the HDO of cellulose at 400 °C with no prereduction. The xylene yield includes the summation of *p*-, *m*-, and *o*-xylene, and the C₉₊ benzene yield includes the summation of propyl benzene, methyl ethyl benzenes, and diethyl benzenes. All values are reported in C%.

Compound	Cellulose Injection Number									
	1	2	3	4	5	6	7	8	9	10
CO and CO ₂										
CO	10.8	4.3	1.0	0.3	0.2	0.2	0.1	0.1	0.2	0.2
CO ₂	9.5	3.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Oxygenates										
Oxygenates	28.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₁ - C ₆										
Methane	0.7	2.1	3.4	3.1	3.5	3.0	3.7	3.5	3.6	4.2
Ethane	0.0	1.4	9.2	8.1	9.7	10.8	10.5	11.9	11.7	11.5
Ethylene	0.7	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0
Propane	0.2	6.8	8.4	9.3	11.0	9.1	10.3	10.7	11.0	10.4
Propylene	0.6	1.1	0.1	0.1	0.2	0.0	0.1	0.1	0.1	0.1
<i>i</i> -Butane	0.1	1.0	2.5	3.1	2.3	2.2	3.0	2.8	3.0	2.5
<i>n</i> -Butane	0.1	11.3	13.9	14.1	13.9	13.0	12.4	11.7	11.1	13.2
<i>i</i> -Pentane	1.1	4.1	8.7	9.0	7.9	8.6	6.6	7.6	6.4	5.3
<i>n</i> -Pentane	1.2	13.6	14.2	12.1	9.5	8.6	6.9	5.8	4.2	3.7
<i>n</i> -Hexane	0.1	3.8	1.4	1.2	0.9	0.3	0.3	0.0	0.2	0.0
Aromatics										
Benzene	0.7	3.3	7.9	7.9	7.4	7.3	6.8	5.5	5.9	6.3
Toluene	1.6	2.0	4.8	5.5	4.1	4.6	4.4	2.6	2.5	0.5
Ethyl Benzene	0.0	0.5	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Xylene	0.2	1.2	1.4	0.6	0.0	0.0	0.0	0.0	0.0	0.0
C ₉₊ Benzene	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Naphthalene	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total C (%)	65.5	70.2	86.7	84.6	80.8	77.7	75.3	72.5	70.1	67.9
H ₂										
Consumption (g _{H₂} /g _{feed})	0.01	0.10	0.15	0.14	0.14	0.13	0.13	0.13	0.12	0.12

Table S3: Product distribution for multiple injections at a 200 mg MoO₃ catalyst loading in the HDO of cellulose at 400 °C with a 1 hr prereduction. The xylene yield includes the summation of *p*-, *m*-, and *o*-xylene, and the C₉₊ benzene yield includes the summation of propyl benzene, methyl ethyl benzenes, and diethyl benzenes. All values are reported in C%.

Compound	Cellulose Injection Number			
	1	2	3	4
CO and CO ₂				
CO	5.4	1.1	0.3	0.5
CO ₂	2.8	0.1	0.1	0.3
Oxygenates				
Oxygenates	0.0	0.0	0.0	0.0
C ₁ - C ₆				
Methane	3.9	4.2	3.3	3.3
Ethane	1.9	4.8	6.5	7.3
Ethylene	0.8	0.2	0.3	0.1
Propane	6.3	9.0	8.8	8.8
Propylene	1.4	0.3	0.4	0.0
<i>i</i> -Butane	1.2	0.9	1.9	0.3
<i>n</i> -Butane	11.7	13.0	16.7	16.4
<i>i</i> -Pentane	7.0	3.5	5.8	5.5
<i>n</i> -Pentane	14.1	15.7	14.5	12.2
<i>n</i> -Hexane	2.2	4.3	3.9	3.1
Aromatics				
Benzene	4.5	3.5	4.5	2.7
Toluene	2.1	2.3	3.4	2.5
Ethyl Benzene	0.5	0.4	0.3	0.1
Xylene	1.6	1.6	1.7	1.2
C ₉₊ Benzene	0.8	0.8	0.6	0.1
Naphthalene	0.2	0.1	0.0	0.0
Coke	23.6	9.3	3.3	0.0
Total C (%)	100.2	85.4	86.5	74.6
H ₂				
Consumption (g _{H₂} /g _{feed})	0.12	0.13	0.14	0.13

Table S4: Product distribution for multiple injections at a 200 mg MoO₃ catalyst loading in the HDO of lignin at 400 °C with a 1 hr prereduction. The xylene yield includes the summation of *p*-, *m*-, and *o*-xylene, and the C₉₊ benzene yield includes the summation of propyl benzene, methyl ethyl benzenes, and diethyl benzenes. All values are reported in C%.

Compound	Lignin Injection Number			
	1	2	3	4
CO and CO ₂				
CO	1.7	0.1	0.0	0.0
CO ₂	2.4	0.0	0.1	0.0
Oxygenates				
Oxygenates	0.0	0.0	0.0	0.0
C ₁ - C ₆				
Methane	6.8	6.3	6.0	6.6
Ethane	0.3	3.1	4.2	3.4
Ethylene	0.1	0.1	0.1	0.0
Propane	1.7	3.4	2.4	1.7
Propylene	0.3	0.1	0.0	0.1
<i>i</i> -Butane	0.5	0.8	0.6	0.5
<i>n</i> -Butane	1.0	1.7	1.9	1.4
<i>i</i> -Pentane	1.0	1.5	1.2	1.3
<i>n</i> -Pentane	1.4	1.5	1.9	1.9
<i>n</i> -Hexane	0.8	0.2	0.9	0.8
Aromatics				
Benzene	2.7	8.9	3.4	4.6
Toluene	4.1	7.1	4.5	6.0
Ethyl Benzene	3.5	0.3	4.1	4.2
Xylene	1.5	1.0	1.7	1.0
C ₉₊ Benzene	2.2	0.0	1.5	2.2
Naphthalene	0.1	0.0	0.1	0.2
Coke	13.8	3.3	6.3	0.0
Total C (%)	98.4	94.5	94.2	88.7
H ₂				
Consumption (g _{H₂} /g _{feed})	0.05	0.06	0.06	0.06

Table S5: Product distribution for multiple injections at a 200 mg MoO₃ catalyst loading in the HDO of corn stover at 400 °C with a 1 hr prereduction. The xylene yield includes the summation of *p*-, *m*-, and *o*-xylene, and the C₉₊ benzene yield includes the summation of propyl benzene, methyl ethyl benzenes, and diethyl benzenes. All values are reported in C%.

Compound	Corn Stover Injection Number			
	1	2	3	4
CO and CO ₂				
CO	5.0	4.6	1.9	0.4
CO ₂	10.4	2.7	0.2	0.0
Oxygenates				
Oxygenates	0.0	0.0	0.0	0.0
C ₁ - C ₆				
Methane	3.3	8.1	7.4	9.6
Ethane	0.9	1.5	8.7	9.7
Ethylene	0.4	0.2	0.3	0.0
Propane	3.9	6.5	7.1	6.6
Propylene	2.5	0.8	0.2	0.0
<i>i</i> -Butane	0.1	1.0	0.8	1.0
<i>n</i> -Butane	3.7	5.2	5.6	6.2
<i>i</i> -Pentane	0.8	2.3	3.0	2.5
<i>n</i> -Pentane	2.3	4.6	4.6	5.5
<i>n</i> -Hexane	0.3	0.8	0.5	0.6
Aromatics				
Benzene	1.2	2.2	3.0	2.9
Toluene	2.4	3.6	3.9	3.8
Ethyl Benzene	1.3	1.9	1.9	1.3
Xylene	1.2	1.6	1.7	1.6
C ₉₊ Benzene	1.4	1.4	0.8	0.5
Naphthalene	0.1	0.1	0.0	0.0
Coke	18.4	3.0	4.0	0.0
Total C (%)	101.7	95.0	98.4	94.2
H ₂				
Consumption (g _{H₂} /g _{feed})	0.05	0.08	0.10	0.11

References

- [1] Jing Zhang, Michael W. Nolte, and Brent H. Shanks. Investigation of primary reactions and secondary effects from the pyrolysis of different celluloses. *ACS Sustainable Chemistry & Engineering*, 2(12):2820–2830, 2014.