ELECTRONIC SUPPLEMENTARY INFORMATION

Hydrodeoxygenation of Cellulose Pyrolysis Model Compounds using Molybdenum Oxide and Low Pressure Hydrogen

Michael W. Nolte, Alireza Saraeian 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 Tandem Micropyrolyzer

To elaborate on the details provided in the main article, the tandem micropyrolyzer is essentially two reactors in series. Feed is introduced into the top reactor where it is pyrolyzed or volatilized in a H_2 atmosphere. The vapors are swept into the second reactor containing a fixed catalyst bed. The effluent from the catalyst bed is swept in the gas chromatograph (GC) for separation and analysis. For liquid feedstocks, a syringe was filled with 0.2 μL of model compound and then directly injected into the top reactor through a septum. Solid feedstock was loaded into stainless steel sample cups, which could then be placed into the reactor. For cellulose, a typical sample mass was around 300 μg, while for the model compounds (glycolaldehyde, 5-hydroxymethylfurfural, and levoglucosan) the sample was 150-200 μg. The cups were held above the reactor for at least 30 seconds to purge out any air. After purging, the cups were dropped by gravity into the top reactor. The gas flow rate through the reaction system was maintained at 120 mL/min H_2.

A GC-MS/TCD/FID (Agilent 7890B GC, Agilent 5977A Mass Selective Detector, Thermal Conductivity Detector, Flame Ionization Detector) system was used for product identification and quantification. The GC oven program was as follows: 1) hold for 7.5 min at 30 °C, 2) ramp at 10 °C/min to 300 °C. The MS and FID were used for the identification and quantification of condensable oxygenates and aromatic hydrocarbons and GC separation was achieved using a medium polarity DB-1701 column (Agilent VF-1701ms, 0.25 mm × 60 m). The light hydrocarbons (alkanes and alkenes) were separated using a GS-Gaspro column (Agilent GS-Gaspro, 0.32 mm × 60 m) and quantified using the TCD. The light hydrocarbons were identified using pure gas standards.

Fixed catalyst beds were constructed by loading a measured amount of MoO_3 and sand into quartz tubes (3 mm ID). Quartz wool was used to secure the beds in place.

S1.2 Coke Measurement

Coke yield was measured by quantifying the CO_2 generated during an oxidative treatment of post-reaction catalyst beds. The coke measurement was performed *in situ* using the tandem micropyrolyzer system. After a reaction, the carrier gas was switched from H_2 to 60 mL/min

He. After H_2 had been fully purged from the GC system, 1 mL/min of air was introduced into the reactor through a secondary gas inlet located in between the two reactors. During the oxidative treatment, the catalyst bed temperature was ramped up to 550 °C to ensure all soft and hard coke would be oxidized. The CO_2 yield was quantified by tracking the mass fragment of 44 m/z with the MS.

S2 Detailed Product Distributions

Table S1: Product distribution from the hydrodeoxygenation of cellulose pyrolysis vapors over MoO_3 at different MoO_3:cellulose mass loadings. Reaction conditions: 120 mL/min H_2, 300 μg cellulose, 500 °C pyrolysis, 400 °C catalyst bed, catalyst pre-reduced 1 hr. The C_8 aromatic yield includes the summation of ethylbenzene and p-, m-, and o-xylene, and the C_{9+} aromatic yield includes the summation of propyl benzene, methyl ethyl benzenes, diethyl benzenes, and naphthalene. The oxygenates yield includes all products which contained at least one oxygen atom (excluding CO and CO_2). All values are reported in C%.

Compound	Catalyst:Cellulose Mass Ratio			
	2:1	10:1	20:1	200:1
CO	5.0	4.8	4.1	4.2
CO_2	3.2	2.7	2.9	4.5
Methane	1.2	1.8	3.3	0.7
Ethane	0.5	3.4	4.0	2.0
Propane	0.1	0.9	3.5	15.9
i-Butane	0.0	0.1	0.4	3.8
n-Butane	0.5	1.4	3.7	10.0
Pentanes	0.9	2.3	7.6	20.5
Hexanes	0.4	1.8	6.7	5.0
C_5-C_6 cyclic alkanes	0.1	0.5	2.4	8.9
Ethylene	0.9	4.5	2.9	0.0
Propylene	1.6	5.0	5.4	0.0
1-Butene	0.7	1.2	1.2	0.0
$trans$-2-Butene	0.7	2.1	3.0	0.0
cis-2-Butene	0.3	1.4	1.6	0.0
Pentenes	1.0	3.1	2.0	0.0
Hexenes	2.6	23.0	16.4	0.0
C_5-C_6 cyclic alkenes	2.2	6.2	3.5	0.0
Benzene	0.6	2.0	2.7	8.2
Toluene	0.5	1.7	2.0	4.2
C_8 Aromatics	0.3	1.9	2.6	1.5
C_{9+} Aromatics	0.8	8.3	8.1	0.0
Oxygenates	48.4	8.7	0.0	0.0
Total	72.5	88.8	89.9	89.2

Table S2: Product distribution of the oxygenated compounds from the hydrodeoxygenation of cellulose pyrolysis vapors over MoO_3 at different MoO_3:cellulose mass loadings. Reaction conditions: 120 mL/min H_2, 300 μg cellulose, 500 °C pyrolysis, 400 °C catalyst bed, catalyst pre-reduced 1 hr. The oxygenates yield includes all products which contained at least one oxygen atom (excluding CO and CO_2). All values are reported in C%.

	Catalyst:Cellulose Mass Ratio			
Compound	2:1	10:1	20:1	200:1
Oxygenates	48.4	8.7	0.0	0.0
Formaldehyde	1.1	0.0	0.0	0.0
Acetaldehyde	4.3	0.3	0.0	0.0
Furan	0.5	0.5	0.0	0.0
Acetone	3.0	0.5	0.0	0.0
Methyl furan	2.9	2.0	0.0	0.0
2-Butanone	1.2	0.3	0.0	0.0
Glycolaldehyde	0.1	0.0	0.0	0.0
2,5-dimethylfuran	4.4	4.5	0.0	0.0
1-methyl-2-Cyclohexen-1-ol	0.5	0.0	0.0	0.0
2-Pentanone	0.9	0.2	0.0	0.0
Acetic acid	2.4	0.0	0.0	0.0
Hydroxyacetone	0.4	0.0	0.0	0.0
3-Penten-2-one	1.0	0.0	0.0	0.0
3-Hexanone	1.0	0.2	0.0	0.0
5-Hexen-2-one	0.8	0.0	0.0	0.0
Cyclopentanone	2.2	0.0	0.0	0.0
2(5H)-Furanone	1.0	0.0	0.0	0.0
2-methylcyclopentanone	1.3	0.0	0.0	0.0
3-Hexen-2-one	1.0	0.0	0.0	0.0
3-Methylcyclopentanone	0.6	0.0	0.0	0.0
2-Cyclopenten-1-one	5.3	0.0	0.0	0.0
Furfural	0.5	0.0	0.0	0.0
2-Propylfuran	0.9	0.0	0.0	0.0
2-methyl-2-Cyclopenten-1-one	4.5	0.0	0.0	0.0
2-Acetylfuran	2.1	0.0	0.0	0.0
5-methylfurfural	0.9	0.0	0.0	0.0
3-methyl-2-Cyclopenten-1-one	3.2	0.0	0.0	0.0
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.5	0.1	0.0	0.0

Table S3: Oxygenate product distribution from the hydrodeoxygenation of cellulose pyrolysis model compounds over MoO_3. Reaction conditions: 120 mL/min H_2, 0.2 μL or 150-200 μg feed injection, 0.8 mg MoO_3, 400 °C catalyst bed, catalyst pre-reduced 1 hr.

Furfural		HMF	
Product	Yield (C%)	Product	Yield (C%)
Furan	3.4	2-Methylfuran	5.0
2-Methylfuran	45.9	2,5-Dimethylfuran	33.9
C_{10} Condensation	0.4	5-Methylfurfural	1.4
Oxygenates	49.7	Oxygenates	40.3

MG		GA	
Product	Yield (C%)	Product	Yield (C%)
Acetaldehyde	5.2	Acetaldehyde	22.9
Propanal	9.4	Furan	3.4
Acetone	58.7	Acetone	3.4
Oxygenates	73.3	Oxygenates	29.7

S3 X-Ray Diffraction (XRD)

XRD experiments were performed using a Siemens D500 X-Ray diffractometer operated from 10-90 2θ (Figure S1). It can be seen that after one cellulose pulse, the bulk catalyst is predominately MoO_3. However, after the fourth cellulose injection, the bulk catalyst is reduced to MoO_2. Similar results have been reported in the literature by Prasomsri *et al.*, whereby by MoO_3 is reduced to MoO_2 at longer time on stream (*Energy & Environmental Science*, 2014, **7**, 2660–2669).
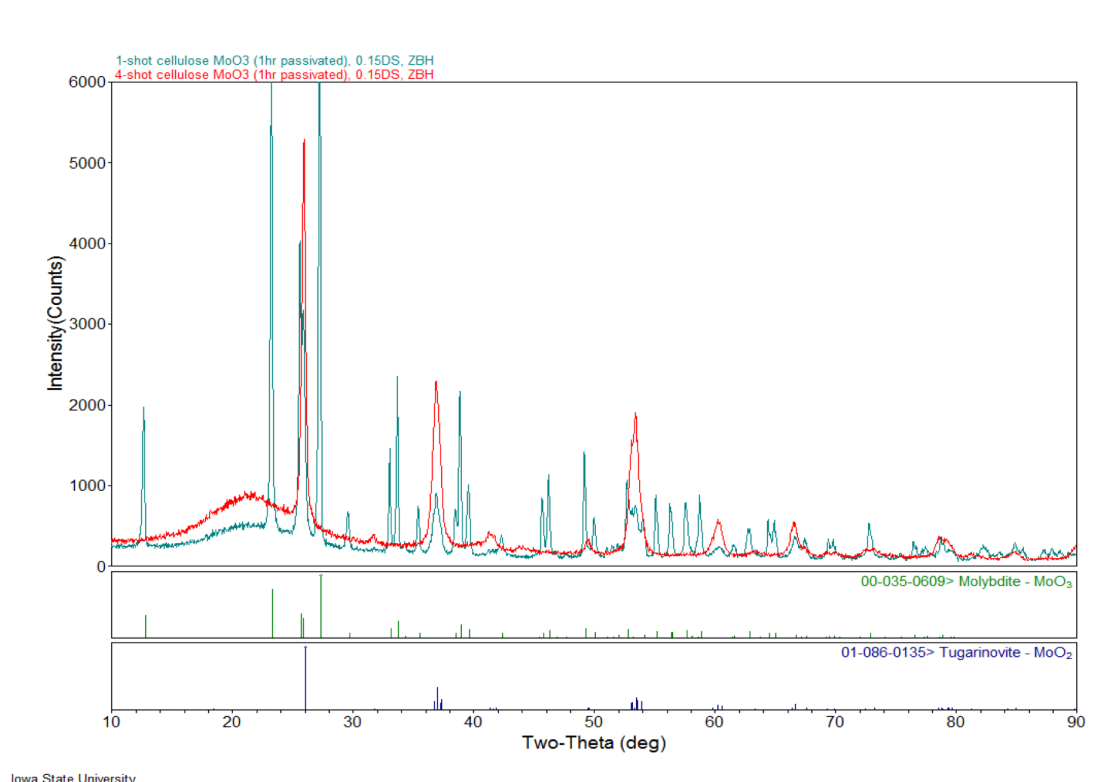

Figure S1: X-Ray diffractograms of used MoO_3 catalyst after 1 and 4 cellulose injections. Reaction conditions: 120 mL/min H_2, 300 μg cellulose injection, 60 mg MoO_3, 400 °C catalyst bed, catalyst pre-reduced 1 hr.