Electronic Supplementary Information for

Catalytic deoxygenation during cellulose fast pyrolysis using acid-base bifunctional catalysis

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Product analysis

The conditions for the online product analysis were: a) temperature of GC injector set at 300 ˚C; b) temperature ramp consisting of an initial hold at 35 ˚C for 3 minutes, then ramping to 300 ˚C at a rate of 5 ˚C/min followed by a hold at 300 °C for 4 minutes; and c) constant column flow rate of 1 ml/min. The flow rate through the reactor was controlled by the split ratio. A capillary column of ZB 1701 (60 m × 0.250 mm and 0.250 µm film thickness) was used to separate the condensable products. For simultaneous identification and quantification, two identical ZB 1701 columns were used. One was connected to a MS (5975C, Agilent Technologies, USA) for product identification and the other one was connected to an FID for product quantification. The calibration method for the condensable vapor products was described in a previous publications.[1] A Porous Layer Open Tubular (PLOT) column (60 m x 0.320 mm) (GS-GasPro, Agilent, USA) was used to separate non-condensable gas (NCG) products, which were then quantified by TCD. The NCG products in the current study include CO, CO_2, C_2H_4 and C_3H_6. A standard gas mixture (Praxair, USA) consisting of CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and C_4H_8 was used for the calibration.

Deoxygenation over serpentine with different loadings

Table S1 shows the product distribution from cellulose catalytic pyrolysis over serpentine 1M at different loadings. Significant deoxygenation did not occur unless a minimum catalyst to cellulose loading of 2.52:1 was used. Among the cases examined, the highest yield of condensed vapor products was observed at a loading of 3.86:1.

Table S1. Product distribution from cellulose fast pyrolysis over serpentine 1M at different loadings.

Products[a]	Serpentine 1M[b]	Serpentine 1M[c]	Serpentine 1M[d]	Serpentine 1M[e]
Formaldehyde	0.42	0.62	0.85	1.17
Acetaldehyde	2.96	5.38	7.08	8.22
Furan	0.65	1.01	1.34	1.66
Propenal	0.61	0.88	1.14	1.22
Acetone	0.37	0.75	1.03	1.50
Methylglyoxal	2.79	1.91	1.69	1.04
2-methyl furan	0.35	0.64	0.86	0.97
Methyl vinyl ketone	2.41	3.19	4.45	4.16
Glycolaldehyde	4.69	0.99	1.25	1.12
Acetic acid	0.27	0.95	0.93	0.34
Acetol	0.85	0.74	0.59	0.68
Furfural	2.90	3.87	4.85	3.27
2 furanmethanol	0.48	0.85	0.51	0.27
3 furanmethanol	0.19	0.93	0.98	1.18
2-hydroxy cyclopent-2-en-1-one	1.01	0.96	0.77	0.33
5-methyl furfural	1.73	2.77	3.22	2.06
2(5H) furanone	0.27	0.39	0.39	0.29
MW 114 DAXP 2	0.52	0.00	0.06	0.40
Methyl cyclopentenolone	0.31	0.35	0.29	0.08
Other DAXP 2	0.55	0.38	0.00	0.06
Levoglucosenone	0.37	0.30	0.19	0.27
Cyclic hydroxy lactone	4.04	1.65	1.19	0.04
1,4,3,6-dianhydro-a-d-glucopyranose	0.47	0.14	0.15	0.01
5-hydroxy methyl furfural	1.12	0.21	0.06	0.04
Dianhydro glucopyranose	0.52	0.16	0.16	0.10
Other AXP	0.09	0.05	0.06	0.07
Levoglucosan	6.62	0.14	0.10	0.07
Levoglucosan-furanose	0.46	0.04	0.00	0.02
MW 86[f]	1.36	0.80	0.80	0.32
$C_6H_8O_4$_1[f]	0.10	0.00	0.00	0.25
$C_6H_8O_4$_2[f]	0.00	0.05	0.09	0.06
$C_6H_8O_4$_3[f]	0.17	0.12	0.09	0.18

$C_4H_6O_2$[f]	0.28	0.27	0.26	0.24
C_6H_6O[f]	0.18	0.21	0.23	0.21
$C_6H_6O_2$[f]	0.18	0.32	0.19	0.17
$C_5H_4O_2$[f]	0.35	0.64	0.74	0.67
$C_6H_{10}O$[f]	0.12	0.22	0.23	0.21
$C_6H_6O_2$[f]	0.42	0.68	0.67	0.60
$C_5H_4O_2$[f]	0.08	0.34	0.33	0.30
$C_5H_4O_2$[f]	0.16	0.39	0.32	0.29
$C_5H_6O_2$[f]	0.08	0.10	0.13	0.12
$C_6H_6O_2$[f]	0.00	0.19	0.21	0.18
C_6H_6O[f]	0.00	0.50	0.57	0.51
$C_6H_4O_3$[f]	0.05	0.07	0.09	0.08
$C_5H_6O_2$[f]	0.19	0.62	0.55	0.50
$C_{10}H_6O_2$[f]	0.00	0.00	0.04	0.04
Ethylene	0.11	0.19	0.30	0.38
Propene	0.24	0.42	0.57	0.72
CO	4.18	7.18	6.24	7.64
CO_2	7.41	10.06	10.59	11.04
Char+coke	31.24	42.96	39.05	41.17
Overall vapor products[g]	42.11	36.40	40.63	36.65
Summation	84.95	96.60	96.51	96.51
Oxygen content of vapor products	41.87	35.76	35.01	34.16
H/C_{eff}	0.24	0.44	0.50	0.60
HHV	18.98	22.53	23.16	23.83

a. all yields are in terms of carbon; b. catalyst loading: 1.12:1; c. catalyst loading: 2.52:1; d. catalyst loading: 3.86:1; e. catalyst loading: 5.08:1; f. molecular weight determined by MS; and g. CO, CO_2 and water not included.

Deoxygenation over different acid, base, acid-base bi-functional materials

Table S2. Product distribution from cellulose fast pyrolysis over acid and base materials with the same total acid and/or total base amount.

Products[a]	Serpentine 1M[b]	Silica-alumina[c]	Strong acid[d]	HA MgO[e]	HA CaO[f]	Strong acid /HA MgO[g]
Formaldehyde	0.85	0.20	0.42	0.27	0.76	0.54
Methanol	-	-	-	-	0.51	0.85
Acetaldehyde	7.08	2.11	1.27	2.49	2.34	4.58
Furan	1.34	0.88	0.59	0.17	0.26	0.51
Propenal	1.14	0.45	0.30	0.63	0.38	0.68
Acetone	1.03	0.20	0.20	0.31	0.33	0.63
Methylglyoxal	1.69	1.50	0.65	2.02	1.80	2.50
2-methyl furan	0.86	0.41	0.20	0.13	0.11	0.29
Methyl vinyl ketone	4.45	1.17	0.84	1.42	1.60	3.64
Glycolaldehyde	1.25	2.90	1.47	6.13	8.35	2.81
Acetic acid	0.93	0.49	0.38	0.27	0.43	0.51
Acetol	0.59	0.29	0.17	1.43	2.05	1.76
MW 86[h]	0.80	1.69	2.39	0.40	1.04	1.18
Furfural	4.85	2.80	2.07	0.95	0.81	2.16
2 furanmethanol	0.51	0.17	0.41	0.20	0.23	0.51
3 furanmethanol	0.98	0.12	0.05	0.13	0.26	0.32
2-hydroxy cyclopent-2-en-1-one	0.77	0.51	0.32	0.87	1.32	1.40
5-methyl furfural	3.22	0.54	0.07	0.21	0.17	1.01
2(5H) furanone	0.39	0.18	0.06	0.25	0.43	0.42
MW 114 DAXP 2	0.06	0.30	1.16	0.06	0.11	0.20
Methyl Cyclopentenolone	0.29	0.12	0.11	0.56	0.34	0.40
Other DAXP 2	0.00	0.08	0.42	0.06	0.18	0.20
Levoglucosenone	0.19	0.54	17.46	0.14	0.12	0.35
Cyclic hydroxy lactone	1.19	1.73	1.93	2.15	2.04	3.92
$C_6H_8O_4$_1[h]	0.00	0.00	0.07	0.00	0.24	0.12
$C_6H_8O_4$_2[h]	0.09	0.00	0.19	0.34	0.43	0.38
$C_6H_8O_4$_3[h]	0.09	0.00	0.34	0.58	0.54	0.34
1,4,3,6-dianhydro-a-d-	0.15	0.23	2.93	0.28	0.32	0.45

glucopyranose						
5-hydroxy methyl furfural	0.06	0.19	0.61	0.75	0.92	1.19
Dianhydro glucopyranose	0.16	0.30	2.27	0.05	0.15	0.07
Other AXP	0.06	0.41	0.35	0.49	0.18	0.08
Levoglucosan	0.10	2.25	5.81	23.09	18.04	3.01
Levoglucosan-furanose	0.00	0.31	0.30	1.04	0.57	0.04
$C_4H_6O_2$[h]	0.26	-	-	-	-	-
C_6H_6O[h]	0.23	-	-	-	-	-
$C_6H_6O_2$[h]	0.19	-	-	-	-	-
$C_5H_4O_2$[h]	0.74	-	-	-	-	-
$C_6H_{10}O$[h]	0.23	-	-	-	-	-
$C_6H_6O_2$[h]	0.67	-	-	-	-	-
$C_5H_4O_2$[h]	0.33	-	-	-	-	-
$C_5H_4O_2$[h]	0.32	-	-	-	-	-
$C_5H_6O_2$[h]	0.13	-	-	-	-	-
$C_6H_6O_2$[h]	0.21	-	-	-	-	-
C_6H_6O[h]	0.57	-	-	-	-	-
$C_6H_4O_3$[h]	0.09	-	-	-	-	-
$C_5H_6O_2$[h]	0.55	-	-	-	-	-
$C_{10}H_6O_2$[h]	0.04	-	-	-	-	-
Ethylene	0.30	0.12	0.14	0.18	0.15	0.29
Propene	0.57	0.16	0.12	0.00	0.17	0.37
CO	6.24	4.79	3.63	2.85	1.52	4.25
CO_2	10.59	4.96	5.78	5.82	1.74	10.25
Char+coke	39.03	36.61	24.63	25.44	34.08	32.00
Overall vapor products[g]	40.63	23.33	46.07	50.81	47.67	37.69
Summation	96.50	69.70	80.12	82.17	85.01	84.19
Oxygen content of vapor products	35.01	41.59	41.40	46.64	46.28	40.07
H/C_{eff}	0.50	0.23	0.08	0.15	0.19	0.42
HHV	23.16	19.13	18.53	16.71	16.95	20.53

a. all yields are in terms of carbon; b. catalyst loading: 3.86:1; c. catalyst loading: 0.93:1; d. catalyst loading: 2.07:1; e. catalyst loading: 1.26:1; f. catalyst loading: 1.03:1; g. catalyst loading: 2.07/1.26:1; h. molecular weight determined by MS; and g CO, CO_2 and water not included

Deoxygenation over transitional metal materials

Table S3. Product distribution from cellulose fast pyrolysis over transitional metal materials

Products[a]	MoO_3[b]	$FeSO_4.7H_2O$[c]	Fe_2O_3[d]
Formaldehyde	0.29	0.29	0.30
Acetaldehyde	1.46	1.13	3.51
Furan	0.90	0.51	0.25
Propenal	0.50	0.29	0.55
Acetone	0.66	0.23	0.57
Methylglyoxal	0.64	0.57	1.49
2-methyl furan	0.10	0.21	0.17
Methyl vinyl ketone	0.83	1.14	2.44
Glycolaldehyde	4.99	1.35	2.65
Acetic acid	0.05	0.31	2.04
Acetol	0.21	0.20	1.35
MW 86	1.26	1.29	0.46
Furfural	1.30	2.86	0.96
2 furanmethanol	0.51	0.43	0.30
3 furanmethanol	0.16	0.09	0.47
2-hydroxy cyclopent-2-en-1-one	0.09	0.30	1.40
5-methyl furfural	0.48	0.80	0.54
2(5H) furanone	0.21	0.18	0.38
MW 114 DAXP 2	0.39	0.83	0.05
Methyl cyclopentenolone	0.39	0.10	0.58
Other DAXP 2	0.20	0.47	0.20
Levoglucosenone	2.09	12.75	0.32
Cyclic hydroxy lactone	1.52	1.65	1.54
$C_6H_8O_4$_1	0.18	0.02	0.15

$C_6H_8O_4$_2	0.31	0.25	0.16
$C_6H_8O_4$_3	0.44	0.53	0.13
1,4,3,6-dianhydro-a-d-glucopyranose	1.70	2.15	0.39
5-hydroxy methyl furfural	0.34	0.20	1.00
Dianhydro glucopyranose	1.46	1.61	0.01
Other AXP	0.26	0.57	0.03
Levoglucosan	15.18	11.28	7.97
Levoglucosan-furanose	0.25	0.68	0.24
Overall vapor products	39.53	45.28	32.58
Oxygen content of vapor products[e]	45.46	42.67	43.27
H/C_{eff}	0.13	0.08	0.29
HHV	17.05	17.96	18.68

a. all yields are in terms of carbon; b. catalyst loading: 4.45:1; c. catalyst loading: 3.66:1; d. catalyst loading: 3.87:1; e. CO, CO_2 and water not included.

It was reported that MoO_3 was active in atmospheric hydrodeoxygenation of cellulose or lignin pyrolysis derived oxygenates with unsaturated hydrocarbons formed during hydrodeoxygenation.[2] In the current study, MoO_3 was used as catalyst for cellulose fast pyrolysis. However, the results showed only a small amount of deoxygenation and a sacrifice of about half of the vapor products, which suggested the presence of hydrogen was necessary for MoO_3 to be effective in the oxygen removal. Iron in acid treated olivine, which might be in oxide or sulfate form, was proposed to be active sites for deoxygenation during biomass fast pyrolysis.[3] In the current study, both Fe_2O_3 and $FeSO_4$ were tested for catalytic deoxygenation. As shown in Table S3, the Fe_2O_3 and $FeSO_4$ behaved similar as single base or single acid materials, respectively. Their deoxygenation performance was not as promising as the acid-base bifunctional catalyst.

References

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