Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Does the presence of lignin affect the pyrolytic decomposition of cellulose? A condensed phase computational investigation

Arul Mozhi Devan Padmanathan[a], Rahul Vaidya[a] and Samir H Mushrif [a*]

*Email: mushrif@ualberta.ca

[a] Department of Chemical and Materials Engineering, University of Alberta, 9211-116 Street Northwest, Edmonton, Alberta T6G 1H9, Canada.

Supporting Information

Content

Literature review

Table S1: Studies that do not show any significant interactions between the biomass components during pyrolysis.

Title	Authors	Year	Equipment	Temperature	Feed	Interactions between biomass components
Pyrolysis characteristics of biomass and biomass components	Raveendran et al.	1995	TG/Packed bed	1000°C (50°C/min)	14 native biomass & synthetic	No interactions. Char, liquid and gas yields match additive model.
Kinetics of Biomass Pyrolysis: a Reformulated Three-Parallel-Reactions Model	Manya et al.	2003	TG	900°C (20°C/min)	Sugarcane bagasse/waste wood (washed & untreated)	No interactions. Weight loss predicts match additive model.
Further Applications of a Revisited Summative Model for Kinetics of Biomass Pyrolysis	Gomez et al.	2004	TG	900°C (20°C/min)	pine, beech, thistle (washed & untreated)	No interactions. Weight loss predicts match additive model.
In-Depth Investigation of Biomass Pyrolysis Based on Three Major Components: Hemicellulose, Cellulose and Lignin	Yang et al.	2005	TG	105°C-900°C (10°C/min)	Synthetic mixture & Palm oil waste	No interactions. Biomass compents were predicted from weight loss measurements by additive model.
TG study on pyrolysis of biomass and its three components under syngas	Wang et al.	2007	TG	300°C-600° C (max 20°C/min)	sawdust	No interactions. Weight loss predicted by additive model. Lumped activation energy for native biomass within the range of its components.
TGA and macro-TGA characterisation of biomass fuels and fuel mixtures	Skreiberg et al.	2010	TG and macro-TG	60°C-900°C (max 100°C/min)	Wood, coffe waste, demolition wood and mixtures	No interactions. Combustion characteristics and gas yields showed qualitative additive behaviour.
Experimental Study of Biomass Pyrolysis Based on Three Major Components: Hemicellulose, Cellulose, and Lignin	Qu et al.	2011	Tube furnace	350°C-600° C	rice straw, corn stalk, peanut vine	No interactions. Char, gas and bio-oil yield trends are predicted by additive model.
Thermogravimetric Pyrolysis and Gasification of Lignocellulosic Biomass and Kinetic Summative Law for Parallel Reactions with Cellulose, Xylan, and Lignin,	Yoon et al.	2012	TG-GC	140°C-900°C (10°C/min)	Conifers & synthetic	No interactions. Total gas yields and carbon coversion predicted by addditive model.
Relationship between thermal behaviour of lignocellulosic components and properties of biomass	Pang et al.	2014	TG	900°C (10°C/min)	11 native biomass & Synthetic	No interactions. Peak decomposition temperature and weight loss predicted by additive model.

Table S2: Studies that show interactions between the biomass components during pyrolysis.

Title	Authors	Year	Equipment	Temperature	Feed	Interactions between biomass components
Influence of inorganic matter on wood pyrolysis at gasification temperature	Hosoya et al.	2007	Glass tubular furface	800°C	Cedar (washed & untreated)	Yes. Hydrolysable sugar (yield and MW) affected.
The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis	Demirbas et al.	2007	Electrically heated tubular furnace	352°C-552°C (10°C/s)	Olive husk, hazelnut shells, spruce and beech wood	Yes. Drastic change in LGA product yields.
Solid/liquid- and vapor-phase interactions between cellulose- and lignin-derived pyrolysis products	Hosoya et al.	2009	Ampoule reactor	600°C	Synthetic	Yes. Change in tar, water and char yields.
Influence of the interaction of components on the pyrolysis behavior of biomass,	Wang et al.	2011	TG-FTIR	300°C-800°C	Synthetic	Yes. Extended LGA formation temperature range, 2-furfural and acetic acid yields change.
Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin?	Couhert et al.	2011	Electrically heated flow reactor	950°C	Synthetic & native (beech, spruce, ricehusk, wood bark, grass)	Yes. Gas (CO, CO2, CH4, H2, C2H2, C2H4) yields cannot be predicted by additive model.
Pyrolytic Reactions of Lignin within Naturally Occurring Plant Matrices: Challenges in Biomass Pyrolysis Modeling Due to Synergistic Effects	George et al.	2014	Wire mesh pyrolysis	400°C-900°C (1°C/s &1000°C/s)	Synthetic & native (silver berchwood, sugarcane baggase)	Yes. Char yields are altered.
Cellulose-Lignin interactions during slow and fast pyrolysis	Hilbers et al.	2015	TGA/Py-GC-MS	350°C & 500°C	Synthetic	Yes. Enhanced LGA and reduced dehydration reactions.
Cellulose−Hemicellulose and Cellulose−Lignin Interactions during Fast Pyrolysis	Zhang et al.	2015	Py-GC-MS	500°C	Synthetic & native [Cornstover, pine, red oak, switchgrass (washed + untreated)]	Yes, interctions in herbaceous cellulose-lignin samples. No interactions between synthetic, native cellulose-hemicellulose and woody cellulose-lignin samples.
Cellulose-lignin interactions during fast pyrolysis with different temperatures and mixing methods	Wu et al.	2016	Py-GC-MS	500°C, 600°C & 700°C	Synthetic and native pretreated	Yes, LGA yield promoted while C1-C3 products are inhibited.
Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass,	Yu et al.	2017	Wire mesh reactor	50° C to 900° C(30° C/min)	Spruce, oak, pine	Yes, at high temperatures additive model cannot predict tar, char and other product yields. However at 325°C, no interactions.
Effects of cellulose, hemicellulose and lignin on biomass pyrolysis kinetics	Zhu et al.	2020	TGA	800° C(10° C/min)	Synthetic	Yes, change in decomposition temperature and other kinetic parameters.

Molecule and system visualizations

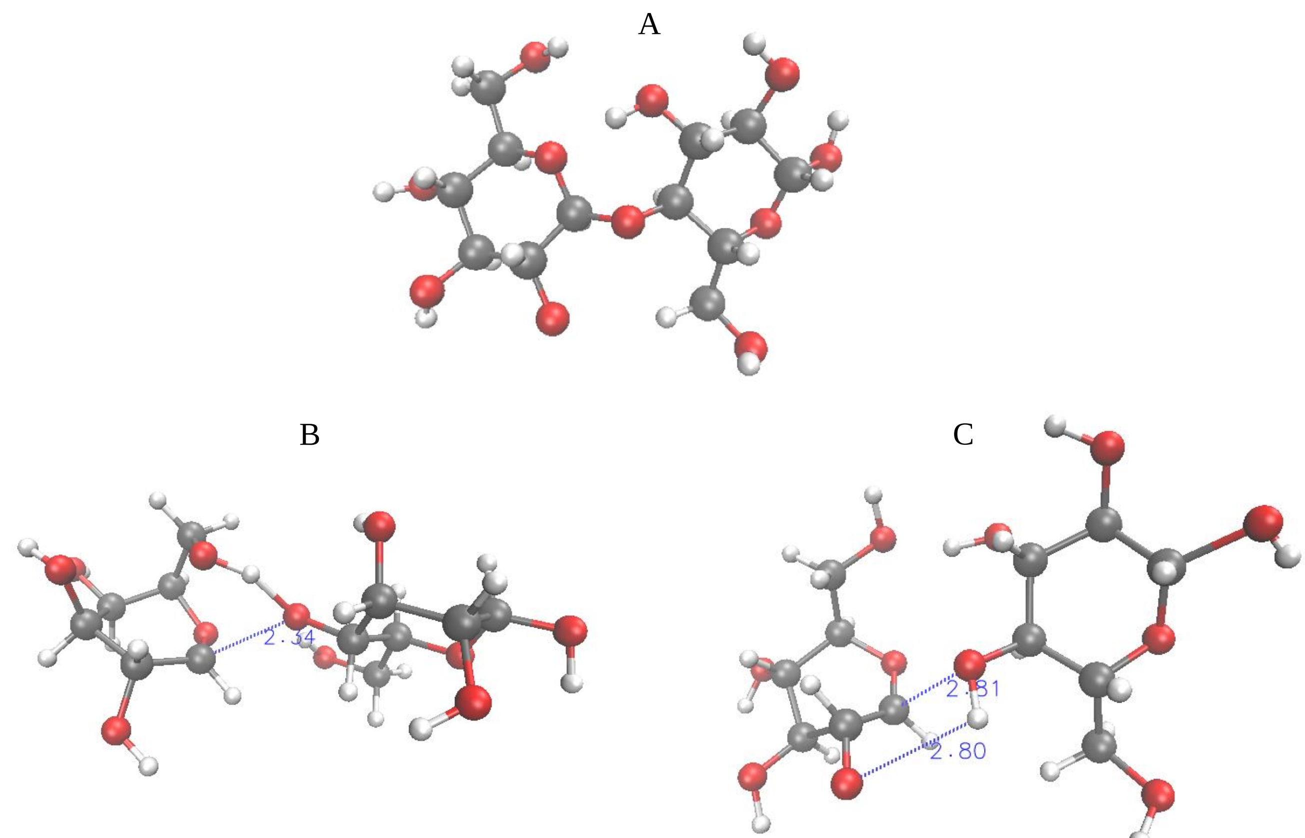


Figure S1: DFT calculated structures of (A) Cellobiose molecule and transition states in gas phase for (B) Transglycosylation (C) Ring contraction mechanisms.

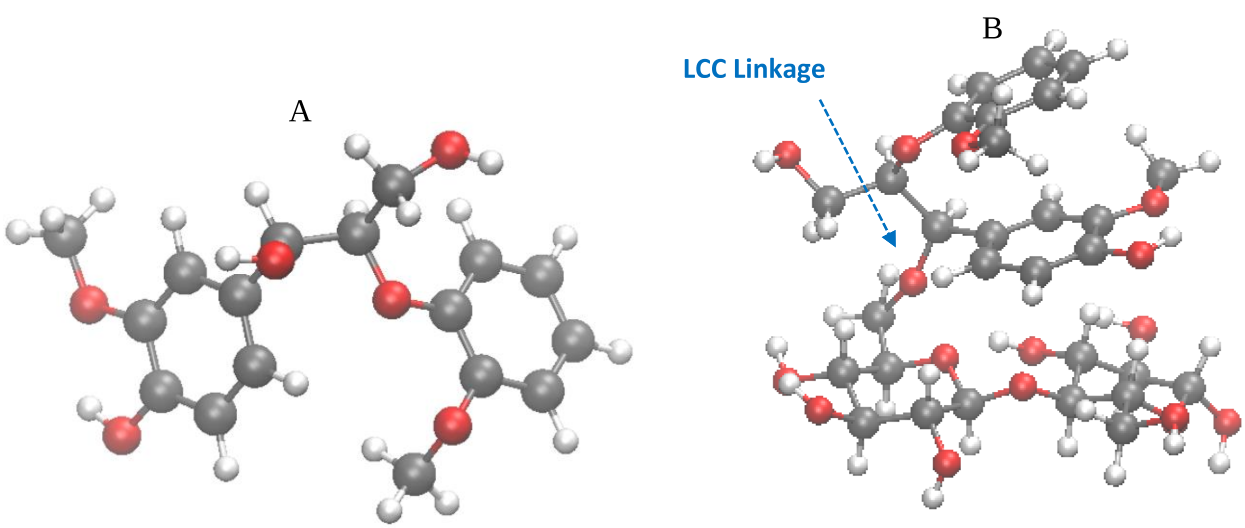


Figure S2: DFT calculated structures of (A) Quinone methide intermediate (lignin dimer) (B) Lignin-Carbohydrate complex (LCC) molecule.

Molecule Coordinates

Cellulose

C	14.95	10.4	14.25
C	19.06	13.32	15.52
C	19.47	14.69	14.99
C	21	14.81	15.02
C	16.38	9.86	14.09
C	16.5	8.33	14.23
C	17.97	7.87	14.07
C	18.89	8.73	14.94
C	18.65	10.21	14.6
C	22.25	11.5	14.13
C	21.36	12.52	14.85
C	19.84	12.24	14.75
H	19.26	13.23	16.59
H	14.54	10.15	15.22
H	19.08	14.84	13.98
H	14.29	9.96	13.51
H	21.37	14.82	16.05
H	16.65	10.07	13.08
H	16.11	8.02	15.19
H	18.26	7.96	13.02
H	18.66	8.57	15.99
H	18.83	10.33	13.52
H	21.88	10.49	14.29
H	22.27	11.68	13.06
H	21.65	12.55	15.89
H	19.59	12.3	13.69
H	15.38	6.91	13.5
H	20.67	16.64	14.85
H	18.48	6.03	13.79
H	15.29	12.23	14.87
H	20.43	8.4	13.75
H	17.52	12.19	15.35
H	23.54	11.17	15.53
H	18.11	15.51	16.12
O	15.75	7.74	13.19
O	21.6	13.8	14.3
O	21.26	16	14.43
O	18.07	6.53	14.5
O	14.94	11.81	14.09

O	20.26	8.39	14.69
O	17.33	10.52	14.94
O	19.55	10.98	15.33
O	17.68	13.13	15.26
O	23.56	11.57	14.67
O	19.02	15.71	15.86

Transition state -Transglycosylation mechanism

C	19.91	13.16	15.78
C	21.01	14.04	15.18
C	20.44	15.44	14.92
C	17.03	9.89	16.19
C	16.7	9.73	14.68
C	16.56	8.28	14.15
C	17.94	7.6	13.91
C	18.92	8.52	13.17
C	18.84	9.92	13.7
C	17.2	14.81	13.48
C	18.29	14.67	14.55
C	18.63	13.22	14.94
H	20.26	12.13	15.83
H	21.89	14.06	15.83
H	16.29	10.54	16.66
H	20.11	15.9	15.86
H	16.98	8.93	16.69
H	15.72	10.19	14.56
H	16.04	8.31	13.19
H	17.84	6.7	13.31
H	19.93	8.18	13.34
H	19.65	10.25	14.35
H	16.87	15.84	13.41
H	17.62	14.56	12.5
H	18.04	15.18	15.47
H	18.78	12.65	14.02
H	21.09	17.14	14.52
H	14.85	7.64	15.04
H	17.56	6.99	15.66
H	17.86	11.26	15.89
H	17.81	9	11.64
H	18.85	13.22	17.4
H	16.02	13.83	14.67
H	20.73	13.98	13.31
O	19.41	15.32	14
O	21.39	16.24	14.39

O	15.81	7.46	15.05
O	18.4	7.21	15.19
O	18.3	10.46	16.45
O	18.64	8.54	11.78
O	17.59	10.47	13.85
O	17.58	12.65	15.71
O	19.62	13.68	17.07
O	16.1	13.96	13.72
O	21.36	13.57	13.9

Transition state – Ring contraction mechanism

C	18.35	13.48	17.76
C	17.14	13.09	16.87
C	17.47	13.28	15.37
C	18.79	12.44	12.46
C	19.16	10.98	12.9
C	18.11	10.09	13.65
C	17.95	8.73	13
C	21.23	9.62	15.28
C	21.13	10.21	13.97
C	20.51	15.27	15.74
C	19.71	13.97	15.66
C	19.64	13.18	16.99
H	18.38	12.91	18.69
H	16.88	12.04	17.03
H	19.48	12.8	11.71
H	17.92	12.35	15.04
H	19	13.14	13.24
H	19.5	10.43	12.02
H	18.41	9.94	14.7
H	17.33	8.64	12.12
H	21.95	8.8	15.31
H	21.97	10.12	13.3
H	20.46	15.79	14.79
H	20.05	15.94	16.47
H	20.23	13.36	14.93
H	20.49	13.45	17.61
H	15.64	13.73	15.18
H	16.82	11.39	13.13
H	17.53	7.15	13.95
H	17.07	13.23	12.82
H	20.45	11.34	16.38
H	17.69	15.22	17.4
H	21.91	14.52	16.87

H	16	13.98	18.14
O	18.39	14.32	15.21
O	16.36	13.49	14.59
O	16.81	10.61	13.66
O	18.34	7.6	13.66
O	17.44	12.71	12.1
O	20.6	9.97	16.28
O	20.28	11.25	13.74
O	19.61	11.76	16.79
O	18.28	14.86	18.06
O	21.87	15.03	16.07
O	16.04	13.91	17.18

Quinone Methide intermediate (Lignin dimer)

C	16.19	15.02	16.99
C	16.22	17.14	16.07
C	16.5	17.32	14.7
C	17.36	18.39	14.32
C	17.87	19.28	15.29
C	17.55	19.11	16.65
C	16.73	18.04	17.04
C	16.14	16.55	12.4
C	15.14	17.57	11.83
C	15.92	15.17	11.73
C	16.74	14	12.27
C	17.72	13.38	11.46
C	18.44	12.27	11.94
C	19.54	11.89	9.85
C	18.19	11.8	13.24
C	17.22	12.4	14.05
C	16.49	13.5	13.56
H	16.74	15.3	17.89
H	16.92	14.66	16.26
H	15.54	14.19	17.24
H	17.64	18.56	13.3
H	18.5	20.1	14.99
H	17.95	19.8	17.38
H	16.49	17.89	18.08
H	17.17	16.81	12.17
H	14.17	17.46	12.31
H	14.97	17.35	10.77
H	14.96	19.4	12.44
H	16.19	15.28	10.68
H	14.46	14.02	11.19

H	17.88	13.76	10.46
H	18.6	11.79	9.3
H	20.25	11.2	9.39
H	19.93	12.9	9.7
H	19.51	10.52	12.96
H	17.01	12.01	15.04
H	15.72	13.95	14.17
O	15.43	16.1	16.48
O	15.93	16.42	13.82
O	15.58	18.9	11.9
O	14.56	14.8	11.74
O	19.39	11.57	11.22
O	18.92	10.74	13.67

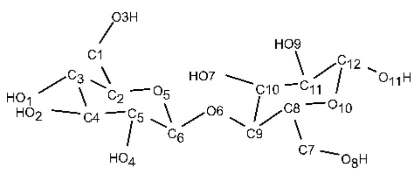
Lignin-carbohydrate complex (LCC) molecule

C	16.25	1.32	2.45
C	18.27	2.59	2.9
C	19.05	3.27	3.86
C	20.22	3.94	3.47
C	20.61	3.97	2.12
C	19.84	3.3	1.15
C	18.67	2.61	1.54
C	18.65	4.4	5.93
C	19.54	4.23	7.17
C	17.18	4.79	6.24
C	16.22	4.55	5.09
C	16	5.56	4.12
C	14.98	5.4	3.15
C	15.61	7.37	1.96
C	16.66	4.15	8.98
C	13.52	6.26	6.67
C	13.14	7.65	6.14
C	12.29	7.54	4.86
C	14.31	3.3	4.21
C	15.38	3.42	5.11
C	15.27	3.55	9.21
C	15.28	2.01	9.44
C	13.89	1.48	9.26
C	13.33	1.92	7.9
C	13.28	3.46	7.92
C	10.1	4.74	5.62
C	11.43	5.47	5.46
C	12.3	5.32	6.73
C	14.14	4.28	3.22

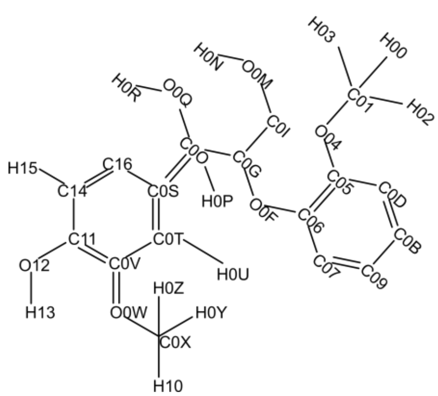
H	15.65	2.09	1.98
H	15.55	0.71	3.01
H	16.72	0.69	1.7
H	20.86	4.42	4.21
H	21.52	4.48	1.84
H	20.14	3.31	0.12
H	18.12	2.1	0.78
H	19.04	5.23	5.34
H	19.3	3.33	7.72
H	19.33	5.03	7.87
H	21.36	3.5	7.27
H	17.18	5.87	6.43
H	16.62	6.43	4.15
H	15.61	8.05	2.82
H	15.31	7.94	1.08
H	16.62	7.01	1.79
H	14.26	5.82	6.02
H	17.26	4.13	9.89
H	12.59	8.17	6.91
H	17.17	3.59	8.2
H	12.83	7.02	4.06
H	13.29	4.91	1.7
H	13.64	2.46	4.28
H	15.54	2.67	5.87
H	14.79	4.04	10.05
H	16.04	1.64	8.75
H	13.23	1.74	10.09
H	13.97	1.6	7.09
H	12.71	3.8	8.79
H	9.55	5.14	6.47
H	10.31	3.69	5.82
H	11.94	5.03	4.61
H	11.68	5.57	7.6
H	15.6	0.85	10.99
H	11.38	8.74	3.7
H	15.36	0.14	9.33
H	11.53	1.46	8.51
H	14.54	5.58	8.09
H	8.6	4.19	4.56
H	13.88	9.01	5.1
O	17.17	1.9	3.36
O	18.67	3.19	5.19
O	20.9	4.2	6.79
O	16.68	4.24	7.47
O	14.7	6.3	2.15

O	15.69	1.78	10.79
O	11.14	6.85	5.2
O	11.98	8.81	4.43
O	13.15	4.17	2.29
O	14.38	0.12	9.27
O	12.05	1.36	7.71
O	14.6	3.87	8
O	12.68	3.94	6.76
O	14.05	6.41	7.97
O	9.3	4.83	4.45
O	14.27	8.39	5.71

Non-bonded parameters

<table>
<tr><th>Molecule</th><th>Atom name</th><th>σ (nm)</th><th>Ɛ (kJ mol)</th></tr>
<tr><td rowspan="5">

Cellobiose (cellulose dimer)</td><td>C1/C2/C3/C4/C5/C6/C7/C8/C9/C10/C11</td><td>0.350</td><td>0.276</td></tr>
<tr><td>H11/H12/H21/H31/H41/H51/H61/H71/H72/ H81/H91/H101/H111/H121</td><td>0.250</td><td>0.126</td></tr>
<tr><td>HO2/HO3/HO4/HO6/HO7/HO8/HO9/HO11</td><td>0.000</td><td>0.000</td></tr>
<tr><td>O2/O3/O4/O6/O7/O8/O9/O11</td><td>0.312</td><td>0.711</td></tr>
<tr><td>O1/O5/O10</td><td>0.290</td><td>0.586</td></tr>
</table>

<table>
<tr><th>Molecule</th><th>Atom name</th><th>σ (nm)</th><th>Ɛ (kJ mol)</th></tr>
<tr><td rowspan="6">

Quinone Methide Intermediate (lignin dimer)</td><td>C05/C06/C07/C09/C0B/C0D/C0S/C0T/C0V /C11/C14/C16</td><td>0.355</td><td>0.293</td></tr>
<tr><td>C01/C0G/C0I/C0O/C0X</td><td>0.350</td><td>0.276</td></tr>
<tr><td>O0M/O0Q/O12</td><td>0.312</td><td>0.711</td></tr>
<tr><td>O04/O0F/O0W</td><td>0.290</td><td>0.586</td></tr>
<tr><td>H08/H0A/H0C/H0E/H0U/H15/H17/H00/H0 2/H03/H0H/H0J/H0K/H0P/H0Y/H0Z/H10</td><td>0.250</td><td>0.126</td></tr>
<tr><td>H0N/H0R/H13</td><td>0.000</td><td>0.000</td></tr>
</table>