Fast Pyrolysis of Cellulose, Hemicellulose, and Lignin: Effect of Operating Temperature on Bio-oil Yield and Composition and Insights into the Intrinsic Pyrolysis Chemistry

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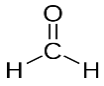
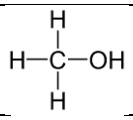
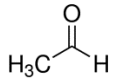
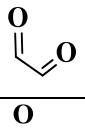
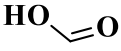
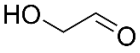
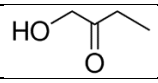
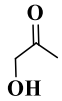
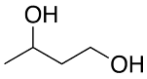
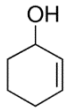
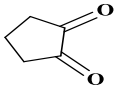
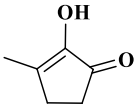
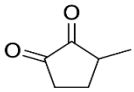
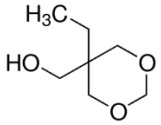
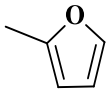
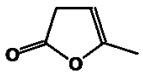
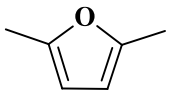
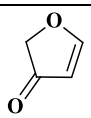
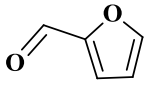
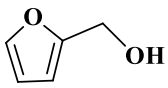
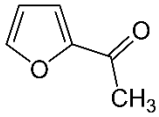
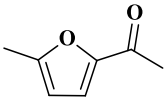
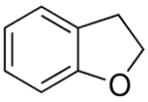
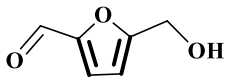
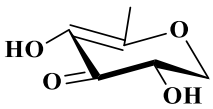
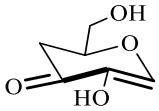
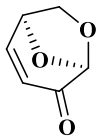
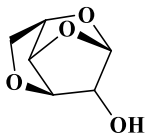
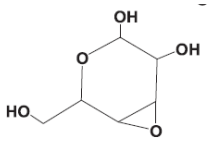
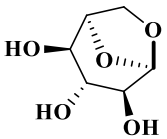
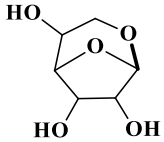
Table 1 of the supporting information

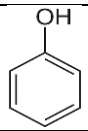
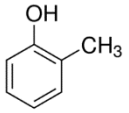
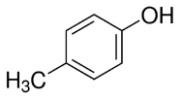
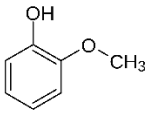
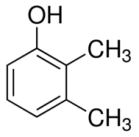
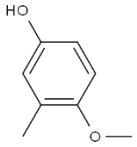
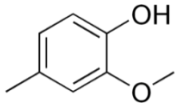
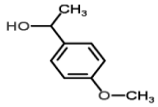
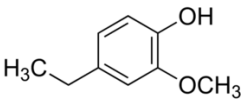
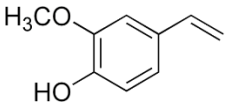
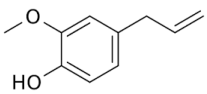
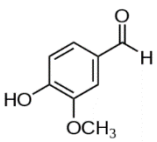
Table 1 depict summary of the products identified through gas chromatography (GC) retention time, mass spectroscopy (MS) during cellulose, xylan, and lignin thin-film pyrolysis. The pyrolysis volatile product such as non-condensable gases, light oxygenates, furanic compounds, pyrans, anhydrosugars, and phenolic compounds are identified using the mass spectrum as well as comparison with pure standards as mentioned previously.[1]

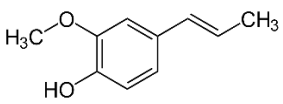
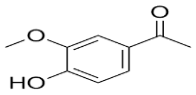
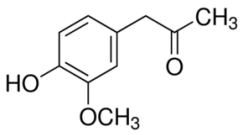
Table T1: Summary of identified pyrolysis products in cellulose, xylan, and lignin thin-film pyrolysis

Compound	**Structure**	**Retention time**	**Molar mass**	**Major ion fragments**		
Non-condensable gases						
				Ion	**Relative height**	**Fragment loss**
Carbon monoxide	:C ≡ O:	4.35	28	28	999	-
Carbon dioxide	O = C = O	5.66	44	44	999	-
Linear oxygenates						
Formaldehyde		2.29	30	**Ion**	**Relative height**	**Fragment loss**
				30	560	-
				29	999	-H (-1)
				28	210	-H (-1)
Methanol		2.7	32	32	745	-
				31	999	-H (-1)
				29	440	$-H_2$ (-2)
Acetaldehyde		2.89	44	44	125	-
				29	999	$-CH_3$ (-15)
Glyoxal		3.50	58	58	67	
				44	190	$-CH_2$ (-14)
				29	999	-
Methyl Glyoxal		3.63	72	72	51	-
				43	999	-CHO (-29)
Formic acid		4.01	46	46	999	-
				45	908	-H (-1)
Glycolaldehyde		6.27	60	60	79	-
				32	485	-CO (-28)
				31	999	-H (-1)
2,3-butanedione		6.57	86	86	180	-
				55	366	$-CH_3O$ (-31)
				43	999	$-C_2H_3O$ (-43)
Acetic acid		7.01	60	60	999	-
				45	910	$-CH_3$ (-15)
				43	868	$-H_2$ (-2)
		7.53	88	88	75	-

1-hydroxy-2-butanone				57	738	-CH_3O (-31)
				29	999	(-59)[b]
Hydroxyacetone		11.06	74	74	110	-
				43	999	(-31)
Butyl glycol		43.58	118	87	210	-CH_3O (-31)
				57	999	(-61)[b]
				45	436	(-73)[b]
2-cyclohene-1-ol		44.08	98	98	306	-
				97	345	-H (-1)
				70	999	-CO(-28)
				55	368	-C_2H_3O (-43)
1,2-cyclopentanedione[a]		44.78	98	98	999	-
				69	161	- CHO (-29)
				55	422	-C_2H_3O (-43)
2-hydroxy-3-methyl-2-cyclopenten-1-one[a]		53.37	112	112	999	–
				83	185	- CHO (-29)
				69	353	-C_2H_3O (-43)
				55	217	(-57)
3-methylcyclopentane, 1,2-dione		53.86	112	112	999	-
				83	181	- CHO (-29)
				69	354	- CH_2 (-14)
				55	317	(-57)[b]
1,3-dioxane-5-methanol, 5-ethyl-		68.92	146	145	25	-H (-1)
				86	494	(-59)[b]
				71	226	(-74)[b]
				57	999	(-88)[b]
Furanic compounds						
Furan		3.79	68	68	999	-
				39	560	- CHO (-29)
2-methylfuran		7.78	82	82	999	-
				53	439	- CHO (-29)
				39	360	- CH_2 (-14)
2(3H), furanone, 5-methyl		13.6	98	98	932	-
				55	999	-C_2H_3O (-43)
				43	785	(-55)[b]
2, 5-dimethylfuran		15.56	96	96	999	-
				95	810	- H (-1)
				81	295	- CH_3 (-15)
				53	362	-C_2H_3O (-43)
Furanone 2, 5(H)		29.38	84	84	999	-
				55	120	- CHO (-29)
				54	490	- CH_2O (-30)
Furfural		34.24	96	96	999	-
				95	950	- H (-1)
2-furanmethanol		38.43	98	98	999	-
				81	570	- OH (-17)
				69	410	- CHO (-29)

				53	328	(-45)[b]
Acetylfuran		43.99	110	110	425	-
				95	999	- CH_3 (-15)
				84	615	(-26)[b]
5-methylfurfural		48.36	110	110	999	-
				109	788	- H (-1)
				81	205	- CHO (-29)
2,3-dihydrobenzofuran		66.07	120	120	999	-
				119	265	- H (-1)
				91	728	- CHO (-29)
Hydroxymethylfurfural		66.85	126	126	999	-
				97	980	- CHO (-29)
				69	226	(-57)[b]
				53	105	(-73 [b]
Pyrans						
2,3-dihydro-3,5-dihydroxy-6-methyl-4H-Pyran-4-one[a]		61.61	144	144	361	-
				101	614	-C_2H_3O (-43)
				73	999	(-71)[b]
1,5-anhydro-4-deoxy-D-glycero-hex-1-en-3-ulose[a]		70.97	144	144	140	-
				113	182	- CH_3O (-31)
				69	999	(-75)[b]
				57	375	(-87)[b]
Anhydrosugars						
Levoglucosenone		58.63	126	126	121	-
				98	999	- CO (-28)
				68	790	- CH_2O (-30)
				53	550	(-73)[b]
1,4:3,6-dihydro-alpha-d-glucopyranose[a]		64.95	144	144	125	-
				98	340	(-46)[b]
				69	999	(-75)[b]
				57	380	(-87)[b]
3,4-Altrosan		73.68	162	98	120	(- 64)[b]
				73	574	-89)[b]
				60	999	(-102)[b]
				57	644	(-105)[b]
Levoglucosan		76.34	162	98	100	(-64)[b]
				73	458	(-89)[b]
				60	999	(-102)[b]
				57	441	(-105)[b]
1,6-anhydroglucofuranose[a]		78.05	162	73	999	(-46)[b]
				69	341	(-89)[b]
				57	185	(-105)[b]

Phenolic compounds						
Phenol		50.47	94	94	999	-
				66	380	- CO (-28)
				39	245	(-55)[b]
2-methylphenol		55.53	108	108	999	-
				90	210	-H_2O (-18)
				79	249	- CHO (-29)
p-Cresol		56.75	108	108	840	-
				107	999	- H (-1)
				79	215	- CHO (-29)
2-methoxyphenol		57.85	124	124	795	-
				109	999	- CH_3 (-15)
				81	684	-C_2H_3O (-43)
2,3-dimethylphenol		61.45	122	122	887	-
				107	999	- CH_3 (-15)
				91	195	- CH_3O (-31)
				77	320	(-45)[b]
4-methoxy-3-methylphenol		63.84	138	138	860	-
				123	999	- CH_3 (-15)
				95	184	-C_2H_3O (-43)
				67	275	(-71)[b]
Creosol		64.83	138	138	999	-
				123	869	- CH_3 (-15)
				95	360	-C_2H_3O (-43)
				77	171	(-61)[b]
2-(4-methoxyphenyl)ethanol		67.39	152	152	175	-
				121	999	- CH_3O (-31)
				77	164	(-75)[b]
4-ethyl-2-methoxyphenol		69.72	152	152	315	-
				137	999	- CH_3 (-15)
				122	137	- CH_2O (-30)
2-methoxy-4-vinylphenol		71.21	150	150	975	-
				135	999	- CH_3 (-15)
				107	673	-C_2H_3O (-43)
				77	660	(-73)[b]
Eugenol		72.76	164	164	999	-
				149	354	- CH_3 (-15)
				131	325	(-33)[b]
				103	360	(-61)[b]
				91	265	(-73)[b]
Vanillin		74.17	152	152	930	-
				151	999	- H (-1)
				123	185	- CHO (-29)
				109	230	-C_2H_3O (-43)

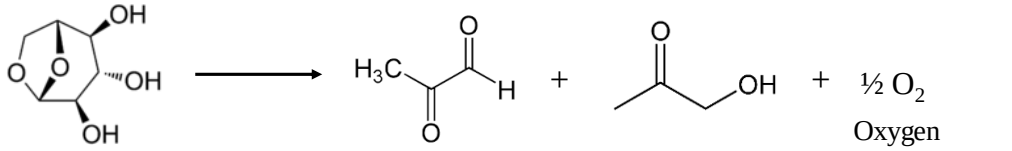
				81	304	(-71)[b]
Isoeugenol		75.48	164	164	999	-
				149	398	- CH_3 (-15)
				131	261	(-33)[b]
				121	210	-C_2H_3O (-43)
				109	205	(-55)[b]
Apocynin		76.44	166	166	425	-
				151	999	- CH_3 (-15)
				123	208	-C_2H_3O (-43)
4-Hydroxy-3-methoxyphenyl acetone		77.47	180	180	290	-
				137	999	-C_2H_3O (-43)
				122	220	- CH_3 (-15)
				94	215	- CO (-28)
				43	490	(-51)[b]

a = Compounds identified using mass spectrometry (MS) only

b = Unknown molecular fragments of the compound detected in MS

Appendix 1

[A]: Levoglucosan (LGA) conversion into Methyl glyoxal (MG) and Hydroxyacetone (HAA) during cellulose thin-film pyrolysis



[1]

$(C_6H_{10}O_5)$ LGA (Mol. Wt. = 162 g/mol)

$(C_3H_4O_2)$ Methyl glyoxal (MG) (Mol. Wt. = 72 g/mol)

$(C_3H_6O_2)$ Hydroxyacetone (HAA) (Mol. Wt. = 74 g/mol)

$\frac{1}{2}O_2$ Oxygen (Mol. Wt. = 16 g/mol)

Reaction [1] show the conversion of LGA into methyl glyoxal and hydroxyacetone along with the oxygen formation. The oxygen generated is apparently utilized insitu and contribute in the formation of other volatile products of cellulose pyroylsis as shown in Appendix 1[B]. The stoichiometry of reaction [A] on weight basis is as follows,

162 gm of LGA gives 72 gm of MG, 74 gm of HAA, and 16 gm of oxygen

Thus, 1 gm of LGA gives 0.444 gm of MG and 0.456 gm of HAA, and 0.098 gm of oxygen

For increase in the pyrolysis temperature from 300 °C to 400 °C:

Decrease in LGA yield = 3.8 wt%

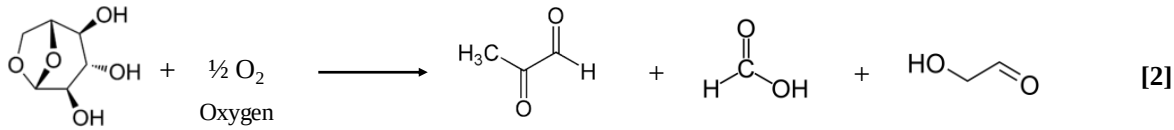
Increase in MG yield = 5.04 wt%; Increase in HAA yield = 1.74 wt%

The yield of LGA required to produce 5.04 wt% of MG = 5.04*0.444 = 2.4 wt%

The yield of LGA required to produce 1.74 wt% of HAA = 1.74*0.456 = 0.79 wt%

Thus, 5.04 wt% of MG and 1.74 wt% of HAA are produced from ~ 3.2 wt% of LGA, which apparently agreed with the decrease in LGA yield (~ 3.8 wt%) in between 300 °C – 400 °C.

[B]: LGA conversion into Methyl glyoxal (MG), Formic acid (FA), and Glycolaldehyde (GL) during cellulose thin-film pyrolysis



[2]

$(C_6H_{10}O_5)$ LGA (Mol. Wt. = 162 g/mol)

$\frac{1}{2}O_2$ Oxygen (Mol. Wt. = 16 g/mol)

$(C_3H_4O_2)$ Methyl glyoxal (MG) (Mol. Wt. = 72 g/mol)

(CH_2O_2) Formic acid (FA) (Mol. Wt. = 46 g/mol)

$(C_2H_4O_2)$ Glycolaldehyde (GA) (Mol. Wt. = 60 g/mol)

Reaction [2] show the LGA combines with the insitu generated oxygen from reaction [1] and apparently converter into methyl glyoxal, formic acid, and glycolaldehyde. The stoichiometry of reaction [2] on weight basis is as follows,

178 gm of LGA/O_2 gives 72 gm of MG, 46 gm of FA, and 60 gm of GA

Thus, 1 gm of LGA/O_2 gives 0.404 gm of MG, 0.258 gm of FA, and 0.337 gm of GA

For increase in the pyrolysis temperature from 400 °C to 500 °C:

Decrease in LGA yield = 4.1 wt%

Increase in MG yield = 3.58 wt%; Increase in FA yield = 5.1 wt%;

Increase in GA yield = 1.85 wt%

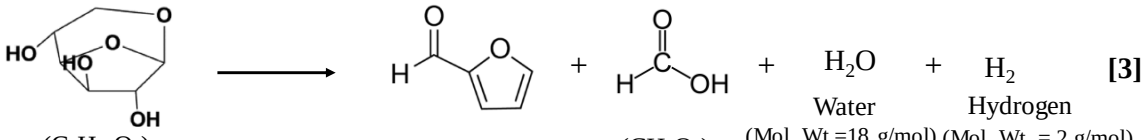
The yield of LGA required to produce 3.58 wt% of MG = 3.58*0.404 = 1.45 wt%

The yield of LGA required to produce 5.1 wt% of FA = 5.1*0.258 = 1.32 wt%

The yield of LGA required to produce 1.85 wt% of GA = 1.85*0.337 = 0.62 wt%

Thus, 3.58 wt% of MG, 5.1 wt% of FA, and 1.85 wt% of GA are produced from ~ 3.4 wt% of LGA, which closely matched with the decrease in LGA yield (~ 4 wt%) in between 400 °C – 500 °C.

[C]: 1, 6-anhydroglucofuranose (AGF) conversion into Furfural and Formic acid (FA) during cellulose thin-film pyrolysis



$(C_6H_{10}O_5)$ AGF (Mol. Wt. = 162 g/mol) → $(C_5H_4O_2)$ Furfural (Mol. Wt. = 96 g/mol) + (CH_2O_2) Formic acid (FA) (Mol. Wt. = 46 g/mol) + H_2O Water (Mol. Wt.=18 g/mol) + H_2 Hydrogen (Mol. Wt. = 2 g/mol) **[3]**

Reaction [3] show the AGF conversion into furfural and formic acid along with water and hydrogen as additional compounds. The hydrogen generated can be utilized insitu for hydrodeoxygenation reaction as shown later in appendix 1[G]. The stoichiometry of reaction [3] on weight basis is as follows,

162 gm of AGF gives 96 gm of furfural, 46 gm of formic acid, 18 gm of water, and 2 gm of H_2

Thus, 1 gm of AGF gives 0.592 gm of furfural, 0.283 gm of formic acid, 0.11 gm of water and 0.01 gm of hydrogen

For increase in the pyrolysis temperature from 300 °C to 400 °C:

Decrease in AGF yield = 1.98 wt%

Increase in Furfural yield = 2.62 wt%

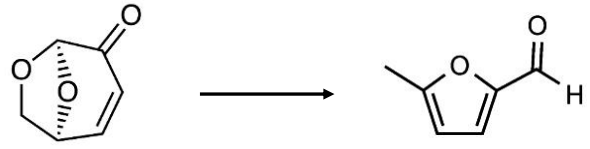
Increase in Formic acid yield = 4.19 wt%

The yield of AGF required to produce 2.62 wt% of furfural = 0.592*2.62 = 1.55 wt%

The yield of AGF required to produce 4.19 wt% of formic acid = 0.283*4.19 = 1.1 wt%

Thus, 2.62 wt% of furfural and 4.19 wt% of formic acid are produced from 2.6 wt% of AGF, which apparently agreed with the decrease in AGF yield (~ 2 wt%) in between 300 °C – 400 °C

[D]: Levoglucosenone (LGO) conversion into 5-Methylfurfural (5-MF) during cellulose thin-film pyrolysis



$(C_6H_6O_3)$ LGO (Mol. Wt. = 126 g/mol) → $(C_6H_6O_2)$ 5-Methylfurfural (5-MF) (Mol. Wt. = 110 g/mol) + ½ O_2 Oxygen (Mol. Wt. = 16 g/mol) **[4]**

Reaction [4] show conversion of LGO into 5-methylfurfural and oxygen. Again, the additional oxygen generated from reaction [4] can utilized into the formation of other pyrolysis volatile products. The stoichiometry of reaction [4] on weight basis is as follows,

126 gm of LGO gives 110 gm of 5-methylfurfural and 16 gm of oxygen

Thus, 1 gm of LGO gives 0.873 gm of 5-methylfurfural and 0.12 gm of oxygen

For increase in the pyrolysis temperature from 300 °C to 400 °C:

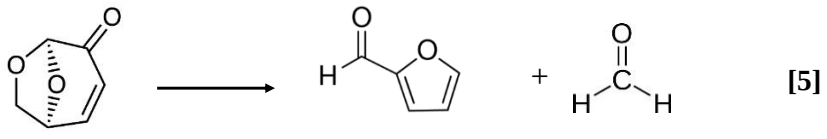
Decrease in LGO yield = 1.6 wt%

Increase in 5-Methylfurfural yield = 0.96 wt%

The yield of LGO required to produce 0.96 wt% 5-Methylfurfural = 0.873*0.96 = 0.84 wt%

Although, the decrease in LGO yield (1.6 wt%) seemed much higher than the increase in 5-methylfurfural, but only 5-methylfurfural yield could closely with LGO yield amongst the entire pyroylsis product distribution, over 300 °C – 400 °C.

[E]: LGO conversion into Furfural and Formaldehyde during cellulose thin-film pyrolysis



$(C_6H_6O_3)$ LGO (Mol. Wt. = 126 g/mol) → $(C_5H_4O_2)$ Furfural (Mol. Wt. = 96 g/mol) + (CH_2O) Formaldehyde (Mol. Wt. = 30 g/mol) **[5]**

Reaction [5] depict the conversion of LGO into furfural and formaldehyde. The stoichiometry of reaction [5] on weight basis is as follows,

126 gm of LGO gives 96 gm of furfural and 30 gm of formaldehyde

Thus, 1 gm of LGO gives 0.761 gm of furfural and 0.238 gm of formaldehyde

For increase in the pyrolysis temperature from 400 °C to 500 °C:

Decrease in LGO yield = 0.21 wt%

Increase in furfural yield = 0.36 wt%

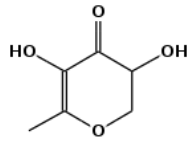
Increase in formaldehyde yield = 0.09 wt%

The yield of LGO required to produce 0.36 wt% of furfural = 0.761*0.36 = 0.27 wt%

The yield of LGO required to produce 0.09 wt% of formaldehyde = 0.238*0.09 = 0.02 wt%

Thus, 0.36 wt% of furfural and 0.09 wt% of formic acid are produced from 0.29 wt% of LGO, which apparently agreed with the decrease in LGO yield (0.21 wt%), over 400 °C – 500 °C.

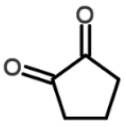
[F]: 2,3-dihydro-3,5-dihydroxy-6-methyl-4HPyran-4-one (DHMDHP) conversion into 1, 2-Cylcopentanedione and Carbon dioxide during cellulose thin-film pyrolysis



$(C_6H_8O_4)$

DHMDHP

(Mol. Wt. = 144 g/mol)



$(C_5H_6O_2)$

1, 2-cyclopentandione

(Mol. Wt. = 98 g/mol)

+ $O=C=O$

(CO_2)

Carbon dioxide

(Mol. Wt. = 44 g/mol)

+ H_2

Hydrogen

(Mol. Wt. = 2 g/mol)

[6]

Reaction [6] show DHMDHP conversion into 1,2-cylcopentanedione and carbon dioxide with hydrogen. The extra hydrogen generated can be utilized insitu and contribute for other product formation. (*cf.* Appendix 1[G]). The stoichiometry of reaction [6] on weight basis is as follows,

Stoichiometry (weight basis):

144 gm of DHMDHP gives 98 gm of 1, 2-cyclopentanedione, 44 gm of carbon dioxide, and 2 gm of hydrogen

Thus, 1 gm of DHMDHP gives 0.68 gm of 1, 2-cyclopentanedione and 0.305 gm of carbon dioxide, and 0.013 gm of hydrogen

For increase in the pyrolysis temperature from 300 °C to 400 °C:

Decrease in DHMDHP yield = 1.92 wt%

Increase in 1, 2-cyclopentanedione yield = 1.44 wt%

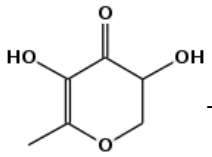
Increase in carbon dioxide yield = 3.62 wt%

The yield of DHMDHP required to produce 1.44 wt% of 1, 2-Cyclopentanedione = 0.68*1.44 = 0.97 wt%

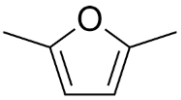
The yield of DHMDHP required to produce 3.62 wt% of carbon dioxide = 0.305*3.62 = 1.1 wt%

Thus, 1.44 wt% of 1, 2-cyclopentanedione and 3.62 wt% of carbon dioxide are produced from 2.07 wt% of DHMDHP, which apparently agreed with the decrease in DHMDHP yield (~ 1.92 wt%) in between 300 °C – 400 °C.

[G]: DHMDHP conversion into 2,5-dimethylfuran during cellulose thin-film pyrolysis



$+ \quad 3H_2 \longrightarrow$



$+ \quad 3H_2O$ **[7]**

$(C_6H_8O_4)$		(C_6H_8O)	
DHMDHP	Hydrogen	2, 5-dimethylfuran	Water
(Mol. Wt. =144 g/mol)	(Mol. Wt.= 2 g/mol)	(Mol. Wt. = 96 g/mol)	(Mol. Wt. = 18 g/mol)

Reaction [7] show that DHMDHP combines with insitu generated hydrogen and produces 2,5-dimethylfuran and water. The stoichiometry of reaction [7] on weight basis is as follows,

150 gm of DHMDHP/H_2 gives 96 gm of 2, 5-dimethylfuran and 54 gm of water

Thus, 1 gm of DHMDHP/H_2 gives 0.64 gm of 2, 5-dimethylfuran and 0.36 gm of water

For increase in the pyrolysis temperature from 400 °C to 500 °C:

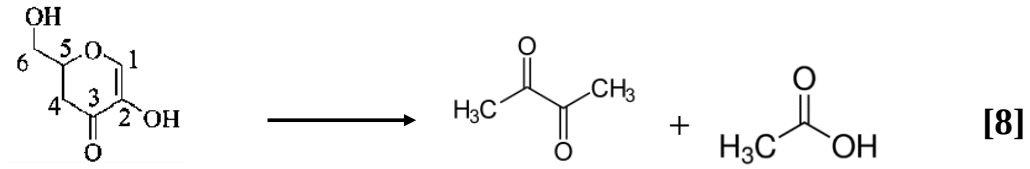
Decrease in DHMDHP yield = 0.51 wt%

Increase in 2, 5-dimethylfuran yield = 0.67 wt%

The yield of DHMDHP required to produce 0.67 wt% of 2, 5-dimethylfuran = 0.67*0.64 = 0.43 wt%

Thus, 0.67 wt% of 2, 5-dimethylfuran is produced from 0.43 wt% of DHMDHP, which is in good agreement with decrease in DHMDHP yield (~ 0.51 wt%) in between 400 °C – 500 °C.

[H]: 1,5-anhydro-4-deoxy-D-glycerohex-1-en-3-ulose (ADGH) conversion into Acetic acid and 2, 3-Butanedione during cellulose thin-film pyrolysis



$(C_6H_8O_4)$ $(C_4H_6O_2)$

ADGH 2, 3-Butanedione Acetic acid

(Mol. Wt. =144 g/mol) (Mol. Wt. = 86 g/mol) (Mol. Wt. = 60 g/mol)

[8]

Reaction [8] depict the conversion of ADGH into 2, 3-buanedione and acetic acid. The stoichiometry of reaction [8] on weight basis is as follows,

144 gm of ADGH gives 86 gm of 2, 3-butanedione and 60 gm of acetic acid

Thus, 1 gm of ADGH gives 0.597 gm of 2, 3-butanedione and 0.416 gm of acetic acid

For increase in the pyrolysis temperature from 300 °C to 400 °C:

Decrease in ADGH yield = 1.5 wt%

Increase in 2, 3-butanedione yield = 1.4 wt%

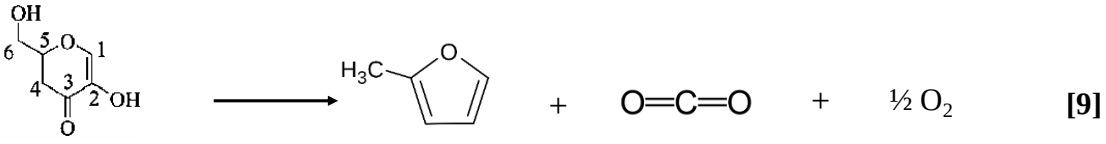
Increase in acetic acid yield = 0.51 wt%

The yield of ADGH required to produce 1.4 wt% of 2, 3-butanedione = 0.597*1.4 = 0.84 wt%

The yield of ADGH required to produce 0.51 wt% of acetic acid = 0.416*0.51 = 0.22 wt%

Thus, 1.4 wt% of 2, 3-butanedione and 0.51 wt% of acetic acid are produced from 1.06 wt% of ADGH, which apparently agreed with the decrease in ADGH yield (~ 1.5 wt%) in between 300 °C – 400 °C.

[I]: ADGH conversion into 2-Methylfuran and Carbon dioxide during cellulose thin-film pyrolysis



$(C_6H_8O_4)$ (C_5H_6O) (CO_2)

ADGH 2, Methyl furan Carbon dioxide Oxygen

(Mol. Wt. =144 g/mol) (Mol. Wt. = 82 g/mol) (Mol. Wt. = 44 g/mol) (Mol. Wt. = 16 g/mol)

[9]

Reaction [9] show the conversion of ADGH into 2-methylfuran, carbon dioxide, and water. The stoichiometry of reaction [9] on weight basis is as follows,

144 gm of ADGH gives 82 gm of 2-methylfuran, 44 gm of carbon dioxide, and 16 gm of oxygen

Thus, 1 gm of ADGH gives 0.569 gm of 2-methylfuran and 0.305 gm of carbon dioxide, and 0.11 gm of oxygen

For increase in the pyrolysis temperature from 400 °C to 500 °C:

Decrease in ADGH yield = 0.55 wt%

Increase in 2-methylfuran yield = 0.42 wt%

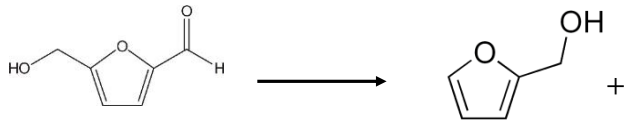
Increase in carbon dioxide yield = 1.13 wt%

The yield of ADGH required to produce 0.42 wt% of 2-methylfuran = 0.569*0.42 = 0.23 wt%

The yield of ADGH required to produce 1.13 wt% of Carbon dioxide = 0.305*1.13 = 0.34 wt%

Thus, 0.42 wt% of 2-methylfuran and 1.13 wt% of Carbon dioxide are produced from 0.57 wt% of ADGH, which apparently agreed with the decrease in ADGH yield (~ 0.55 wt%) in between 400 °C – 500 °C.

[J]: HMF conversion into 2-Furanmethanol and Carbon monoxide during cellulose thin-film pyrolysis



$(C_6H_6O_3)$ + CO **[10]**

$(C_5H_6O_2)$

HMF	2-Furanmethanol	Carbon Monoxide
(Mol. Wt. =126 g/mol)	(Mol. Wt. = 98 g/mol)	(Mol. Wt. = 28 g/mol)

Reaction [10] show the conversion of HMF into 2-furanmethanol and carbon monoxide. The stoichiometry of reaction [10] on weight basis is as follows,

126 gm of HMF gives 98 gm of 2-furanmethanol and 28 gm of carbon monoxide

Thus, 1 gm of HMF gives 0.777 gm of 2-furanmethanol and 0.222 gm of carbon monoxide

For increase in the pyrolysis temperature from 300 °C – 400 °C:

The decrease in HMF yield = 1.5 wt%

Increase in 2-furanmethanol yield = 1.52 wt%

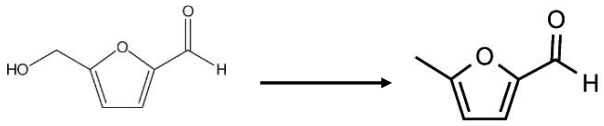
Increase in carbon monoxide yield = 1.61 wt%

The yield of HMF required to produce 1.52 wt% of 2-furanmethanol = 0.777*1.52 = 1.18 wt%

The yield of HMF required to produce 1.61 wt% of carbon monoxide = 0.222*1.61 = 0.35 wt%

Thus, 1.52 wt% of 2-furanmethanol and 1.61 wt% of carbon monoxide are produced from 1.53 wt% of HMF, which apparently agreed with the decrease in HMF yield (~ 1.5 wt%) in between 300 °C – 400 °C.

[K]: HMF conversion into 5-methylfufural during cellulose thin-film pyrolysis



$(C_6H_6O_3)$ HMF (Mol. Wt. =126 g/mol) → $(C_6H_6O_2)$ 5-Methylfurfural (Mol. Wt. = 110 g/mol) + ½ O_2 Oxygen (Mol. Wt. = 16 g/mol) **[11]**

Reaction [11] show the conversion of HMF into 5-mehtylfurfural and oxygen. The stoichiometry of reaction [11] on weight basis is as follows,

126 gm of HMF gives 110 gm of 5-methylfurfural and 16 gm of oxygen

Thus, 1 gm of HMF gives 0.873 gm of 5-methylfurfural and 0.126 gm of oxygen

For pyrolysis temperature in between 400 °C – 500 °C:

The decrease in HMF yield = 1.9 wt%

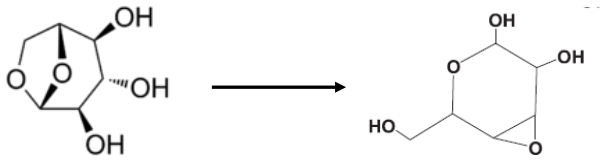
Increase in 5-mehtylfurfural yield = 0.96 wt%

The yield of HMF required to produce 0.96 wt% of 5-mehtylfurfural = 0.873*0.96 = 0.84 wt%

Thus, the comparison between the experimental yields of HMF and 5-methylfurfural showed 1 wt% difference, however, the HMF yield could only closely matched with the 5-methylfurfural yield amongst all the pyrolysis products, over 400 °C – 500 °C.

Appendix 2

[A]: LGA conversion into 3, 4-Altrosan during xylan thin-film pyrolysis



[1]

$(C_6H_{10}O_5)$
LGA
(Mol. Wt. = 162 g/mol)

$(C_6H_{10}O_5)$
3, 4-Altrosan
(Mol. Wt. = 162 g/mol)

Reaction [1] show the conversion of LGA into 3,4-altrosan. The stoichiometry of reaction [1] on weight basis is as follows,

162 gm of LGA gives 162 gm of 3, 4-Altrosan

Thus, 1 gm of LGA gives 1 gm of 3, 4-Altrosan

For increase in the pyrolysis temperature from 200 °C to 300 °C:

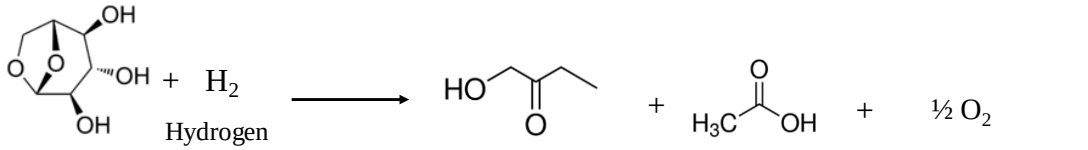
The decrease in LGA yield = 3.01 wt%

Increase in 3, 4-Altrosan yield = 3.5 wt%

The yield of LGA required to produce 3.5 wt% of 3, 4-Altrosan = 1*3.5 = 3.5 wt%

Thus, 3.5 wt % of 3, 4-Altrosan is produced from 3.5 wt% of LGA, which apparently agreed with the decrease in LGA yield (~ 3.05 wt%) in between 200 °C – 300 °C.

[B]: LGA conversion into 1-Hydroxy-2-butanone and Acetic acid during xylan thin-film pyrolysis



[2]

$(C_6H_{10}O_5)$ (Mol. Wt. = 2 g/mol)
LGA
(Mol. Wt. = 162 g/mol)

Hydrogen

$(C_4H_8O_2)$
1-Hydroxy-2-butanone
(Mol. Wt. = 88 g/mol)

$(C_2H_4O_2)$
Acetic acid
(Mol. Wt. = 60 g/mol)

Oxygen
(Mol. Wt. = 16 g/mol)

Reaction [2] show that LGA combines with insitu hydrogen and result in the formation of 1-hydroxy-2-butanone and acetic acid, and oxygen. The oxygen generated apparently used (as insitu) in the formation of other products of xylan thin-film pyrolysis as shown later in appendix 2[D]. The stoichiometry of reaction [2] on weight basis is as follows,

164 gm of LGA/H_2 gives 88 gm of 1-hydroxy-2-butanone, 60 gm of acetic acid, and 16 gm of oxygen

Thus, 1 gm of LGA/H_2 gives 0.536 gm of 1-hydroxy-2-butanone and 0.365 gm of acetic acid

For increase in the pyrolysis temperature from 300 °C to 500 °C:

The decrease in LGA yield = 3.5 wt%

Increase in 1-hydroxy-2-butanone yield = 2.66 wt%

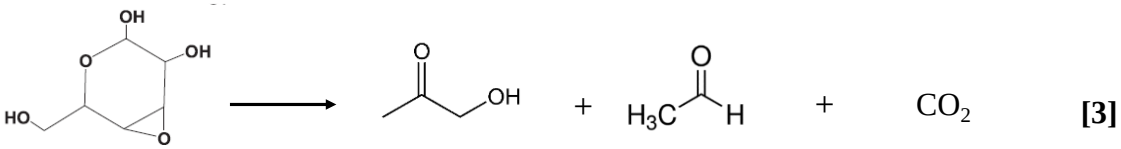
Increase in acetic acid yield = 1.77 wt%

The yield of LGA required to produce 2.66 wt% of 1-hydroxy-2-butanone = 0.536*2.66 = 1.42 wt%

The yield of LGA required to produce 1.77 wt% of acetic acid = 0.365*1.77 = 0.65 wt%

Thus, 2.66 wt % of 1-hydroxy-2-butanone and 1.77 wt% of acetic acid are produced from 2.07 wt% LGA, which closely matched with the decrease in LGA yield (~ 3.05 wt%) in between 300 °C – 500 °C.

[C]: 3, 4-Altrosan conversion into Hydroxyacetone and Acetaldehyde, and Carbon dioxide during xylan thin-film pyrolysis



[3]

($C_6H_{10}O_5$)
3, 4-Altrosan
(Mol. Wt. = 162 g/mol)

($C_3H_6O_2$)
Hydroxyacetone
(Mol. Wt. = 74 g/mol)

(C_2H_4O)
Acetaldehyde
(Mol. Wt. = 44 g/mol)

Carbon dioxide
(Mol. Wt. = 44 g/mol)

Reaction [3] show the conversion of 3, 4-altrosan into hydroxyacetone, acetaldehyde, and carbon dioxide. The stoichiometry of reaction [3] on weight basis is as follows,

162 gm of 3, 4-altrosan gives 74 gm of hydroxyacetone, 44 gm of acetaldehyde, and 44 gm of carbon dioxide

Thus, 1 gm of 3, 4-altrosan gives 0.456 gm of hydroxyacetone, 0.271 gm of acetaldehyde, and 0.271 gm of carbon dioxide

For increase in the pyrolysis temperature from 300 °C to 500 °C:

Decrease in 3, 4-altrosan yield = 4.3 wt%

Increase in hydroxyacetone yield = 4.66 wt%

Increase in acetaldehyde yield = 2.65 wt%

Increase in carbon dioxide yield = 4.4 wt%

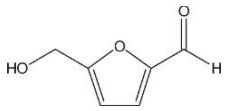
The yield of 3, 4-altrosan required to produce 4.66 wt% of hydroxyacetone = 0.456*4.66 = 2.12 wt%

The yield of 3, 4-altrosan required to produce 2.65 wt% of acetaldehyde = 0.271*2.65 = 0.72 wt%

The yield of 3, 4-altrosan required to produce 4.4 wt% of carbon dioxide = 0.271*4.4 = 1.19 wt%

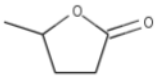
Thus, 4.66 wt % of hydroxyacetone, 2.65 wt% of acetaldehyde, and 4.4 wt% of carbon dioxide are produced from 4.03 wt% of 3, 4-altrosan, which apparently agreed with the decrease in 3, 4-altrosan yield (~ 4.3 wt%) in between 300 °C – 500 °C.

[D]: HMF conversion into 2(3H)-Furanone, 5-methyl and and Carbon dioxide during xylan thin-film pyrolysis



$(C_6H_6O_3)$
HMF
(Mol. Wt. =126 g/mol)

+ ½ O_2
Oxygen
(Mol. Wt. = 16 g/mol)



$(C_5H_6O_2)$
2(3H)-Furanone, 5-methyl-
(Mol. Wt. = 98 g/mol)

+ CO_2
Carbon dioxide
(Mol. Wt. = 44 g/mol)

[4]

Reaction [4] show that HMF combines with the insitu generated oxygen (possible the oxygen generated from reaction [2 & 5] in appendix [B] as shown earlier) and converted into 2(3H)-Furanone, 5-methyl and Carbon dioxide. The stoichiometry of reaction [4] on weight basis is as follows,

142 gm of HMF/O_2 gives 98 gm of 2(3H)-Furanone, 5-methyl and 44 gm of carbon dioxide

Thus, 1 gm of HMF/O_2 gives 0.69 gm of 2(3H)-Furanone, 5-methyl and 0.309 gm of carbon dioxide

For increase in the pyrolysis temperature from 200 °C to 300 °C:

Decrease in HMF yield = 2.2 wt%

Increase in 2(3H)-Furanone, 5-methyl yield = 2.36 wt%

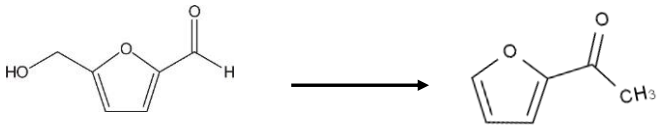
Increase in carbon dioxide yield = 0.15 wt%

The yield of HMF required to produce 2.21 wt% of 2(3H)-Furanone, 5-methyl = 0.69*2.36 = 1.65 wt%

The yield of HMF required to produce 0.15 wt% of carbon dioxide = 0.309*0.15 = 0.05 wt%

Thus, 2.36 wt % of 2(3H)-Furanone, 5-methyl and 0.15 wt% of carbon dioxide are produced from 1.7 wt% of HMF, which closely matched with the decrease in HMF yield (~ 2.2 wt%) in between 200 °C – 300 °C.

[E]: HMF conversion into Acetylfuran during xylan thin-film pyrolysis



$(C_6H_6O_3)$ HMF (or its intermediates) (Mol. Wt. =126 g/mol) → $(C_6H_6O_2)$ Acetylfuran (Mol. Wt. = 110 g/mol) + ½ O_2 Oxygen (Mol. Wt. = 16 g/mol) **[5]**

Reaction [5] show the conversion of HMF into acetylfuran and oxygen. HMF as such cannot form acetylfuran, however, its intermediate can result into acetylfuran formation during cellulose pyrolysis.[2] The stoichiometry of reaction [5] on weight basis is as follows,

126 gm of HMF/intermediates gives 110 gm of acetylfuran and 16 gm of oxygen

1 gm of HMF/intermediates gives 0.873 gm of acetylfuran

For increase in the pyrolysis temperature from 300 °C to 500 °C:

Decrease in HMF yield = 4.4 wt%

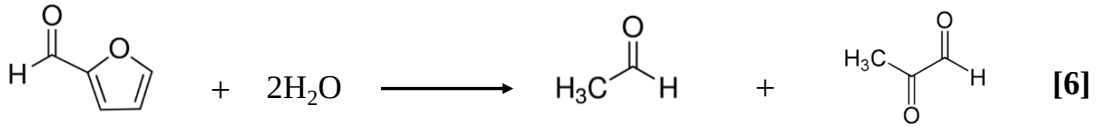
Increase in acetylfuran yield = 3.99 wt%

Increase in formaldehyde yield = 3.68 wt%

The yield of HMF/intermediates required to produce 3.99 wt% of acetylfuran = 0.873*3.99 = 3.48 wt%

Thus, 3.99 wt % of acetylfuran is produced from 3.48 wt% of HMF/intermediates, which apparently agrees with the decrease in HMF yield (~ 4.4 wt%) in between 300 °C – 500 °C.

[F]: Furfural conversion into Hydroxy acetaldehyde and Methyl glyoxal during xylan thin-film pyrolysis



$(C_5H_4O_2)$ Furfural (Mol. Wt. =96 g/mol) + $2H_2O$ Water (Mol. Wt. = 36 g/mol) → $(C_2H_4O_2)$ Hydroxy acetaldehyde (Mol. Wt. = 60 g/mol) + $(C_3H_4O_2)$ Methyl glyoxal (MG) (Mol. Wt. = 72 g/mol) **[6]**

Reaction [6] show that furfural reacted with water and convert into hydroxy acetaldehyde and methyl glyoxal. The stoichiometry of reaction [6] on weight basis is as follows,

132 gm of furfural/H_2O gives 60 gm of hydroxy acetaldehyde and 72 gm of methyl glyoxal

Thus, 1 gm of furfural/H_2O gives 0.454 gm of hydroxy acetaldehyde and 0.545 gm of methyl glyoxal

For increase in the pyrolysis temperature from 200 °C to 400 °C:

Decrease in furfural yield = 7.1 wt%

Increase in hydroxy acetaldehyde yield = 0.7 wt%

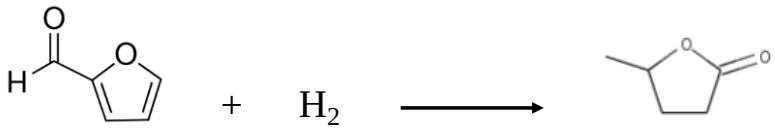
Increase in methyl glyoxal yield = 4.82 wt%

The yield of furfural required to produce 0.71 wt% of hydroxy acetaldehyde = 0.454*0.71 = 0.32 wt%

The yield of furfural required to produce 4.82 wt% of methyl glyoxal = 0.545*4.82 = 2.63 wt%

Thus, 0.7 wt % of hydroxy acetaldehyde and 4.82 wt% of methyl glyoxal are produced from 2.93 wt% of furfural. This is the best match we could obtain for the decrease in furfural in between 200 °C – 400 °C, when compared with the yields of other pyrolysis products.

[G]: Furfural conversion into 2(3H), furanone, 5-methyl during xylan thin-film pyrolysis



$(C_5H_4O_2)$ Furfural (Mol. Wt. =96 g/mol) + H_2 Hydrogen (Mol. Wt. = 2 g/mol) ⟶ $(C_5H_6O_2)$ 2(3H)-Furanone, 5-methyl- (Mol. Wt. = 98 g/mol) **[7]**

Reaction [7] show that furfural hydrogenated with insitu hydrogen and converted into 2(3H), furanone, 5-methyl. The stoichiometry of reaction [7] on weight basis is as follows,

98 gm of furfural/H_2 gives 98 gm of 2(3H)-Furanone, 5-methyl-

Thus, 1 gm of furfural/H_2 gives 1 gm of 2(3H)-Furanone, 5-methyl-

For increase in the pyrolysis temperature from 400 °C to 500 °C:

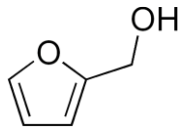
Decrease in furfural yield = 0.37 wt%

Increase in 2(3H)-Furanone, 5-methyl yield = 0.34 wt%

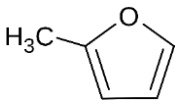
The yield of furfural required to produce 0.34 wt% of 2(3H)-Furanone, 5-methyl = 1*0.34 = 0.34 wt%

Thus, 0.34 wt % of 2(3H)-Furanone, 5-methyl is produced from 0.34 wt% of furfural, which apparently agreed with the decrease in furfural yield (~ 0.37 wt%) in between 400 °C – 500 °C.

[H]: 2-Furanmehtanol conversion into 2-Methylfuran and Oxygen during xylan thin-film pyrolysis



$(C_5H_6O_2)$
2-Furanmethanol
(Mol. Wt. = 98 g/mol)



(C_5H_6O)
2-Methyl furan
(Mol. Wt. = 82 g/mol)

+ ½ O_2
Oxygen
(Mol. Wt. = 16 g/mol)

[8]

Reaction [8] show the conversion of 2-furanmethanol into 2-methylfuran and oxygen. The stoichiometry of reaction [8] on weight basis is as follows,

98 gm of 2-furanmethanol gives 82 gm of 2-methylfuran and 16 gm of oxygen

Thus, 1 gm of 2-furanmethanol gives 0.836 gm of 2-methylfuran and 0.163 gm of oxygen

For increase in the pyrolysis temperature from 400 °C to 500 °C:

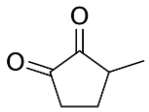
Decrease in 2-furanmethanol yield = 1.42 wt%

Increase in 2-methylfuran yield = 1.41 wt%

The yield of 2-furanmethanol required to produce 1.41 wt% of 2-methylfuran = 0.836*1.41 = 1.18 wt%

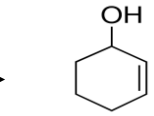
Thus, 1.41 wt% of 2-methylfuran is produced from 1.18 wt% of 2-furanmethanol, which apparently agreed with the decrease in 2-furanmethanol yield (~ 1.42 wt%) in between 400 °C – 500 °C.

[I]: 3-methylcyclopentane, 1,2-dione conversion into 2-cyclohexen-1-ol during xylan thin-film pyrolysis



$(C_6H_8O_2)$
3-methylcyclopentane, 1,2-dione
(Mol. Wt. = 112 g/mol)

+ H_2
Hydrogen
(Mol. Wt. = 2 g/mol)



$(C_6H_{10}O)$
2-Cyclohexen-1-ol
(Mol. Wt. = 98 g/mol)

+ ½ O_2
Oxygen
(Mol. Wt. = 16 g/mol)

[9]

Reaction [9] show that 3-methylcyclopentane, 1,2-dione reacts with hydrogen (as insitu) and converts into 2-cyclohexen-1-ol and oxygen. The stoichiometry of reaction [9] on weight basis is as follows,

114 gm of 3-methylcyclopentane, 1,2-dione/H_2 gives 98 gm of 22-cyclohexen-1-ol and 16 gm of oxygen

Thus, 1 gm of 3-methylcyclopentane, 1,2-dione/H_2 gives 0.859 gm of 2-cyclohexen-1-ol and 0.14 gm of oxygen

For increase in the pyrolysis temperature from 300 °C to 500 °C:

Decrease in 3-methylcyclopentane, 1,2-dione yield = 2.78 wt%

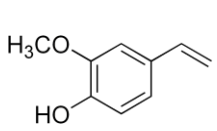
Increase in 2-cyclohexen-1-ol yield = 3.01 wt%

The yield of 3-methylcyclopentane, 1,2-dione required to produce 3.01 wt% of 2-cyclohexen-1-ol = 0.859*3.01 = 2.58 wt%

Thus, 3.01 wt% of 2-cyclohexen-1-ol is produced from 2.58 wt% of 3-methylcyclopentane, 1,2-dione, which apparently agreed with the decrease in 3-methylcyclopentane, 1,2-dione yield (~ 2.78 wt%) in between 300 °C – 500 °C.

Appendix 3

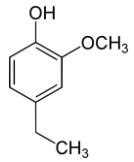
[A]: 2-methoxy-4-vinylphenol conversion into 4-ethyl-2-methoxyphenol during lignin thin-film pyrolysis



($C_9H_{10}O_2$)
2-methoxy-4-vinylphenol
(Mol. Wt. = 150 g/mol)

+ H_2

Hydrogen
(Mol. Wt. = 2 g/mol)



($C_9H_{12}O_2$)
4-ethyl-2-methoxyphenol
(Mol. Wt. = 152 g/mol)

[1]

Reaction [1] show that 2-methoxy-4-vinylphenol reacts with insitu hydrogen and gets converted into 4-ethyl-2-methoxyphenol. The stoichiometry of reaction [1] on weight basis is as follows,

152 gm of 2-methoxy-4-vinylphenol/H_2 gives 152 gm of 4-ethyl-2-methoxyphenol

Thus, 1 gm of 2-methoxy-4-vinylphenol/H_2 gives 1 gm of 4-ethyl-2-methoxyphenol

For increase in the pyrolysis temperature from 350 °C to 450 °C:

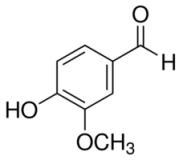
Decrease in 2-methoxy-4-vinylphenol yield = 0.9 wt%

Increase in 4-ethyl-2-methoxyphenol yield = 0.87 wt%

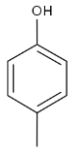
The yield of 2-methoxy-4-vinylphenol required to produce 0.87 wt% of 4-ethyl-2-methoxyphenol = 1.01*0.87 = 0.88 wt%

Thus, 0.87 wt % of 4-ethyl-2-methoxyphenol is produced from 0.88 wt% of 2-methoxy-4-vinylphenol, which apparently agreed with the decrease in 2-methoxy-4-vinylphenol yield (~ 0.9 wt%) in between 350 °C – 450 °C.

[B]: Vanillin conversion into p-Cresol and Carbon dioxide during lignin thin-film pyrolysis



($C_8H_8O_3$)
Vanillin
(Mol. Wt. = 152 g/mol)



(C_7H_8O)
p-Cresol
(Mol. Wt. = 108 g/mol)

+ CO_2

Carbon dioxide
(Mol. Wt. = 44 g/mol)

[2]

Reaction [2] show the conversion of vanillin into p-Cresol and carbon dioxide. The stoichiometry of reaction [2] on weight basis is as follows,

152 gm of vanillin gives 108 gm of p-Cresol and 44 gm of carbon dioxide

Thus, 1 gm of vanillin gives 0.71 gm of p-Cresol and 0.289 gm of carbon dioxide

For increase in the pyrolysis temperature from 350 °C to 450 °C:

Decrease in vanillin yield = 1.6 wt%

Increase in p-Cresol yield = 1.13 wt%

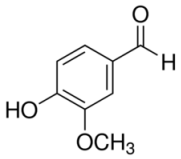
Increase in carbon dioxide yield = 3.79 wt%

The yield of vanillin required to produce 1.13 wt% of p-Cresol = 0.71*1.13 = 0.8 wt%

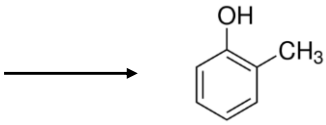
The yield of vanillin required to produce 3.79 wt% of carbon dioxide = 0.289*3.79 = 1.09 wt%

Thus, 1.13 wt % of p-Cresol and 3.79 wt% of carbon dioxide are produced from 1.89 wt% of vanillin, which apparently agreed with the decrease in vanillin yield (~ 1.6 wt%) in between 350 °C – 450 °C.

[C]: Vanillin conversion into 2-Methylphenol and Carbon dioxide during lignin thin-film pyrolysis



($C_8H_8O_3$)
Vanillin
(Mol. Wt. = 152 g/mol)



(C_7H_8O)
p-Cresol
(Mol. Wt. = 108 g/mol)

\+ CO_2

Carbon dioxide
(Mol. Wt. = 44 g/mol)

[3]

Reaction [3] show the conversion of vanillin into 2-methylphenol and carbon dioxide. The stoichiometry of reaction [3] on weight basis is as follows,

152 gm of vanillin gives 108 gm of 2-methylphenol and 44 gm of carbon dioxide

Thus, 1 gm of vanillin gives 0.71 gm of 2-methylphenol and 0.289 gm of carbon dioxide

For increase in the pyrolysis temperature from 450 °C to 550 °C:

Decrease in vanillin yield = 1.62 wt%

Increase in 2-methylphenol yield = 1.24 wt%

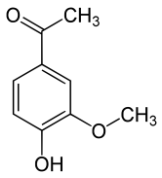
Increase in carbon dioxide yield = 0.9 wt%

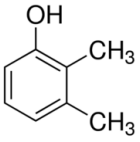
The yield of vanillin required to produce 1.24 wt% of 2-methylphenol = 0.71*1.24 = 0.88 wt%

The yield of vanillin required to produce 0.9 wt% of carbon dioxide = 0.289*0.9 = 0.26 wt%

Thus, 1.24 wt % of 2-methylphenol and 0.9 wt% of carbon dioxide are produced from 1.14 wt% of vanillin, which closely matched with the decrease in vanillin yield (~ 1.62 wt%) in between 450 °C – 550 °C.

[D]: Apocynin conversion into 2, 3-Dimethylphenol and C_1 compound lignin thin-film pyrolysis





+ C_1 compound **[4]**

($C_9H_{10}O_3$) ($C_8H_{10}O$) (Mol. Wt. = 44 g/mol)

Apocynin 2, 3-dimethylphenol

(Mol. Wt. = 166 g/mol) (Mol. Wt. = 122 g/mol)

Reaction [4] show the conversion of apocynin into 2, 3-dimethylphenol and C_1 compound. The C_1 compound here could be one of the unidentified pyroylsis product during lignin thin-film pyrolysis. The stoichiometry of reaction [4] on weight basis is as follows,

166 gm of apocynin gives 122 gm of 2, 3-dimethylphenol

Thus, 1 gm of apocynin gives 0.734 gm of 2, 3-dimethylphenol

For increase in the pyrolysis temperature from 350 °C to 550 °C:

Decrease in apocynin yield = 5.2 wt%

Increase in 2, 3-dimethylphenol yield = 6.47 wt%

The yield of apocynin required to produce 6.47 wt% of 2, 3-dimethylphenol = 0.734*6.47 = 4.74 wt%

Thus, 6.47 wt % of 2, 3-dimethylphenol is produced from 4.74 wt% of apocynin, which is closely matched with the decrease in apocynin yield (~ 5.2 wt%) in between 350 °C – 550 °C.

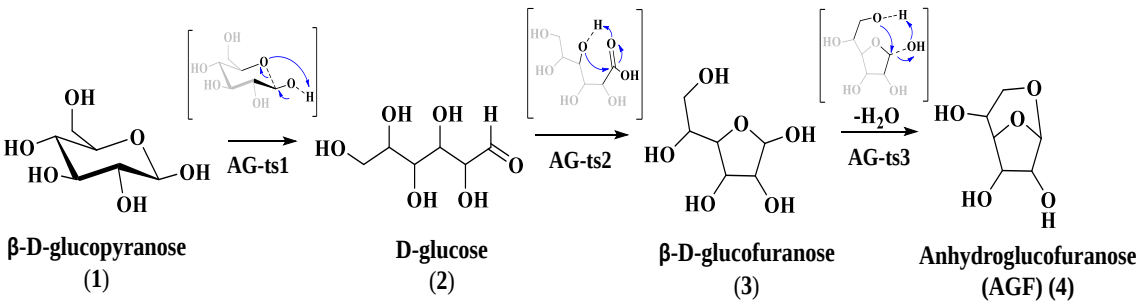
Appendix 4

Density Functional Calculations for Insights into AGF and DAGP formation mechanisms

The activation barriers for AGF and DAGP formation are computed using the methodology reported elsewhere.[1] Density Functional Theoretical (DFT) calculations were performed using the Gaussian *09* code. The reaction schemes for AGF and DAGP formation from glucose, as the reactant, are shown in Figure S1 [A & B]. The transition states of the reaction are shown above the reaction arrow.

AGF formation from β-D-glucopyranose (**1**) involves ring opening to form acyclic D-glucose (**2**), followed by 1,4-acetal bond formation in (**2**) generating β-D-glucofuranose (**3**). The 5-membered glucofuranose (**3**) undergoes 1,6-acetal bond with dehydration in a concerted fashion, forming AGF (**4**).[3-5] Generation of β-D-glucofuranose (**3**) is the most crucial step responsible for AGF formation.[6] DFT computed activation enthalpies of the three steps involved in AGF formation i.e., AG-ts1, AG-ts2 and AG-ts3 are 45.4, 38.3 and 54.7 kcal.mol^{-1}, respectively. The activation enthalpy values indicate that dehydration accompanied by 1,6-acetal bond formation, i.e., AG-ts3, is the rate-limiting-step during AGF formation from glucopyranose.

DAGP is an anhydrosugar comprising of 1,4 and 3,6 acetal bonds of the pyranose ring. [5, 7] An-often referenced mechanism[6] for DAGP formation discarded DAGP formation from β-D-glucopyranose (**1**) due to difference in the orientation of OH group at C_1 in β-D-glucopyranose, which hinders 1,4-acetal bond formation. But β-D-glucopyranose (**1**) can readily undergo ring opening to D-glucose (**2**), which can further cyclize to form α-D-glucopyranose (**5**). This is followed by 1,4-acetal bond formation and simultaneous loss of water from O_1H and H_4 atoms generating 1,4-anhydroglucopyranose (**6**). Loss of another water molecule from (**6**) i.e., O_6H and H_3 atoms, along with 3,6-acetal bond formation results in DAGP (**7**). The activation enthalpies of all the steps in the pathway of DAGP formation from glucose are 45.4, 37.6, 59.2 and 70.7 kcal.mol^{-1}, respectively. Therefore, 3,6-acetal bond formation step (DA-ts3) is the rate-limiting step.



[**A**]

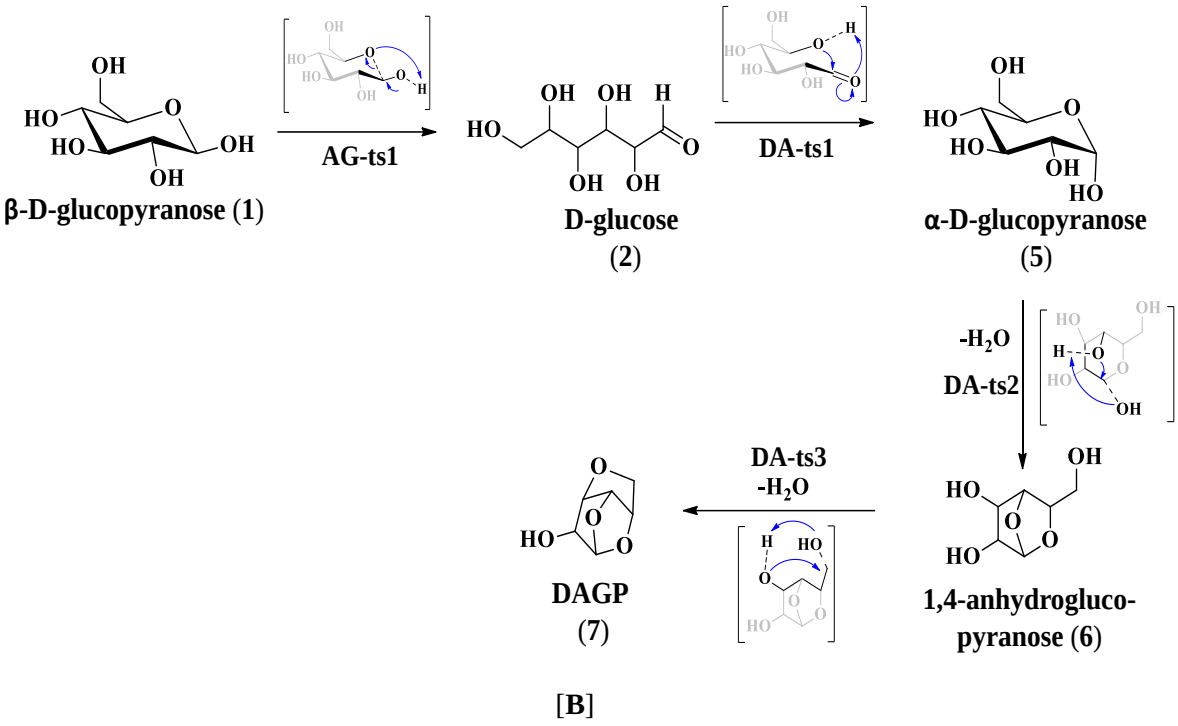


Figure S1: Reaction scheme for [**A**] 1,6-Anhydroglucofuranose (AGF) [**B**] 1,4,3,6-dianhydro-α-D-glucopyranose (DAGP) formation from glucose. The blue arrows in the molecular structures show the electron flow during the reaction. Transition states of the reactions are illustrated above the arrow (in brackets), where the atoms not taking part in the reaction are faded.

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