Supporting Information

Mathematical Modeling of Fast Biomass Pyrolysis and Bio-oil Formation.
Note II: Secondary Gas-Phase Reactions and Bio-oil Formation
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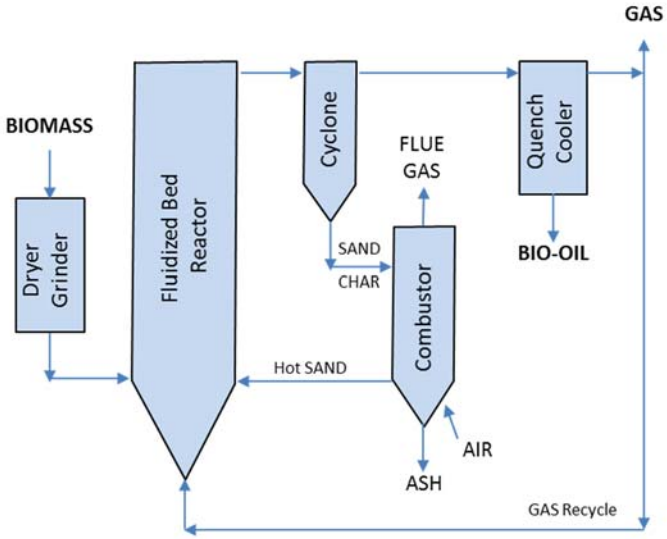

Figure S1. Schematic of a circulating fluidized bed fast pyrolysis process[2].

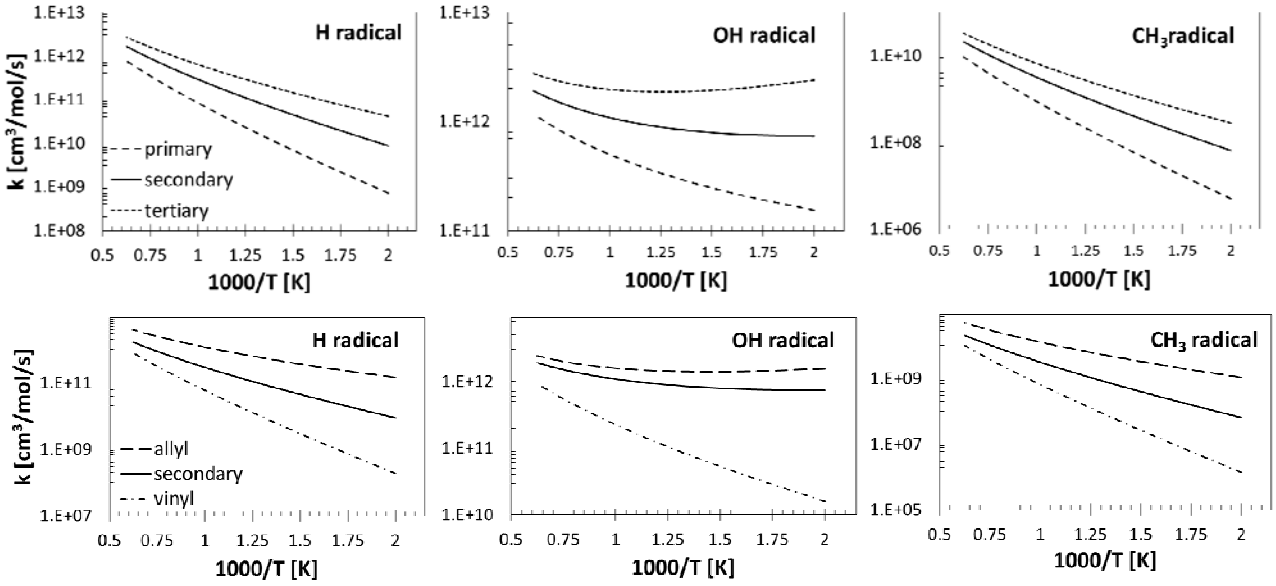

Figure S2. H-abstraction reactions. Rate constants of H, OH and CH_3 (per H-atom) for single primary, secondary, tertiary H-atoms (top) and for secondary H-atoms in alkyl, vinyl and allyl-sites (bottom).

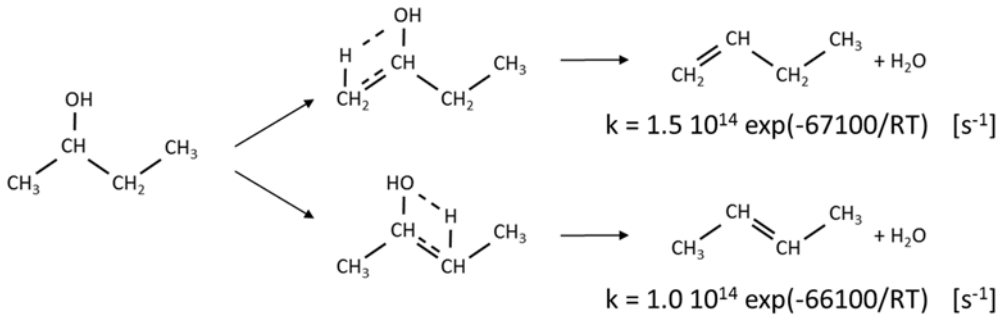

Figure S3. Dehydration reactions of 2-butanol to form 1-butene and 2-butene, via four center molecular reactions.

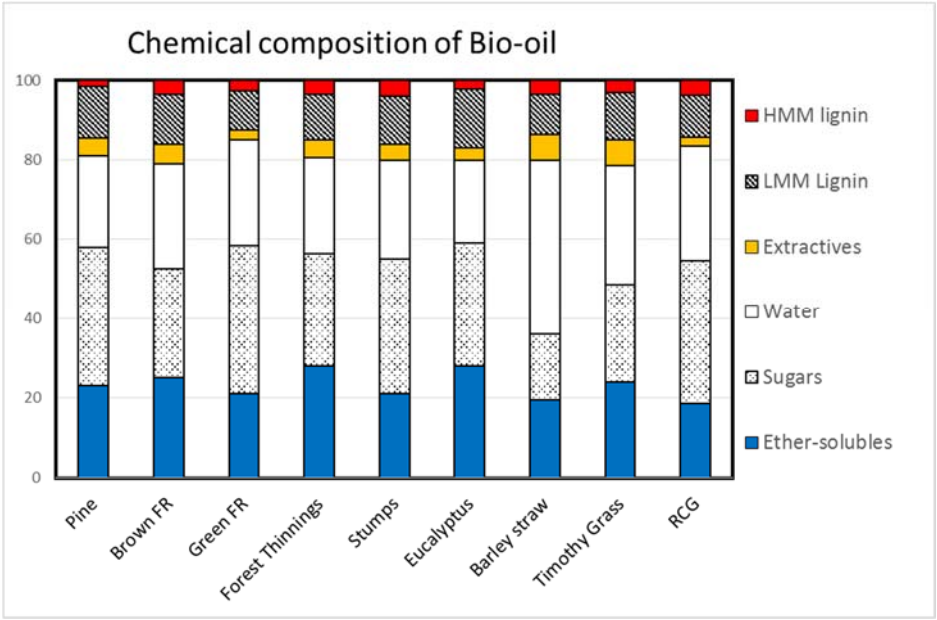

Figure S4. Chemical composition of several bio-oils[86].

Table S1. Multi-step kinetic scheme of biomass pyrolysis

	Pyrolysis Reactions			**Kinetic Parameters A (s^{-1}), Eact**
	Cellulose			
1	CELL	->	CELLA	1.5 10^{14} x exp(-47000/RT)
2	CELLA	->	0.4 HAA + 0.05 GLYOX + 0.15 CH3CHO + 0.25 HMFU + 0.35 ALD3 + 0.15 CH3OH + 0.3 CH2O + 0.61 CO + 0.36 CO2 + 0.05 H2 + 0.93 H2O + 0.02 HCOOH + 0.05 C3H6O2 + 0.05 G{CH4} +	2.5 10^{6}x exp(-19100/RT)
3	CELLA	->	LVG	3.3 x T x exp(-10000/RT)
4	CELL	->	5 H2O + 6 CHAR	6 10^{7} x exp(-31000/RT)
	Hemicellulose			
5	GMSW	->	0.70 HCE1 + 0.30 HCE2	1 10^{10} x exp(-31000/RT)
6	XYHW	->	0.35 HCE1 + 0.65 HCE2	1 10^{10} x exp(-28500/RT)
7	HCE1	->	0.6 XYLAN + 0.2 C3H6O2 + 0.12 GLYOX + 0.2 FURF + 0.4 H2O + 0.08 G{H2} + 0.16 CO	3 x T x exp(-11000/RT)
8	HCE1	->	0.4 H2O + 0.79 CO2 + 0.05 HCOOH + 0.69 CO + 0.01 G{CO} + 0.01 G{CO2} + 0.35 G{H2} + 0.3 CH2O + 0.9 G{COH2} + 0.625 G{CH4} + 0.375 G{C2H4} + 0.875 CHAR	1.8 10^{-3} x T x exp(-3000/RT)
9	HCE2	->	0.2 H2O + 0.275 CO + 0.275 CO2 + 0.4 CH2O + 0.1 C2H5OH + 0.05 HAA + 0.35ACAC + 0.025 HCOOH + 0.25 G{CH4} + 0.3 G{CH3OH} + 0.225 G{C2H4} + 0.4 G{CO2} + 0.725 G{COH2} +	5 10^{9} x exp(-31500/RT)
	Lignins			
10	LIGC	->	0.35 LIGCC + 0.1 COUMARYL + 0.08 PHENOL + 0.41 C2H4 + 1.0H2O + 0.7 G{COH2} + 0.3 CH2O + 0.32 CO + 0.495 G{CH4} +	1 10^{11} x exp(-37200/RT)
11	LIGH	->	LIGOH + 0.5 ALD3 + 0.5 C2H4 + 0.2 HAA + 0.1 CO + 0.1 G{H2}	6.7 10^{12} x exp(-37500/RT)
12	LIGO	->	LIGOH + CO2	3.3 10^{8} x exp(-25500/RT)
13	LIGCC	->	0.3 COUMARYL + 0.2 PHENOL + 0.35 HAA + 0.7 H2O + 0.65 CH4 + 0.6 C2H4 + H2 + 1.4 CO + 0.4 G{CO} + 6.75 CHAR	1 10^{4} x exp(-24800/RT)
14	LIGOH	->	0.9 LIG + H2O + 0.1 CH4 + 0.6 CH3OH + 0.05 G{H2} + 0.3 G{CH3OH} + 0.05 CO2 + 0.65 CO + 0.6 G{CO} + 0.05 HCOOH + 0.85 G{COH2} + 0.35 G{CH4} + 0.2 G{C2H4} + 4.25 CHAR +	1 10^{8} x exp(-30000/RT)
15	LIG	->	0.7 FE2MACR + 0.3 ANISOLE + 0.3 CO + 0.3 G{CO} + 0.3 CH3CHO	4 x T x exp(-12000/RT)
16	LIG	->	0.6 H2O + 0.4 CO + 0.2 CH4 + 0.4 CH2O + 0.2 G{CO} + 0.4 G{CH4} + 0.5 G{C2H4} + 0.4 G{CH3OH} + 2 G{COH2} + 6 CHAR	8.3 10^{-2} x T x exp(-8000/RT)
17	LIG	->	0.6 H2O + 2.6 CO + 1.1 CH4 + 0.4 CH2O + C2H4 + 0.4 CH3OH +	1 10^{7} x exp(-24300/RT)
	Extractives			
18	TGL	->	ACROL + 3 FFA	7 10^{12} x exp(-45700/RT)
19	TANN	->	0.85 FENOL + 0.15 G{PHENOL} +G{CO} + H2O + ITANN	2 10^{1} x exp(-10000/RT)
20	ITANN	->	5 CHAR + 2 CO + H2O + G{COH2}	1 10^{3} x exp(-25000/RT)
	Metaplastic			
21	G{CO2}	->	CO2	1 10^{6} x exp(-24000/RT)
22	G{CO}	->	CO	5 10^{12} x exp(-50000/RT)
23	G{COH2}	->	CO+H2	1.5 10^{12} x exp(-71000/RT)
24	G{H2}	->	H2	5 10^{11} x exp(-75000/RT)
25	G{CH4}	->	CH4	5 10^{12} x exp(-71500/RT)
26	G{CH3OH}	->	CH3OH	2 10^{12} x exp(-50000/RT)
27	G{C2H4}	->	C2H4	5 10^{12} x exp(-71500/RT)
28	G{PHENOL}	->	PHENOL	1.5 10^{12} x exp(-71000/RT)
	H2O Evap.			
29	ACQUA	->	H2O	1 x T x exp(-8000/RT)

Table S2. Formation enthalpy $\Delta H_{f,298}$ [kcal/mol] and entropy $\Delta S_{f,298}$ [cal/mol/K] of major oxygenated species released from biomass pyrolysis.

Chemical Name		ΔH_f	ΔS_f
Glyoxal	$C_2H_2O_2$	-50.6	65.4
Acetaldehyde	C_2H_4O	-39.5	63.0
Acetic Acid	$C_2H_4O_2$	-103.9	67.4
Hydroxy-acetaldehyde	$C_2H_4O_2$	-73.5	73.6
Ethylene-glycol	$C_2H_6O_2$	-92.0	76.3
Acrolein	C_3H_4O	-20.3	67.4
Propanedial	$C_3H_4O_2$	-62.4	73.7
3-Hydroxy-2-oxo-propanal	$C_3H_4O_3$	-102.7	88.4
Propanal	C_3H_6O	-45.3	72.8
1-Propanol	C_3H_8O	-60.9	76.4
2-Propanol	C_3H_8O	-65.5	74.5
Acetol	$C_3H_6O_2$	-87.4	80.6
3-Hydroxypropanal	$C_3H_6O_2$	-80.3	83.3
1,3-Propanediol	$C_3H_8O_2$	-45.5	86.0
Glycerol	$C_3H_8O_3$	-137.1	95.8
Furan	C_4H_4O	-10.2	60.2
Butanedione	$C_4H_6O_2$	-78.4	84.2
C4 O-heterocycles	C_4H_8O	-27.7	73.6
Furfural	$C_5H_4O_2$	-36.1	77.8
Xylosan	$C_5H_8O_4$	-151.6	104.8
Phenol	C_6H_6O	-23.0	75.3
Hydroxymethyl-furfural	$C_6H_6O_3$	-79.8	98.2
Levoglucosan	$C_6H_{10}O_5$	-200.9	113.5
Anisole	C_7H_8O	-17.1	84.0
Syringol	$C_8H_{10}O_3$	-95.3	111.0
Coumaryl alcohol	$C_9H_{10}O_2$	-49.2	109.0
Sinapyl aldehyde	$C_{11}H_{12}O_4$	-70.3	145.0
Heavy Molecular Weight Lignin (HMWL)	$C_{24}H_{28}O_4$	40.0	281.0

Table S3. Biomass pyrolysis, torrefaction, and gasification processes[2].

		Residence time		Product Yields (wt.%)		
Mode	**Temperature [°C]**	**vapor**	**Solid**	**Liquid**	**solid**	**gas**
Fast Pyrolysis	500	1-2 s		75	12	13
Intermediate Pyrolysis	500	5-30 s		50	25	25
Slow (Carbonization)	400	hours-days	Hours	30	35	35
Torrefaction	280		10-60 min	0	80	20
Gasification	750-900	1-5 s		3	1	95

Table S4. Comparison of physical properties of bio-oil and mineral oils: Heavy Fuel Oil (HFO) and Light Fuel Oil (LFO)[84].

	Typical bio oil	HFO 180/420	LFO EN 590
Water (% wt)	20-30	-	-
Solids (% wt)	<0.5	-	-
Ash (%wt)	0.01-0.1	0.08 max	0.01 max
Oxygen (%wt)	35-40	-	-
Nitrogen (wt)	<0.4	0.4	0.02
Sulphur (%wt)	<0.05	1.0 max	0.001 max
Density@15 °C (g/cm^3)	1.10-1.30*	0.99/0.995 max	0.845 max
Viscosity@40 °C (cSt)	15-35*	180/420 max @50 °C	2-4.5
LHV (MJ/kg)	13-18	40.6 min	42.6
Distillability/Stability (heating and long term storage)	Non distillable/Unstable	Distillable/Stable	Distillable/Stable

* depending on water content