

Supplemental Material

S1. Biomass Characterization

S2. Gas phase kinetics of released species

S1. Biomass Characterization

As already mentioned, three reference components are used to describe the composition of the lignins. Fig. S1a shows that the triangle defined by the three pseudocomponents includes the most part of different natural lignins [1, 2]. A single lignin composition can be then easily characterized as a linear combination of the three reference components, which satisfies the C/H/O content of the elemental analysis.

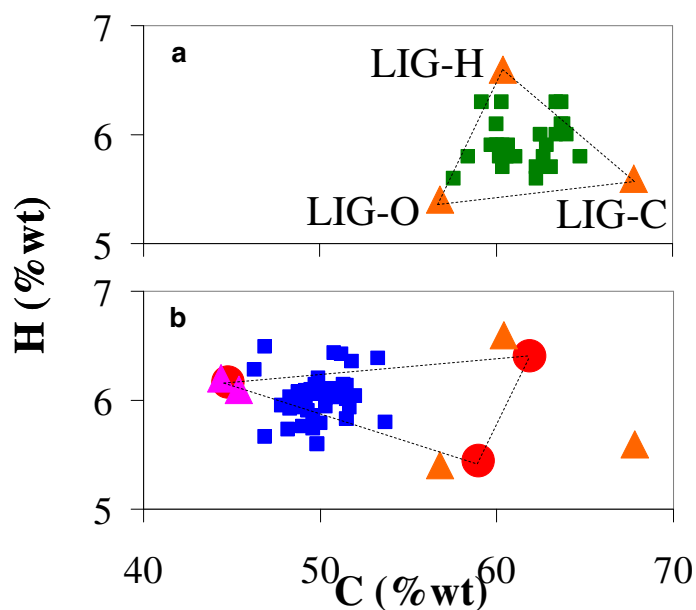


Figure. S1. H and C content of biomasses. Panel a) Comparison between the triangle defined by the lignin pseudocomponents and natural lignins. Panel b) Comparison between the triangle used to characterize the biomass and natural biomasses [1,2].

In the same way, the biomass composition is obtained by linearly combining three reference components (P1, P2 and P3). Fig. S1b shows in the Carbon-Hydrogen plot that most of the biomasses [3] are inside the triangle, whose vertexes are P1, P2 and P3.

P1 is here assumed as 60% cellulose and 40% hemicellulose (statistically the most probable ratio) with a C/H/O = 44.8/6.16/49.06 (%wt). P2 (C/H/O = 59.0/5.44/35.56) and P3 (C/H/O = 61.9/6.4/31.72) are the combination of 80% LIG-O and 20% LIG-C and of 80% LIG-H and 20% LIG-C. Some biomasses lie outside this triangle, anyway, it is possible to modify the reference points and to extend the proposed approach by including new reference species. For instance, the biomasses richer in hydrogen should be conveniently described by using a reference fatty acid, while phenolic components allow to characterize the biomasses with a low hydrogen content.

S2. Gas phase kinetics of released species

Volatile components released from biomasses in the gas phase are subject to successive decomposition and oxidation reactions. The primary propagation reactions of these oxygenated species (reported in Table S1) form intermediate products already considered in a detailed kinetic scheme of pyrolysis and oxidation of hydrocarbons. A very simplified sub-mechanism considers the initiation and the H abstraction reactions of the released species, as reported in Arrhenius form in Table S2. Rate parameters of reverse reactions are evaluated on the basis of thermodynamic consistency. H-abstraction reactions are expressed in a generic form with the indication of the number (N_H) and type of H-atoms to be abstracted. This expression refers to the assumption that the rate constant for the metathesis reaction is only function of the abstracting radical and of the type of the H to be abstracted. Details on this approach can be found in [4].

The whole kinetic scheme together with thermodynamic properties of all involved species are available in the web site [<http://www.chem.polimi.it/CRECKModeling/>]

Chemical name	Formula	ΔH_f°	ΔS_f°
Glyoxal	C ₂ H ₂ O ₂	-50.6	65.42
hydroxyl-acetaldehyde (HAA)	C ₂ H ₄ O ₂	-73.5	73.57
ethylene glycol	C ₂ H ₆ O ₂	-92	76.36
n-propanol	1-C ₃ H ₇ OH	-60.93	76.41
iso-propanol	2-C ₃ H ₇ OH	-65.1	74.3
hydroxyl-oxo-propanal	C ₃ H ₄ O ₃	-102.77	88.45
propanal, 3-hydroxy-	C ₃ H ₆ O ₂	-80.3	83.37
propane-1,3-diol	C ₃ H ₈ O ₂	-96.93	87.16
propanedial	C ₃ H ₄ O ₂	-65.8	79.72
Furan	C ₄ H ₄ O	-8.34	63.87
Tetrahydro-furan (THF)	C ₄ H ₈ O	-44.21	72.26
Butanedione	C ₄ H ₆ O ₂	-78.36	84.28
Xylofuranose (Xylof)	C ₅ H ₈ O ₄	-151.54	104.94
furan-2-carboxaldehyde (Furfural)	C ₅ H ₄ O ₂	-36.14	77.85
levoglucosan (LVG)	C ₆ H ₁₀ O ₅	-200.9	113.67
5-hydroxymethyl-furfural (HMFU)	C ₆ H ₆ O ₃	-79.8	98.2
2,6-dimethoxy-phenol (MGuai)	C ₈ H ₁₀ O ₃	-113.53	134.38
4-(3-hydroxy-1-propenyl)phenol (pCoumaryl)	C ₉ H ₁₀ O ₂	-49.81	110.18
3-(4-hydroxy-3,5-dimethoxy-phenyl)acryl-aldehyde (FE2MAC)	C ₁₁ H ₁₂ O ₄	-116.03	136.83

Table S1. Main volatile species from biomass pyrolysis (units are kcal, mol, K)

(Names in brackets are used in the kinetic scheme of Table S2)

Reactions	A	Eatt	Reactions	A	Eatt
HOCH ₂ CH ₂ OH ↔ CH ₂ OH + CH ₂ OH	3·10 ¹⁶	83000.	CH ₃ (CO) ₂ CH ₃ ↔ 2CH ₃ CO	1·10 ¹⁶	72000.
HOCH ₂ CH ₂ OH ↔ CH ₂ CH ₂ OH + OH	3·10 ¹⁶	93000.	Rfuran > C ₃ H ₃ + CO	1·10 ¹³	38000.
HOCH ₂ CH ₂ OH ↔ CH ₂ O + CH ₃ OH	1·10 ¹³	59000.	Rfuran > CH ₂ CO + C ₂ H	1·10 ¹³	43000.
HOCH ₂ CH ₂ OH ↔ CH ₃ CHO + H ₂ O	1·10 ¹³	59000.	HMFU ↔ CH ₂ O + C ₃ H ₄ O ₂	5·10 ¹²	59000.
HAA ↔ CH ₂ OH + HCO	3·10 ¹⁶	82000.	HMFU > Furfural+ H + HCO	2·10 ¹⁶	79000.
HAA ↔ CH ₂ O + CH ₂ O	5·10 ¹²	60000.	LVG > HAA + CH ₂ CHCHO + OH + HCO	2.5·10 ¹⁶	85000.
Glyoxal ↔ HCO + HCO	3·10 ¹⁶	71000.	LVG > OH+OH+CH ₃ (CO) ₂ CH ₃ +CH ₂ CO	2.5·10 ¹⁶	88000.
C ₂ H ₃ CH ₂ OH ↔ CH ₃ +CH ₂ CH ₂ OH	2·10 ¹⁶	86000.	LVG > C ₆ H ₈ O ₄ + H ₂ O	2.5·10 ¹²	60000.
C ₂ H ₃ CH ₂ OH ↔ C ₂ H ₅ +CH ₂ OH	2·10 ¹⁶	82000.	LVG > HMFU + 2. H ₂ O	2.5·10 ¹²	60000.
C ₂ H ₃ CH ₂ OH ↔ C ₃ H ₆ +H ₂ O	1·10 ¹³	59000.	C ₆ H ₈ O ₄ > HMFU + H ₂ O	2.5·10 ¹²	59000.
C ₂ H ₃ CH ₂ OH ↔ C ₂ H ₆ +CH ₂ O	1·10 ¹³	59000.	Xylof> HAA + HCO + CH ₂ CHO	5·10 ¹⁶	82000.
HOCH ₂ CH ₂ CHO ↔ CH ₂ CH ₂ OH+HCO	3·10 ¹⁶	82000.	pCoumaryl ↔ Rcresol + CH ₂ CHO	1·10 ¹⁶	72000.
HOCH ₂ CH ₂ CHO ↔ CH ₂ OH+CH ₂ CHO	3·10 ¹⁶	81000.	H+ pCoumaryl > Phenol+.5C ₂ H ₄ +.5HCO+.5CH ₂ CH ₂ CHO	1·10 ¹⁰	5000.
HOCH ₂ CH ₂ CHO ↔ CH ₂ CHCHO+H ₂ O	1·10 ¹³	59000.	FE2MAC > MGuai + CO + C ₂ H ₂	2·10 ¹⁶	88000.
OCHCH ₂ CHO ↔ HCO+CH ₂ CHO	1·10 ¹⁶	77000.	H+FE2MAC > C ₂ H ₃ + CO + C ₈ H ₁₀ O ₃	1·10 ¹⁰	5000.
HOCH ₂ CH ₂ CHO ↔ CH ₃ CHO+CH ₂ O	1·10 ¹³	59000.	H+ Mguai > .5Phenol + CH ₃ O + .5C ₈ H ₁₀ O ₃	1·10 ¹⁰	5000.
OCHCHOHCHO > HCO + Glyoxal + H	1·10 ¹⁶	77000.			
H-Abstraction Reactions			H-Abstraction Reactions		
	N _H	type		N _H	type
R+HOCH ₂ CH ₂ OH > RH +.2CH ₃ OH + .2CH ₂ O + .6CH ₃ CHO+.6OH +.2OCHCH ₂ OH +.2H	5	1	R+CH ₃ (CO) ₂ CH ₃ > RH + CH ₃ CO + CH ₂ CO	6	0
R+ HAA > RH + CO + CH ₂ OH	1	8	R + Furan > RH + Rfuran	4	8
R+ HAA > RH+ Glyoxal +H	1	1	R+HMFU > RH + Furfural + CO + H	1	8
R+Glyoxal > RH + CO + HCO	2	8	R+ Furfural > RH + 2 CO + C ₃ H ₃	1	8
R+C ₂ H ₃ CH ₂ OH > RH + C ₂ H ₄ + CH ₂ OH	3	0	R+LVG > RH + CH ₂ O + CH ₂ CHO + OCHCHOHCHO	4	1
R+C ₂ H ₃ CH ₂ OH > RH + .5C ₃ H ₆ + .5OH+ + .5CH ₃ CHO + .5CH ₃	4	1	R+LVG > RH + C ₆ H ₈ O ₄ + OH	0.5	1
R+C ₂ H ₃ CH ₂ OH > RH + CH ₂ O + C ₂ H ₃	1	0	R+LVG > RH + CO + OH + CH ₂ O + CH ₃ (CO) ₂ CH ₃	0.5	1
R+HOCH ₂ CH ₂ CHO > RH + CH ₂ CH ₂ OH + CO	1	8	R+C ₆ H ₈ O ₄ > RH + HMFU +OH	1	1
R+HOCH ₂ CH ₂ CHO > RH +.5CH ₂ CHCHO + +.5OH +.5CH ₃ CHO +.5HCO	4	1	R+ Xylof > RH + OH + H ₂ O + C ₃ H ₄ O ₂	2	1
R+HOCH ₂ CH ₂ CHO > RH + CH ₂ O + CH ₂ CHO	1	0	R+ Xylof> RH + CH ₂ CHO + HAA + CO	2	1
R+OCHCH ₂ CHO > RH + CO + CH ₂ CHO	2	8	R+ Xylof> RH + OCHCHO + .5CH ₂ CHCHO + .5OH + CH ₃ CHO + .5HCO	2	1
R+ pCoumaryl > RH + CH ₂ CO + Rcresol	1	8	R+ MGuai > RH+ .5Phenol + HCO + .5MGuai	6	0
R+OCHCHOHCHO > RH + CO + Glyoxal +H	2	8			

Table S2. Primary propagation reactions of released species. (Units are: s, l, mole, cal and K)

References

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