Extractives extend the applicability of multistep kinetic scheme of biomass pyrolysis

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Supplemental Material

1- Estimation of optimal characterization parameters

Based on the elemental analysis, the biomass characterization method estimates a biochemical composition in terms of seven reference components. The predicted biomass composition must satisfy only the three H, C, and O balances, therefore there are 5 degrees of freedom converted into 5 splitting parameters. These parameters define the three reference mixtures whose relative concentration is derived by the H/C/O balances.

As already discussed in the paper, optimal splitting or characterization parameters can be obtained by minimizing the square deviations between the predicted and experimental values of cellulose, hemicellulose, lignin, and extractives. Optimal splitting parameters were obtained with the feasible boundary conditions between 0 and 1. TGL is expected to increase with the H content of the biomass sample, while TANN will increase when H content is decreasing. A non-linear regression method [1, 2] was applied in order to find the optimal splitting parameters taking also into account the relative H_i and C_i content of the biomass sample:

$$\alpha = \alpha_1 + \alpha_2 . C_i + \alpha_3 . H_i \quad [1]$$

$$\beta = \beta_1 + \beta_2 . C_i + \beta_3 . H_i \quad [2]$$

$$\gamma = \gamma_1 + \gamma_2 . C_i + \gamma_3 . H_i \quad [3]$$

$$\delta = \delta_1 + \delta_2 . C_i + \delta_3 . H_i \quad [4]$$

$$\varepsilon = \varepsilon_1 + \varepsilon_2 . C_i + \varepsilon_3 . H_i \quad [5]$$

The parity or scatter diagrams reported in Figure S1 clearly show that the relative amount of cellulose and hemicellulose is different in grass/cereal and wood samples. Therefore, the splitting parameter α (ratio between cellulose and holocellulose) could be better optimized by dividing the overall biomass samples into two different classes. Table A1 reports the optimized splitting parameters for the overall database, for grass and cereals, and for hardwood and softwood samples.

Figure S2 clearly confirms how the optimal splitting parameter α, widely scattered when considering the overall set of data, become more correlated with hydrogen content when considering the two separate biomass classes. Namely, the ratio between cellulose and holocellulose ranges between 0.6-0.7 for wood, while it is lower than 0.6 for the grass and cereals.

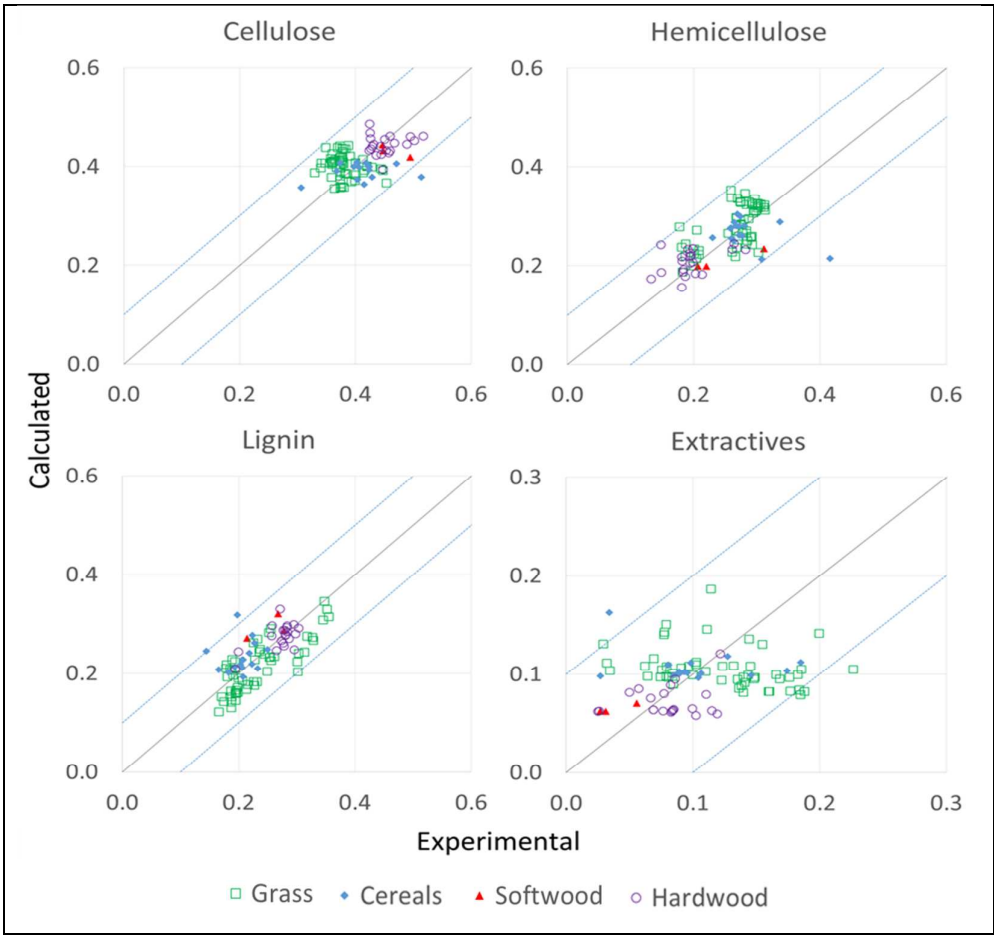


***Figure S1**. Parity diagrams of experimental and predicted biomass composition in terms of cellulose, hemicellulose, lignin, and extractives.*

		α	β	γ	δ	ε
OPT1: Overall	1	-0.586	0.995	1.015	0.294	0.734
	2	2.255	-0.012	-0.045	0.986	-0.372
	3	0.000	0.162	-0.005	0.002	0.021
OPT2: Wood	1	1.503	2.079	12.697	-1.750	-2.339
	2	-0.037	-2.160	-25.284	3.428	1.303
	3	-13.807	-0.207	12.461	13.422	41.335
OPT3: Grass	1	0.626	0.155	6.944	-2.249	-3.501
	2	0.877	-2.110	-13.983	0.731	3.038
	3	-8.681	29.643	13.707	33.856	45.092

***Table A1**. Optimized parameters for different ligno-celullosic feedstocks*

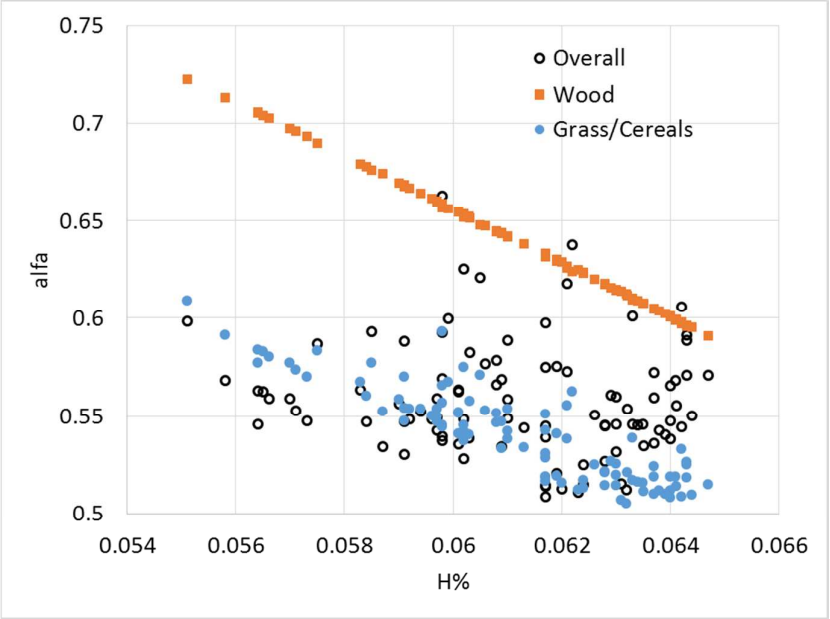


***Figure S2**. Optimal splitting parameter α (ratio between cellulose and holocellulose) as a function of H% for the overall database, for the wood, and for the grass/cereal samples*

Based on the splitting parameters of Table A1, it is possible to derive simple correlations to define the mass fractions of reference components. These correlations, simply obtained by linear regression methods [1,2], are reported in Table A2, in the following form for each reference species:

$$REF_K = \alpha_0 + \alpha_1.C_i + \alpha_{11}.C_i^2 + \alpha_2.H_i + \alpha_{22}.H_i^2 + \alpha_{12}.C_i.H_i \qquad (K=1, 7)$$

Figure S3 shows that the validity range of these expressions, to maintain the feasibility of biomass composition, is indeed quite limited. This is due to the prediction of unfeasible values above zero of some reference species outside this region. Figure S4 shows iso-lines of the surface of estimated amounts for TANN and TGL, thus indicating the region of feasibility values. The resulting intersection of the two feasible regions is indeed very limited. In order to enlarge this region of applicability of the characterization method, it should be necessary to drastically modify the regressions accounting for these feasibility boundaries. This is outside the purposes of this work. For this reason, and to warrant a complete respect of the H/C/O balances, it is preferable to refer to the three reference mixtures and to solve the corresponding linear system of equations.

GRASS Linear characterization																	
CELL	=	6.153	+	-21.875	Ci	+	20.483	Ci^2	+	6.803	Hi	+	3.925	Hi^2	+	-11.744	Ci* Hi
HECELL	=	4.178	+	-18.098	Ci	+	18.187	Ci^2	+	30.983	Hi	+	7.512	Hi^2	+	-42.778	Ci* Hi
LIGH	=	-1.411	+	4.574	Ci	+	-3.935	Ci^2	+	5.047	Hi	+	10.413	Hi^2	+	-7.619	Ci* Hi
LIGO	=	-10.653	+	53.328	Ci	+	-62.901	Ci^2	+	-85.335	Hi	+	-54.471	Hi^2	+	173.332	Ci* Hi
LIGC	=	12.623	+	-52.992	Ci	+	56.568	Ci^2	+	6.285	Hi	+	-2.564	Hi^2	+	-20.184	Ci* Hi
TGL	=	-3.898	+	11.971	Ci	+	-10.847	Ci^2	+	14.575	Hi	+	3.230	Hi^2	+	-7.411	Ci* Hi
TANN	=	-5.993	+	23.091	Ci	+	-17.554	Ci^2	+	21.642	Hi	+	31.954	Hi^2	+	-83.595	Ci* Hi

WOOD Linear characterization																	
CELL	=	11.814	+	-46.121	Ci	+	47.910	Ci^2	+	33.934	Hi	+	22.352	Hi^2	+	-79.165	Ci* Hi
HECELL	=	5.124	+	-22.635	Ci	+	23.302	Ci^2	+	25.813	Hi	+	19.902	Hi^2	+	-34.972	Ci* Hi
LIGH	=	-14.550	+	61.143	Ci	+	-70.524	Ci^2	+	-75.695	Hi	+	-49.969	Hi^2	+	212.321	Ci* Hi
LIGO	=	-16.513	+	72.616	Ci	+	-75.716	Ci^2	+	-16.957	Hi	+	-70.433	Hi^2	+	19.080	Ci* Hi
LIGC	=	18.745	+	-84.434	Ci	+	96.927	Ci^2	+	68.397	Hi	+	35.378	Hi^2	+	-165.043	Ci* Hi
TGL	=	-1.574	+	4.203	Ci	+	-3.779	Ci^2	+	10.470	Hi	+	10.271	Hi^2	+	-7.296	Ci* Hi
TANN	=	-2.045	+	15.229	Ci	+	-18.120	Ci^2	+	-45.961	Hi	+	32.499	Hi^2	+	55.075	Ci* Hi

***Table A2**. Correlations obtained by linear regression of the optimized values.*

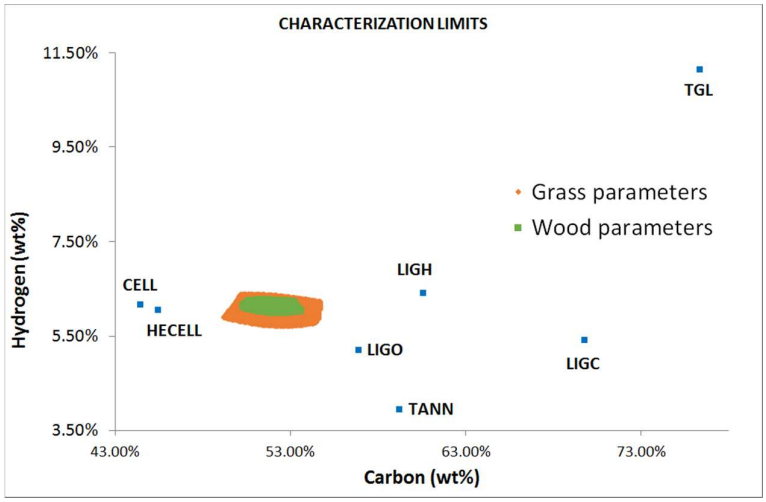


***Figure S3**. Characterization limits for both grass and wood set of equations. The colored area represent the region in which all reference species maintain feasible values.*

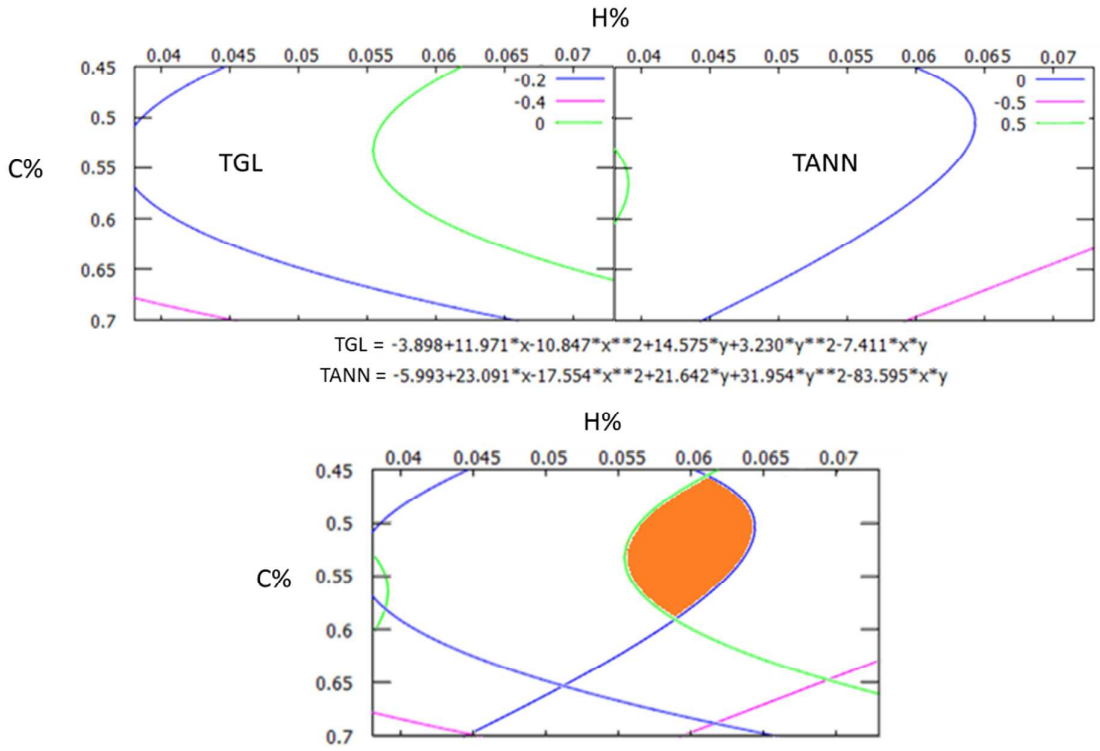


***Figure S4**. Grass/Cereal Samples. Contour map of TGL and TANN estimated values. Feasible region is obtained from the intersection of TANN and TGL feasible surfaces.*

Referring to the large scatter of extractive species, it is important to highlight that predicted extractives are the sum of two reference components, tannins and triglycerides, whose compositions are highly different. Figure S5 clearly shows how tannin species decreases when hydrogen content of the biomass increases, while the reverse is observed for the triglycerides. Figure S6 highlights the correlation between these extractive species. Comparisons reported in the scatter diagram of Figure S1 only refers to the sum of these two classes. Experimental data with a distinction between these two classes of components would be useful to improve the characterization method and to reduce the large scatter of extractives.

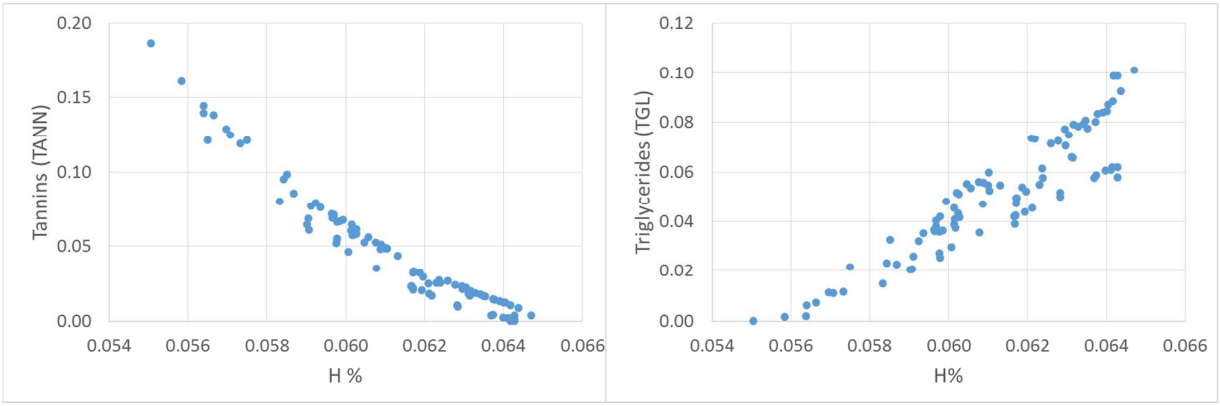


***Figure S5**. Tannin and triglyceride species versus biomass hydrogen content.*

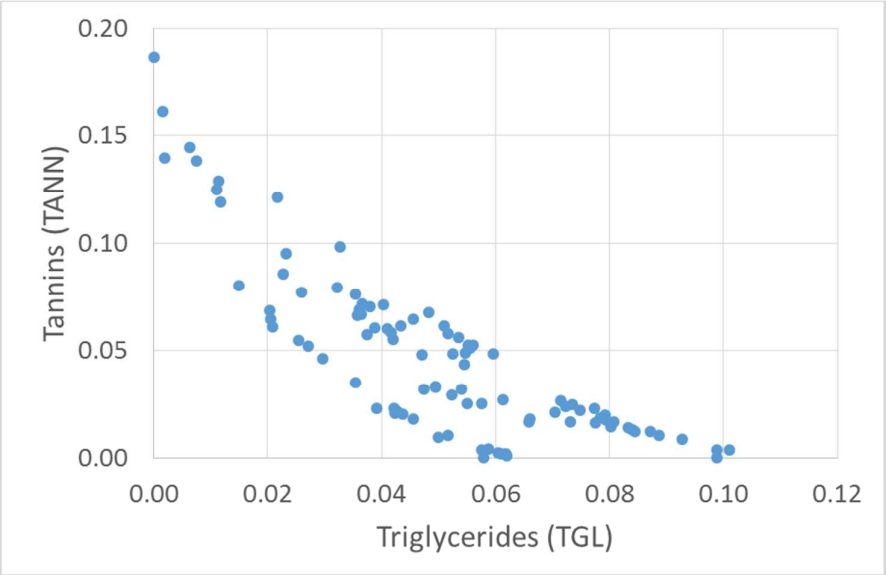


***Figure S6**. Correlation between tannin and triglyceride species*

References

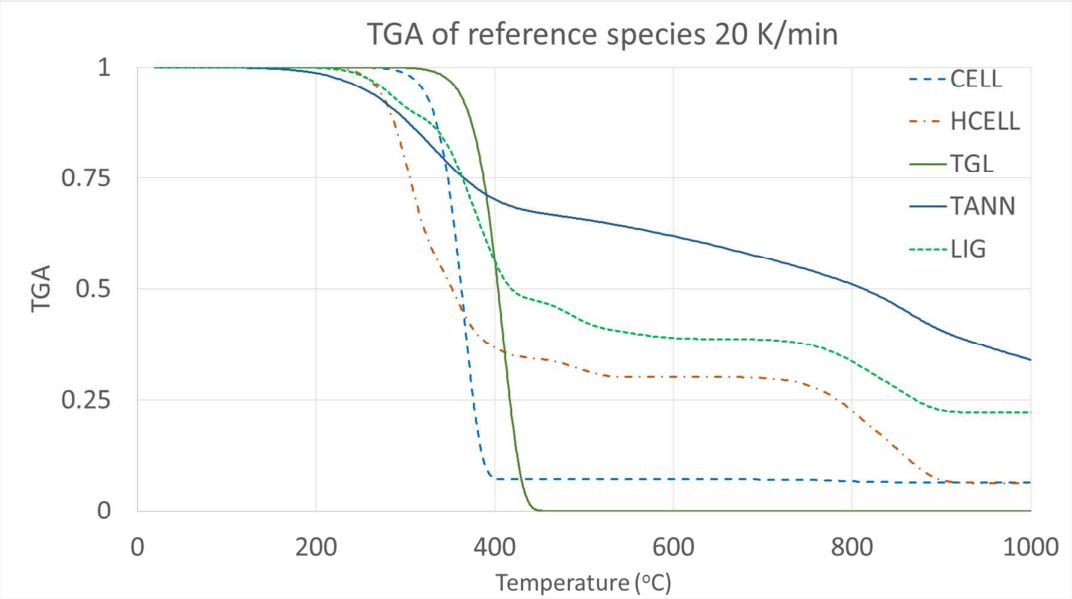
1. Buzzi-Ferraris, G. and F. Manenti, *Outlier detection in large data sets.* Computers & chemical engineering, 2011. **35**(2): p. 388-390.
2. Buzzi-Ferraris, G. and F. Manenti, *BzzMath: Library overview and recent advances in numerical methods.* Computer Aided Chemical Engineering, 2012. **30**(2): p. 1312-1316.

2- Multistep Kinetic Scheme

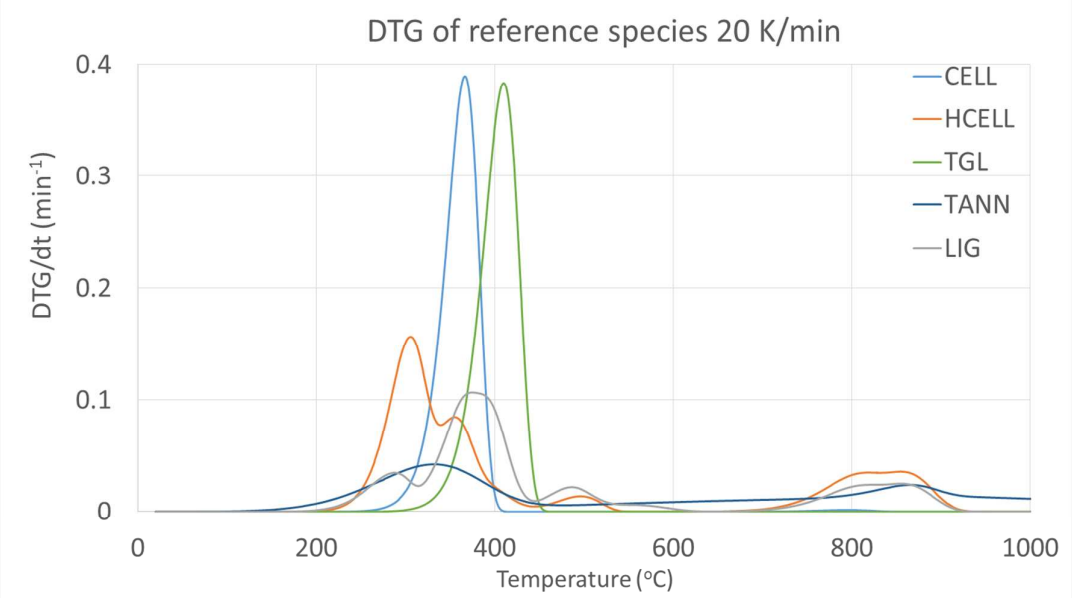
$$k = A \cdot 10^{\beta} \cdot T^{\alpha} \cdot e^{\left(-\frac{Eact.}{R \cdot T}\right)}$$ (T in Kelvin, Eact in cal/mol)

Pyrolysis Reactions			Kinetic Parameters
Cellulose			**/A/β/α/Eact/**
CELL	>	CELLA	/4/13/0/45000/
CELLA	>	0.45HAA + 0.2 GLYOX + 0.1 MECHO + 0.25 HMFU + 0.3 ALD3 + 0.15 CH3OH + 0.4 CH2O + 0.31 CO + 0.41 CO2 + 0.05 H2 + 0.83 H2O + 0.02 HCOOH + 0.2 CH4S + 0.05 CH2S + 0.61 CHAR	/2/6/0/19100/
CELLA	>	LVG	/4/0/1/10000/
CELL	>	5 H2O + 6 CHAR	/6.5/7/0/31000/
Hemicellulose			
HECELL	>	0.5 HCE1 + 0.5 HCE2	/1/10/0/31000/
HCE1	>	0.025 H2O + 0.5 CO2 + 0.025 HCOOH + 0.5 CO + 0.8 CH2O + 0.125 ETOH + 0.1 CH3OH + 0.25 C2H4 + 0.125 CH2S + 0.275 CO2S + 0.4 COH2S + 0.45 CH3OHS + 0.325 CH4S + 0.875 CHAR	/1.2/9/0/30000/
HCE1	>	0.25 H2O + 0.8 CO2 + 0.05 HCOOH + 0.1 CO + 0.15 COS + 0.15 CO2S + 0.2 CH2S + 0.3 CH2O + 1.2 COH2S + 0.625 CH4S + 0.375 C2H4S + 0.875 CHAR	/0.15/0/1/8000/
HCE1	>	XYLAN	/3/0/1/11000/
HCE2	>	0.2 H2O + 0.175 CO + 0.275 CO2 + 0.5 CH2O + 0.1 ETOH + 0.2 HAA + 0.025 HCOOH + 0.25 CH4S + 0.3 CH3OHS + 0.275 C2H4S + 0.4 CO2S + 0.925 COH2S + 1.0 CHAR	/0.5/10/0/33000/
Lignins			
LIGC	>	0.35 LIGCC + 0.1 COUMARYL + 0.08 FENOL + 0.41 C2H4 + 1.0H2O + 0.7 COH2S + 0.3 CH2O + 0.32 CO + 0.495 CH4S + 5.735 CHAR	/1.33/15/0/48500/
LIGH	>	LIGOH + 0.5 ALD3 + 0.5 C2H4 + 0.25HAA	/0.67/13/0/37500/
LIGO	>	LIGOH + CO2	/0.33/9/0/25500/
LIGCC	>	0.3 COUMARYL + 0.2 FENOL + 0.35 HAA + 0.7 H2O + 0.65 CH4S + 0.6 C2H4S + 1 COH2S + 0.4 CO + 0.4 COS + 6.75 CHAR	/1.67/6/0/31500/
LIGOH	>	1 LIG + 0.9 H2O + 0.1 CH4 + 0.6 CH3OH + 0.1 CH2S + 0.3 CH3OHS + 0.05 CO2 + 0.55 CO + 0.6 COS + 0.05 HCOOH + 0.85 COH2S + 0.35 CH4S + 0.2 C2H4S + 4.15 CHAR	/1/8/0/30000/
LIGOH	>	1.5 H2O + 0.8 CO + 0.1 CH4 + 0.2 CH2S + 1 COS + 4.2 COH2S + 1.65 CH4S + 0.3 C2H4S + 0.5 CH3OHS + 10.15 CHAR	/0.33/2/0/15000/
LIG	>	FE2MACR	/4/0/1/12000/
LIG	>	0.95 H2O + 0.2 CH2O + 0.4 CH3OH + 1 CO + 0.2 CH4 + 0.05 HCOOH + 0.45 COS + 0.5 COH2S + 0.4 CH4S + 0.65 C2H4S + 0.2 MECHO + 0.2 ALD3 + 5.5 CHAR	/0.4/9/0/30000/
LIG	>	0.6 H2O + 0.4 CO + 0.2 CH4 + 0.4 CH2O + 0.2 COS + 0.4 CH4S + 0.5 C2H4S + 0.4 CH3OHS + 2 COH2S + 6 CHAR	/0.083/0/1/8000/
Condensed Tannins			
CTANN	>	1 FENOL + 1 ITANN	/5/1/0/11000/
ITANN	>	6 CHAR + 3 CO + 3 H2O	/1.5/-2/0/6100/
Triglycerides			
TAG	>	ACRO + 3 FFA	/7/12/0/45700/
Metaplastic Species			
CO2S	>	CO2	/1/6/0/24000/
COS	>	CO	/0.5/13/0/50000/
COH2S	>	CO+H2	/5/11/0/71000/
CH2S	>	H2	/5/11/0/75000/
CH4S	>	CH4	/5/12/0/71667/
CH3OHS	>	CH3OH	/2/12/0/50000/
C2H4S	>	C2H4	/5/12/0/71667/
Moisture Evaporation			
ACQUA	>	H2O	/1.0/0/1/ 7644/

3-


TGA of reference species 20 K/min
TGA
Temperature (°C)
CELL
HCELL
TGL
TANN
LIG
1
0.75
0.5
0.25
0
0
200
400
600
800
1000

4-


DTG of reference species 20 K/min
DTG/dt (min-1)
Temperature (°C)
CELL
HCELL
TGL
TANN
LIG
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000