

Biomass pyrolysis reactions and products as studied by simultaneous thermal analysis techniques

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INTRODUCTION

From heterogeneous biomass, pyrolysis allows producing more homogeneous tar (oils) or char (carbonaceous solids) that are then easily stored and transported. The process conditions are known to affect the tar / char ratio and compositions [1,2]. A key step is the release of volatiles during the biopolymers early decomposition.

Among the thermal analysis techniques, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) are the best suited to simulate at the lab scale the pyrolysis processes. In the present study, influences of heating rate, sample mass, and grain size on the slow pyrolysis of cellulose, lignin, xylan and resinous wood samples were studied.

ENERGETICS OF BIOMASS PYROLYSIS

Tested materials: Cellulose, xylan, lignin, commercial pellets from resinous source (ground and sieved, resulting 0.125-0.250mm size fraction was used for the test).

Samples were heated in a SETARAM DSC131 Evo using an alumina pan between 25°C and 700°C at 10°C/min under nitrogen.

At low temperature, endothermic effects are observed due to free water evaporation. Resinous pellets exhibit an endotherm starting at 350.2°C and corresponding to cellulose depolymerization. It is followed by an exothermic effect attributed to presence of lignin.

As xylan represents only 10% of the hemicellulose [3] content of resinous wood, its thermal effect is not observed.

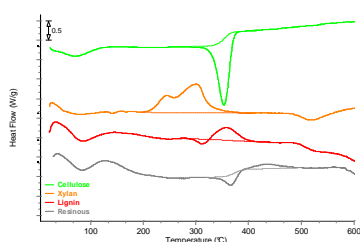


Figure 1 – superimposition of the HeatFlow = f(Temperature) data

Sample	Heat of pyrolysis (J/g)	Temperature at peak maximum (°C)
Cellulose	260.7	353.9
Xylan	-321.1	300.0
Lignin	-72.2 (14.4 -86.6)	310.9 / 360.3
Resinous	2.5 (41.5 -39.0)	432.4 / 368.0

Table 1 – results of integration and characteristic temperatures

PARAMETERS AFFECTING THE CHARCOAL YIELD

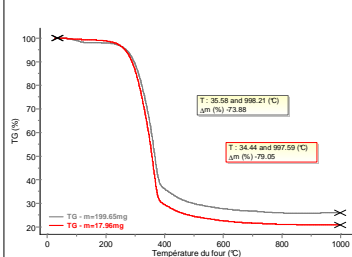


Figure 2 – Weight loss curves (%) for the comparison of different initial masses

Thermogravimetry allows acquiring data on pyrolysis steps involving mass losses [4].

Commercial pellets from resinous source were ground and sieved. The resulting 125-250µm and >500µm grain size fractions were used for the test. Samples were heated in a SETARAM SETSYS Evolution TGA using a platinum holder between 25°C and 1000°C at varying heating rates under 50mL/min helium flow.

The mass of remaining charcoal at 1000°C vs. initial sample mass ratio is determined for each test. It allows stating that the main parameters affecting charcoal yield are a high heating rate, a low sample mass and a low grain size.

Sample mass (mg)	Heating Rate (°C/min)	Grain size (µm)	Mass residue at 1000°C (%)
17.96	10	125-250	20.95
199.65	10	125-250	26.12
17.73	1	125-250	22.29
18.04	50	125-250	20.49
20.37	10	>500	21.77

Table 2 – residual masses

ANALYSIS OF THE EVOLVED GASES

Modern thermogravimetric systems allow evolved gases to be transferred to gas analyzers for identification.

Cellulose, xylan, lignin, and 125-250µm resinous samples were heated in a platinum holder between 25°C and 1000°C at 10°C/m in under 50mL/min helium flow. The released gases were continuously sent to a Thermo Nicolet 380 on-line FTIR equipped with a gas flow cell. The transfer line was heated to 200°C. Each spectrum was obtained with a resolution of 4 cm⁻¹.

In the case of cellulose, the maximum rate of decomposition was detected at 356°C. Figure 3 exhibits the FTIR spectra obtained at that temperature, showing the presence of water, carbon dioxide and formaldehyde in the flue gas. The other main gases are furfural and carbon monoxide. The temperatures T_{max} at which the intensity of their characteristic vibration bands was the highest are listed in Table 3.

The production of CO₂ is mainly caused by the cracking and reforming of carbonyl C=O and carboxyl COOH functional groups [5]. Depending on its chemical structure, each biopolymer thus goes through its own CO₂ production mechanism, as showed by Figure 4.

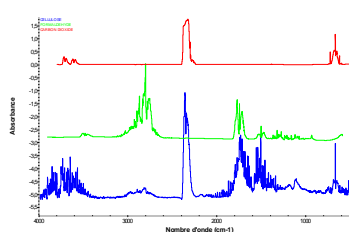


Figure 3 – Experimental FTIR spectrum obtained at 356°C (blue), compared to library spectra of CO₂ (red) and formaldehyde (green)

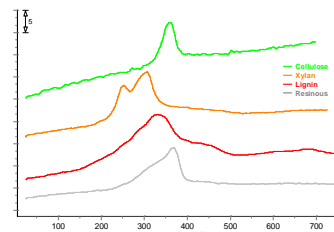


Figure 4 – Intensity variations of the stretching vibration band of CO₂ as a function of temperature for the 4 tested samples

Wavenumber (cm ⁻¹)	Assignment (Bond)	Vibration	Compound	T _{max} (°C)
2143-2223	C-O	Stretching	CO	364
2020-2138	C-O	Stretching		
2237-2397	C=O	Stretching	CO ₂	360
671	C=O	Bending		
3425-3991	O-H	Stretching	H ₂ O	364
1282-2010	O-H	In-plane rocking		
1712	C=O	Stretching	Furfural	350
754	C-H	Bending		
1651-1834	C=O	Stretching	Formaldehyde	360
2590-3132	C-H	Bending		

Table 3 – characteristic vibration bands of some of the detected chemicals in the flue gas during cellulose pyrolysis

CONCLUSION

Adapted analytic tools are necessary to achieve the challenges faced while improving biomass pyrolysis processes. While calorimetry allows acquiring key thermodynamic data such as heat of pyrolysis and heat capacity of biomass materials, thermogravimetry allows understanding the chemistry and kinetics of the involved decompositions. By coupling these techniques with gas analysis, the data offered allow selecting the best suited pyrolysis process conditions.

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[2] H. Luik, L. Luik, L. Tiikma and N. Vink, J. Anal. Appl. Pyrolysis, 79 (2007) 205.

[3] A. KHELFA, 2009, Etude des étapes primaires de la dégradation thermique de la biomasse lignocellulosique, Thesis (PhD), University of Metz.

[4] M.V. Gil et al., Bioresource Technology 101 (2010) 8859–8867.

[5] H. Yang and al, Fuel, Vol.86, pp. 1781-1788, 2007.