

Slow and Flash Pyrolysis of *Eucalyptus globulus* Wood

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Abstract: The analytical methods TG and Py-capillary-GC-MS were used to study the slow and flash pyrolysis of *Eucalyptus globulus* wood. The TG analysis in air and in nitrogen showed that the percentage content of char and ash were, respectively 10.09 and 10.81%. In the slow pyrolysis the evolution of organic degradation products occurred mainly between 165 and 380°C with the maximum evolution rate at 342°C. Flash pyrolysis was used during 60 s at 300, 400, 500 and 600°C. In these temperatures we have identified the presence of valuable chemicals such as carboxylic acids, resin acids, ketones, phenols, furans, alkanes, alkenes and polycyclic aromatic hydrocarbons.

Key words: *Eucalyptus globulus* wood, pyrolysis, TGA, DTG, Py-capillary-GC-MS

INTRODUCTION

The biomass material (mainly wood and plants) is more and more considered as an important resource for alternative fuels with significant environmental advantages, chemical products and precursors used for the preparation of Carbon Molecular Sieves (CMS) for separating small molecular gases (Guerrero *et al.*, 2005; Chang and Sung, 2006; Bello *et al.*, 2002; Mohan *et al.*, 2006; Beaumontt and Schwob, 1984; Lima *et al.*, 2004; Rochal *et al.*, 2002). Compared to other renewable energy sources, biomass possesses the advantage of being less cost intensive.

Biomass is constituted from 88-99.9% of organic compounds. Typically, all tree wood consists of various forms of celluloses (40-50% dry weight of wood, d.w.w.), hemicelluloses (20-30%, d.w.w.), lignins (20-30%, d.w.w) and extractive compounds (4-10%, d.w.w.) (Libby, 1962). Cellulose is a linear crystalline polysaccharide. The polymer is formed from repeating units of cellobiose, a disaccharide of β -linked glucose moieties. Hemicelluloses are polysaccharides of variable composition containing both five carbon (including xylose and arabinose) and 6 carbon monosaccharide units (including galactose, glucose and mannose). The lignins are highly branched, substituted, mononuclear polymers of phenylpropane units, derived from coniferyl, sinapyl and p-coumaryl alcohols (Yaman, 2004). Generally the physical and chemical properties of wood depend on the species, the age of the tree and the part of the tree considered but all wood are practically similar in their elementary chemistry (C: 51%, H: 6% and O: 43%) (Kafani *et al.*, 1996).

The geographic, climatic and pyrolysis conditions exert certain influence on biomass quality and the amount of charcoal, bio-oil and gases obtained by pyrolysis of biomass. The gases are mainly hydrogen, carbon monoxide, carbon dioxide and methane, whereas the bio-oil contains complexes compounds with higher boiling point. Biomass pyrolysis produces charcoal, bio-oil and gases via a complex process called the Broido-Shafizadeh mechanism (Varhegyi *et al.*, 1994). Understanding the chemical composition during the pyrolysis wood is a key feature in determining potential uses for and the value of, a specific biomass resource. Pyrolysis of the biomass constitutes a viable source of more than 230 organic chemicals (Kifani *et al.*, 1996). The knowledge of pyrolysis products can also facilitate the research on the development of the bio-fuel, preparation of cheap chemicals and char for the preparation of carbon molecular sieves (Bello *et al.*, 2002).

The objective of this study, is to investigate the influence of the temperature during *Eucalyptus globulus* wood pyrolysis. The study of the thermal degradation can provide information on the chemical composition during a pyrolysis of this wood. The wood species of *Eucalyptus globulus* are very rife in the Mediterranean region. Thermogravimetric and pyrolysis-capillary gas chromatography-mass spectrometric methods were employed in this investigation.

MATERIALS AND METHODS

The thermobalance: The thermal analysis was carried out using a Setaram thermobalance model TGA 92 (vertical

balance mechanism) operating in nitrogen with a flow rate of 60 mL min⁻¹ through the furnace. The uniformity of the sample was maintained by using 10.0 mg of sample spread uniformly over the silica crucible. The runs were carried out under in dynamic conditions between 30 and 900°C at a constant heating rate of 10°C min⁻¹.

Py-GC-MS: The experiments were conducted with a CDS pyroprobe 2000 coupled with an HP Agilent 6890 gas chromatography equipped with an HP-5MS capillary column (cross linked 5% Ph-Me siloxane, 30 m length, 0.25 mm diameter, 0.25 µm film thickness) held at 60°C, connected to a mass selective detector (HP Agilent 5973) operating in the electron mode at 70 eV energy. The source and quadrupole were, respectively held at 230 and 250°C, respectively. The mass scanning range was: 50-350 uma. The carrier gas used was helium with a column flow rate of 1 mL min⁻¹. About 3.0 mg of sample were placed into the quartz tube of the pyroprobe. Flash pyrolysis was used during 60 s at 300, 400, 500 and 600°C. The mass transfer line was kept at 280°C. The GC oven program temperature started at 50°C then increased at the rate of 3°C min⁻¹ to the temperature of 150°C and then increased at the rate of 10°C min⁻¹ to the final temperature of 300°C.

Samples: The *Eucalyptus globulus* wood was obtained from plantations located at Oum-El-Bouaghi town in the East of Algeria. The bark free wood, of 24 years of age, was first cut in small chips, air dried for a week and ground to size range less than 0.250 mm.

RESULTS AND DISCUSSION

TG and DTG analysis: The TG profiles of *Eucalyptus globulus* wood in air and in nitrogen are presented in Fig. 1. The two degradations were very similar between 20 and 380°C. The nature of TG curves in combination with the corresponding DTG curves (Fig. 2) gives a clear indication of number of stages of the thermal degradation. The initial loss of moisture from the samples started at around 32°C and continued up to about 118°C with a maximum at 64°C. The changes observed in the DTG curves between 124 and 161°C were attributed to the volatile fraction such as formic acid acetic acid and methanol (Beall and Eikner, 1970). The most important losses occurred between 165 and 380°C. Those changes were attributed to the thermal degradation of the main constituents of wood (hemicelluloses, cellulose and lignin). A peak at higher temperatures (342°C) is mainly due to the decomposition of the cellulose and the shoulder, at lower temperatures (300°C), can be attributed to the decomposition of the hemicelluloses. A peak due

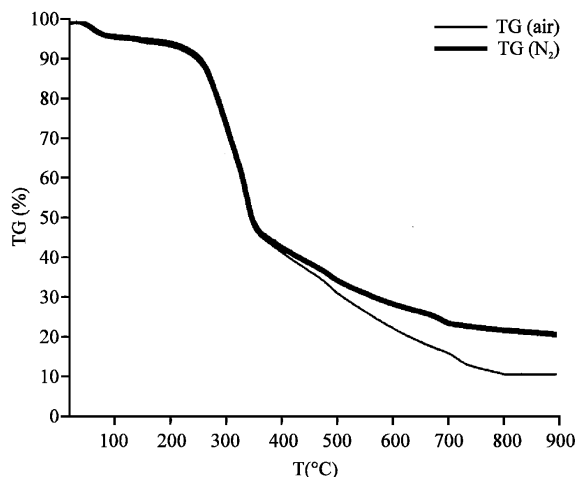


Fig. 1: TG curves in nitrogen and in air of *Eucalyptus globulus* wood

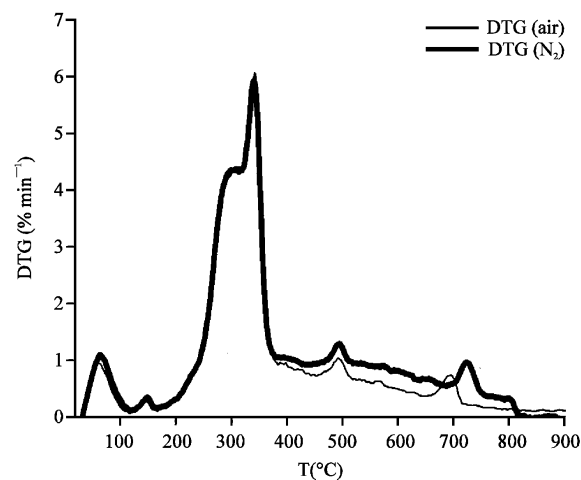


Fig. 2: DTG curves in nitrogen and in air of *Eucalyptus globulus* wood

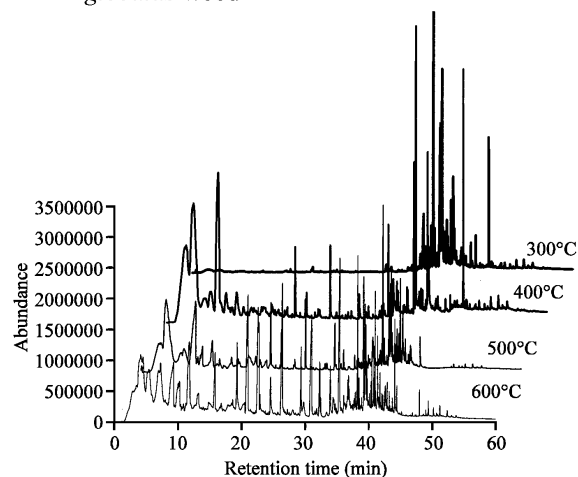
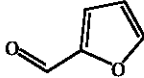
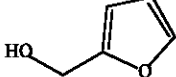
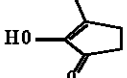
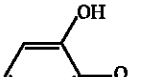
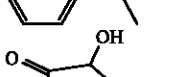
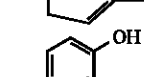
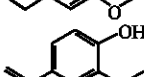
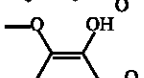
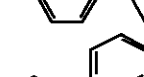
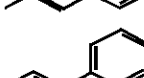
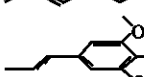
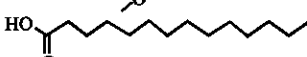
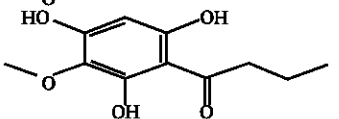



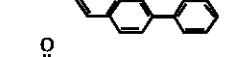





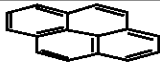


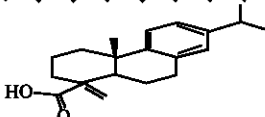


Fig. 3: Py-GC/MS chromatogram of *Eucalyptus globulus* wood at 300, 400, 500 and 600°C

Table 1: The volatile pyrolysis products of *Eucalyptus globulus* wood identified by Py-GC-MS at 600°C

Peak number	*R.t (min)	^b Mw	Compound	Reference	Origin
01	4.41	96	2-Furaldehyde		H+C
02	5.23	98	2-furanmethanol		H+C
03	10.00	112	2-cyclopentan-1-one, 2-hydroxy-3-methyl		C
04	11.65	124	Phenol, 2-methoxy		L
05	13.07	126	3-cyclopentan-1-one, 3-ethyl-2-hydroxy		C
06	19.15	152	Phenol, 4-ethyl-2-methoxy		L
07	20.86	150	Phenol, 2-methoxy-4-vinyl		L
08	22.47	154	Phenol, 2,6-dimethoxy		L
09	24.46	164	Phenol, 2-methoxy-4-[1-propenyl]		L
10	24.46	164	Phenol, 2-methoxy-4-[1-propenyl]		L
11	35.41	194	Phenol, 2,6-dimethoxy-4-[1-propenyl]		L
12	36.68	228	n-Tetradecanoic acid		E
13	36.83	226	1-Butanone, 1-[2,4,6-trihydroxy, 3-methoxy phenyl]		L
14	37.88	204	Naphtalene, 1-phenyl		E
15	38.54	268	Nonadecane		E
16	39,23	254	Hexadecenoic acid, Z-11		E
17	39.45	204	Naphtalene, 2-phenyl		E
18	39.57	256	n-Hexadecanoic acid		E
19	39.70	252	1-Octadecene		E
20	39.78	394	Octacosane		E
21	40.49	202	Fluoranthene		E
22	40.81	266	1-Nonadecene		E

Continue Table 1

23	41.06	202	Pyrene		E
24	41.30	282	9-Octadecenoic acid		E
25	41.84	226	Hexadecane		E
26	44.13	300	Podocarpa-8, 11,13-trien-15-oic acid,13-isopropyl		E

^aRetention time; ^bMolecular weight; C: Cellulose; H: Hemicellulose; L: Lignin; E: Extractive

the lignin degradation cannot be observed, because lignin degrades throughout the temperature range in both cases (Muller *et al.*, 2003).

From the TG curves and based on the original biomass weight, the percentage composition of *Eucalyptus globulus* wood at the end of the volatilisation was determined as follows: Moisture (4.82%), organic volatiles (74.28%), char (10.09%) and ash (10.81%). The char from *Eucalyptus* wood possesses already a primary molecular sieve structure and can be used to prepare CMS with high selectivity for CQ₂ and CH₄ (Bello *et al.*, 2002).

Py-GC-MS analysis: The pyrolysis was carried out at 300, 400, 500 and 600°C at 60 s. The Py-capillary-GC-MS chromatograms are given in Fig. 3. The Analysis of these chromatograms confirms that, the chemical composition of the pyrolysis wood is temperature dependent. At 300°C the phenol derivatives represent only 8% of the pyrolysis products. The peaks observed at this temperature have retention times higher than 30 min. The same peaks appeared at the pyrolysis temperatures of 400, 500 and 600°C. These peaks are assigned mainly to the extractive fraction. But as the pyrolysis temperature increases the number of peaks that appear at lower retention times increases (Fig. 3). At 600°C, the chemical composition of the pyrolysis wood becomes very complex. This it is due to the total degradation of the principal constituents of wood.

The identities of the compounds detected at 600°C are listed in Table 1. The product peaks were assigned by automatic library search NIST98. The library match quality was higher than 98% for all selected compounds. The main degradation products obtained in this study were divided into the following compound groups: Carboxylic acids, resin acids, ketones, phenols, furans, alkanes, alkenes and Polycyclic Aromatic Hydrocarbons (PAHs) (Chang and Sung, 2006; Ralph and Hatfield, 1991; Pimenta *et al.*, 1998; Del Ryo *et al.*, 2005; Elder and Soltes, 1980; Alen *et al.*, 1996; Statheropoulous *et al.*, 1997). The thermal degradation of the extractive fraction which contains resin acids produces PAHs (Rogge *et al.*, 1998).

Phenols are considered as important chemical products of the degradation of *Eucalyptus globulus* wood. More than 33% of the pyrolysis products are

phenol derivatives (Table 1). They have been commercially synthesized from petroleum resources; however, the production of petroleum-based phenols is quite expensive. Hence, phenols derived from bio-oil have been looked at as a potential substitute for petroleum-based phenols (Kawser and Nash, 2000).

CONCLUSION

The TG analysis in nitrogen and in air showed that *Eucalyptus globulus* wood percentage content of char and ash were 10.09 and 10.81%, respectively. TG and DTG analysis proved that the evolution of organic degradation products occurs mainly between 165 and 380°C and has its maximum evolution rate at 342°C. In the Py-capillary-GC-MS analysis at 300, 400, 500 and 600°C during 60 s, it was found that *Eucalyptus globulus* wood contains a series of important and useful chemicals compounds: carboxylic acids, resin acids, ketones, phenols, furans, alkanes, alkenes and polycyclic aromatic hydrocarbons. These compounds evolved and identified were related to their origin (e.g., extractive, cellulose, hemicelluloses or lignin). Phenols are considered as important chemical products of the degradation of *Eucalyptus globulus* wood. Its important char composition is potentially useful for the preparation of carbon molecular sieves.

ACKNOWLEDGEMENT

The authors thank the laboratory of chemistry and applications of the University of Metz (France) for the technical support.

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