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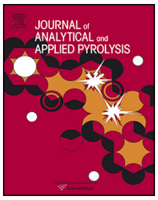

Investigations into the pyrolytic behaviour of birch wood and its main components: Primary degradation mechanisms, additivity and metallic salt effects

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ABSTRACT

The effect of mineral addition on biomass thermal decomposition was investigated in slow pyrolysis conditions (10 °C min^{-1}). The tests were carried out on the biomass components, their mixtures and real wood (birch wood), using thermogravimetric analyses (TGA) and pyrolysis coupled to mass spectrometry technique (Py-MS). The main criteria chosen to study the additivity of thermal behaviour were: the mass loss of the samples (C.R %), the temperature of the maximum mass loss (T_m) and the initial degradation temperature (T_i). Furthermore, to highlight the primary reactions of thermal behaviour of the studied samples, the chemical composition of emitted vapours was analysed and the influence of some mineral salts ($MgCl_2$, $NiCl_2$) on pyrolysis primary mechanisms was also investigated. Considering the large data sets collected (integrated MS intensities of 19 selected ions), principal component analysis (PCA) was used to provide a tool to simplify pyrolysis data interpretation. Considering mineral effects, it is possible to favour some primary mechanisms: dehydration (inducing to char formation); ring opening (with gas and light vapours formation) and depolymerisation (with sugars, pyrans and furans formation). $MgCl_2$ catalyses inter (or intra) molecular dehydration. However, $NiCl_2$ does not catalyse the mentioned primary reactions but appreciably modifies the emitted gas and vapours composition. With the help of the PCA calculations, the effect of metallic salts on xylan and ternary mixtures was evidenced.

1. Introduction

To decrease the amount of CO_2 emission from energy conversion, biomass as a renewable and CO_2-neutral resource has raised great interest. Especially wood and agricultural residues ("*Second generation" technology*) like straw are widely distributed and easily accessible at relatively low costs. Of these lignocellulosic materials wood is favourably used because of its higher density (higher energy content per volume), lower amount of ash, and of its very low amount of nitrogen.

Cellulosic biomass normally consists of biopolymeric species: cellulose, hemicellulose and lignin, in the proportions 35–50%, 15–25% and 15–30%, respectively [1]. In principle, there are two main ways to release heat and energy from wood: direct combustion, or thermochemical conversion into gases and liquids that can be used in gas turbines or diesel engines. Also, upgrading of wood to quality fuels such as methanol or hydrogen, or production of fine chemicals is a research topic.

It was found, in previous publications [2–5] that the whole process of biomass pyrolysis can be divided into the following four ranges: <220 °C, moisture evolution; 220–315 °C, predominantly hemicellulose decomposition; 315–400 °C, cellulose decomposition; >400 °C, lignin decomposition. There is no significant interaction among the three components in pyrolysis. The behaviour of natural biomass was different from that of synthesized biomass based on the three main components; the activation energy of the former is much less than that of the latter, which might be attributed to the catalytic effect of mineral matter that occurs in the natural biomass [5–9]. Therefore, an investigation of the influence of mineral matter on biomass pyrolysis is beneficial.

From earlier studies [2,6,10–16], it is well known that the addition of inorganic salts to wood samples result in a wide variety of changes in the pyrolysis process. An attractive option is to insert the catalyst inside the wood matrix by impregnation before thermochemical conversion [6,9,17–19]. Using this method, the catalytic material is highly dispersed in the biomass and freshly renewed when it is introduced into the reactor. The last few research studies on catalyst impregnation in wood for biomass pyrolysis or gasification were mainly centred on relating the effectiveness of

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Table 1
Ultimate analysis of studied samples.

	C	**H**	**O**	**N**	Residue
C.Ald	43.1	6.1	50.5	0	0.3
X.Flk	35.4	5.7	52	<0.3	4.0
L.CIMV	60.94	6.13	31.73	<0.3	0.9
R.biomass	43.8	5.95	47.14	<0.3	2.88
Birch	45.87	6.15	45.81	<0.3	1.87

alkali and alkaline earth metallic species. These catalysts have been reported to be very active in tar removal [20,21], as the conversion of condensable hydrocarbons leads to an increase in gas yield [22]. Examples of inorganic ions that have been added to biomass are Na^+, Li^+, K^+ and Ca^{2+} [22–24]. However, these species volatilize at low temperatures, causing significant problems in terms of fouling, erosion and corrosion of the plant components [25,26].

Today, the influence of inorganic salts on the pyrolysis of wood is studied with multiple aims: e.g. to increase the yield of charcoal, to develop analytical pyrolysis as a quantitative method for the analysis of pulps [27], to dispose heavy metal containing wood waste [28], to increase the yield of valuable fine chemicals from biomass pyrolysis, and to provide a model that comprises the influence of inorganic salts (ash) on the pyrolysis kinetics [10]. In this study, the pyrolysis of birch wood samples was investigated with a focus on the catalytic effect of inorganic species (Mg^{2+}, Ni^{2+}) on the distribution pattern of the pyrolysis products. In addition, the effect of mineral salts on pyrolysis mechanisms was studied by treating the aqueous impregnated samples. Given the large data sets collected in Py-MS analysis, we have used a chemometric evaluation tool (principal component analysis (PCA)) to help the interpretation of the diverse experimental results.

2. Experimental

2.1. Materials and sample impregnation

Birch wood (or Birch) used in this study was provided by the laboratory of Toulouse “Surfaces cellulaires et signalisation chez les végétaux”. Cellulose (Microgranular cellulose) was purchased from Sigma–Aldrich Company (C.Ald). Because commercial hemicellulose can hardly be purchased, xylan has been widely used as a representative of the hemicellulose component in pyrolysis process. Moreover, the choice fell on xylan because it appears to be more reactive and is very sensitive to the degradation and dehydration reactions between 200 and 300 °C [64]. It is the main source of volatile products (essentially furfurals and acetaldehyde) and plays an important role in the initiation and propagation of pyrolysis reactions. Here, xylan was purchased from Fluka Company (X.Flk). Lignin CIMV (L.CIMV) was extracted from birch wood via AVIDEL process [29]. CIMV is the name of the company which exploits this process. Reconstituted biomass (R.biomass) has been prepared by combining the 3 main biomass components in the proportions of birch wood (C.Ald: 40 wt% X.Flk: 39 wt%, L.CIMV: 21 wt%). The ultimate analysis of those samples is listed in Table 1.

The elements associated with the biomass (minerals) were selected so as to represent the families of chemical elements able to have an influence. It will be interesting to make a distinction between minerals present naturally in biomass and added minerals not present naturally. We chose magnesium to represent family of alkaline-earth metals [30] (this mineral is present in natural biomass) and nickel [31] for transition metals family. Nickel has been widely investigated as a catalyst of biomass gasification and pyrolysis because of its comparatively low price and high activity. This mineral is not present in the natural state in biomass (and can be present in a very small content). We then chose to associate these elements with the biomass in the shape of a common salt: chlorides. The chlorides offer many possibilities, they are easily soluble and they do not release, during their decomposition, gases which could distort our results (example: carbonates give CO_2 while breaking up).

Table 2
The relative standard deviation (%RSD) of the selected *m*/*z*.

m/*z*	%RSD
18	18
28	8
30	6
43	3
44	10
45	6
60	5
96	10
98	10
114	15
154	11

Wood main components and both ternary mixtures (birch wood and synthetic mixture) were impregnated with Ni(II) chloride hexahydrat 99% (Aldrich) and Mg(II) chloride hexahydrat 99% (Merck). 5 g of each sample was impregnated by the different chloride salts using 50 mg of metallic cations (1% mass in respect to the sample amount) dissolved in 30 ml of distilled water. The mixture was gently stirred at 75 °C during 7 h for cellulose, xylan and both mixtures, at 50 °C for lignin during several days, and then dried at 100 °C for 12 h.

In the following, impregnated samples will be noted as follows: Cell-Metal for cellulose samples, R.biomass-Metal for reconstituted biomass samples, etc. For example: Cell-Ni and Cell-Mg for cellulose impregnated with $NiCl_2$ and $MgCl_2$, respectively, or R.biomass-Mg for reconstituted samples impregnated with $MgCl_2$.

2.2. Experimental methods

The pyrolysis of biomass components was first carried out in a thermogravimetric analyser (SETARAM TGA92). To minimise the difference of heat and mass transfer, the sample weight was kept at ~30 mg. The sample was heated from ambient temperature to 95 °C (kept temperature during 15 min) then up to 500 °C with the heating rate of 10 °C min^{-1}. Purified argon (99.9995%) at a flow rate of 60 ml min^{-1} was used as the carrier gas to provide an inert atmosphere for pyrolysis and to remove the gaseous and condensable products, thus minimising any secondary vapour–phase interactions.

The used Py-MS system consisted of pyrolysis analyser corresponding to Pyroprobe 2000 CDS pyrolyser (with the Py-GC/MS apparatus, using an empty column (Fused Silica Kapillars, 10 m × 0.25 mm)) and a mass selective detector (Agilent-HP 5973). The Py-MS interface temperature was maintained at 200 °C. The inert gas used was helium with a flow rate of 20 ml min^{-1}. Approximately 6 mg of each sample were heated in the pyrolyser from 25 to 500 °C with a heating rate of 10 °C min^{-1}. The electron impact source was tuned at 70 eV and the mass range for the MS data acquisition was 4–300 amu. The experimental uncertainties for some of the MS evolution profiles are reported in Table 2. These uncertainties are the root-mean-squares deviations calculated for six tests on untreated biomass, expressed as percent of peak maximum. The calculation of %RSD has been established for 11 fragments. The fragments were chosen considering four groups: 3 groups for characteristic fragments of each biomass biopolymer ($m/z = 30$ and 98 for cellulose degradation, $m/z = 43$ and 114 for xylan degradation and m/z 154 for lignin degradation) and a last group for common fragments ($m/z = 18$, 28, 44 and 96,. . .).