



Analytical pyrolysis of hot water pretreated forest biomass



Étienne Le Roux^a, Papa Niokhor Diouf^b, Tatjana Stevanovic^{a,*}

^a Centre de Recherche sur les Matériaux Renouvelables, Department of Wood and Forest Science, Faculty of Forestry, Geography and Geomatic, Laval University, Pavillon Gene-H.-Kruger, 2425 Rue de la Terrasse, G1V 0A6 Quebec, QC, Canada

^b Service de recherche et d'expertise en transformation des produits forestiers (SEREX), 25 rue Armand-Sinclair, porte 5, G5J 1K3 Amqui, QC, Canada

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ABSTRACT

Fast pyrolysis is a promising technology to promote wood biomass utilization. This thermochemical process produces mainly a liquid bio-oil. Currently, a direct application of bio-oil as fuel is limited due to its poor physicochemical properties.

Pressurized Hot Water Treatment (PHWT) has been applied on white spruce and trembling aspen whole wood chips prior to production of pyrolysis oil. The effect of PHWT and the influence of the fast pyrolysis parameters on the bio-oil composition and products distribution were investigated by analytical pyrolysis coupled with gas chromatography/mass spectrometry (Py–GC/MS), it was carried out at two heating rates (100 °C/min and 1000 °C/min) and in temperature ranges from 350 °C to 500 °C for trembling aspen and from 400 °C to 550 °C for white spruce. The pyrolysis products were identified to belong to eleven chemical groups: syringyl derivatives, guaiacyl derivatives, other phenolics, anhydrosugars, low molecular weight acids, fatty acids, furans, pyrans, ketones, aldehydes and alcohols.

The results of the analytical pyrolysis indicate that the higher yield is obtained from pretreated than from untreated biomass. The effect of the pretreatment is more important for the 1000 °C/min heating rate than for 100 °C/min. The composition analysis revealed that the higher peak area% of anhydrosugar were obtained from PHWT biomass at 1000 °C/min while the phenols were the major constituents of the pyrolysis products obtained at lower, 100 °C/min heating rate. It is also demonstrated that the acids are still found in pyrolysis products even after pretreatment. The Py–GC/MS results obtained in this study indicate that pretreatment affected the hardwood and softwood in quite different ways.

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1. Introduction

The world energy consumption has considerably risen during the last forty years and the same trend will remain until 2035 according to the International Energy Agency [1]. Amongst the energy resources, fossil fuels are predominant. Nevertheless the future depletion of fossil resources, the high costs of petroleum, the global warming, and the energy security issues require decreasing the oil dependence. It is therefore urged to replace fossil fuels by more eco-friendly resources. Biomass represents one of the alternatives, since it is a renewable, abundant and low cost resource. It is already used by the pulp and paper industry as a feedstock for chemicals and fuels. Forest biomass transformation into bio-oil can offer some solutions to this industry which is presently facing one of its most important crises.

Various forms of woody biomass are available from wood processing such as sawdust, barks, branches, twigs, etc. The research has been focused on the integration of woody biomass valorization in an integrated biorefinery process [2]. Fast pyrolysis is one of the most promising technologies to promote woody biomass valorization [3,4]. Pyrolysis is a thermochemical degradation occurring in an inert atmosphere. It produces mainly 60–75 wt% of a liquid bio-oil, 15–25 wt% of biochar and 10–20 wt% of non-condensable gas [5]. The bio-oil could be a valuable feedstock for chemical production or fuels. However the bio-oil is a complex mixture. Its chemical composition and distribution depend on the origin of the biomass and the parameters of the pyrolysis. The main constituents of a crude bio-oil originate from the thermal decomposition of three principal components of lignocellulosic biomass, hemicelluloses, cellulose and lignins. Crude bio-oil composition is well studied by several analytical tools such as GC/MS [6] and it could be resumed to: 30% water, 30% phenolics, 20% aldehydes and ketones, 10% alcohols and 10% others compounds [7]. Due to its composition, the crude bio-oil presents some physical properties which

* Corresponding author. Tel.: +1 418 656 2131x7337; fax: +1 418 656 2091.
E-mail address: Tatjana.Stevanovic@sbf.ulaval.ca (T. Stevanovic).

impede its direct application. Indeed, the degradation products of carbohydrates, particularly those from hemicelluloses, give an acidic character to the bio-oil (pH around 2–3). The thermal degradation generates also other oxygenated compounds. They are susceptible to react during storage and transport operations. The viscosity of the bio-oil may thus be modified. Moreover, the water content reduces the heating value of the bio-oil.

To eliminate these drawbacks, a pretreatment of the biomass is one of the solutions proposed in the literature [8,9]. In our previous work [10], two woody biomasses, trembling aspen (*Populus tremuloides*) and white spruce (*Picea glauca*), were torrefied in the presence of water in a pressure vessel. Chemical, proximate and elementary analyses were performed on the pretreated wood and the harsher the pretreatment, the higher reduction of hemicelluloses content was determined. At the same time, a partial solubilization of lignins was observed for the hardwood. These alterations of the feedstock would certainly modify the chemical composition and distribution of the constituents in the bio-oil produced. Py-GC/MS analysis is an appropriate analytical technique for investigation of the thermal behavior of a biomass. The Py-GC/MS technique is combining an analytical pyroprobe with a gas chromatograph coupled with a mass spectrometer. This analytical technique is used to achieve biomass fast pyrolysis and allows on-line analysis of the pyrolysis products in order to get information on their distribution.

Despite the fact that the Py-GC/MS analysis of untreated wood is well documented, there are only a few studies on pretreated wood analyses [11,12]. This study is focusing on the thermochemical behavior of the pretreated biomass during a fast pyrolysis. The Py-GC/MS analyses were performed at two heating rates, 100 °C/min and 1000 °C/min, corresponding to the heating rates commonly applied in fast pyrolysis. The experiments were carried out applying the parameters simulating common conditions of woody biomass fast pyrolysis with an aim to investigate the effect of a PHWT pretreatment on the chemical composition and the distribution of the constituents.

2. Experimental

2.1. Wet torrefied biomass production

Two woody biomasses were studied, hardwood trembling aspen (*P. tremuloides*) and softwood white spruce (*P. glauca*). The wood chips, produced from whole logs without debarking, were obtained from Groupe BSL sawmill located in Amqui, Quebec, Canada. They were received oven dried to 8% moisture content. The wood samples were subjected to a PHWT pretreatment in a 2 L stirred pressure reactor (Parr 4522) at 175 °C, 195 °C and 215 °C. A severity factor, S , was calculated taking into account the time (t) and the pretreatment temperature (T) [13,14] as explained by Eqs. (1) and (2) in which TREF is 373 K:

$$S = \log R \quad (1)$$

$$R = \int_0^t \exp\left(\frac{T - \text{TREF}}{w}\right) dt \quad (2)$$

Thus, for PHWT performed at 175 °C, 195 °C and 215 °C, the severity factors were calculated to be 3.9, 4.6 and 5.2 [10]. The results of chemical analysis of untreated and pretreated wood [10] are presented in Table 1.

The solid residues were collected, washed with hot water (1 L), and air dried. The pretreatment was triplicated for each severity. Prior to pyrolysis analysis, the pretreated and untreated wood chips, were successively milled in a cutting mill (Pulverisette 19, Fritsch), and in a hammer mill (Mikrom-Batam) in order to obtain sawdust with a particle size under 1 mm.

2.2. Pyrolysis–gas chromatography/mass spectrometry

The analytical pyrolysis was performed using a CDS Pyroprobe 2000 heated coil pyrolyzer. The fast pyrolysis was performed at 350 °C–400 °C–450 °C–500 °C and 400 °C–450 °C–500 °C–550 °C for trembling aspen and white spruce, respectively, and held at these temperatures for 3.0 min. Two heating rates were selected, 100 °C/min and 1000 °C/min. These rates were chosen to study the fast pyrolysis process under its entire heating rate range. The organic volatile species were analyzed in a GC/MS system (Varian CP-3800, Varian Saturn 2200). The pyrolysis products were separated in capillary column VF-5 ms (30 m × 0.25 mm × 0.25 μm inner diameter). Helium was the carrier gas with a flow rate of 1 mL/min. About 1 mg of biomass sample was pyrolyzed at 100 °C/min with a split ratio of 50:1. The experiments at the heat rate of 1000 °C/min were first performed with the same parameters but some compounds, particularly sugars, seemed to stick to the column. Therefore, the sample weight and the split ratio were changed respectively to 0.15 mg and 100:1 for the heating rate of 1000 °C/min. The column oven program was: 9 min and 4 min at 45 °C for the heating rate of 100 °C/min and 1000 °C/min respectively, followed by an increase to 280 °C (5 °C/min) and hold at that temperature for 10 min. The gases were then sent into a mass spectrometer operating in Electron Ionization mode at 70 eV. The mass spectra were obtained from m/z 40 to 400 with a scan rate of 1 scan/s. The identification of the chromatographic peaks was based on the NIST library and on the data available in the literature [15–18]. All samples, untreated wood samples and triplicates samples from each pretreatment severity were pyrolyzed twice.

When analysis the Py-GC/MS results only the relevant part of the chromatogram was considered. Indeed, the compounds detected after the retention times of 45 min and 40 min for the pyrolysis performed at 100 °C/min and 1000 °C/min heating rates, were considered as irrelevant. They were not related to the thermal degradation of lignocellulosic biomass but to the Py-GC/MS analysis system. Thus, the calculations concerned only peaks detected before these retention times.

For each identified compound, the peak area values and the peak area% were normalized per mg of sample dry weight and used for discussion. The peak area value of a compound which is considered to be proportional to its concentration is used to discuss the changing of its yields under different pyrolysis conditions [19,20]. The peak area% of a product is used to discuss the changing of the compound distribution under different pyrolysis conditions.

3. Results and discussions

Fig. 1 present an example of pyrogram of untreated trembling aspen pyrolyzed at 450 °C with a heating rate of 1000 °C/min. Biomass fast pyrolysis products are composed of permanent gases and condensable gases which consist of water, volatile compounds and non-volatile oligomers which will form bio-oil after condensation [19]. During the condensation, recombination reactions between the products may also occur. In the case of an analytical Py-GC/MS, the organic condensable products are separated thus avoiding recombination reactions instead of being collected in the form of bio-oil as is the case for fast pyrolysis. Only monomers and few dimers are detected by the mass spectrometer. Therefore, the compounds identified by Py-GC/MS analysis represent only a fraction of the real constituents of the bio-oil which will be produced by pyrolysis from the studied biomass. Nevertheless, this analysis helps to estimate the yield change under different pyrolysis conditions and predict the chemical distribution of the pyrolysis products. The compounds identified from pyrolysis are classified into nine chemical groups, including phenolics,

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