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# Pilot-scaled fast pyrolysis conversion of eucalyptus wood fines into products: discussion toward possible applications in biofuels, materials and precursors

*Mailson Matos*[1]*; Bruno D. Mattos*[2]*; Pedro H. G. de Cademartori*[3]*; Tainise V. Lourençon*[2]*; Fabrício A. Hansel*[4]*; Patrícia R. S. Zanoni*[4]*; Carlos I. Yamamoto*[1]*; Washington L. E. Magalhães*[1,4*]

[1] Integrated Program in Engineering & Materials Science, Federal University of Paraná, Polytechnic Center, Curitiba 81531-990, Brazil.

[2] Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, FI-00076 Aalto, Finland.

[3] Programa de Pós-Graduação em Engenharia Florestal (PPGEF) - Departamento de Engenharia e Tecnologia Florestal, Universidade Federal do Paraná, Curitiba 80210-170, Brazil.

[4] Embrapa Florestas, Estrada da Ribeira, Km 111, Colombo 83411-000, Brazil.

* Corresponding author: Mailson Matos, mailsondematos@ufpr.br

**Abstract.** Based on a circular bioeconomy strategy, eucalypt wood fines rejected from a Kraft pulp line were used as starting material in a pilot-scaled fast pyrolysis process. The bio-oil and its coproducts were characterized regarding their physical, chemical and thermal aspects. We put in perspective their properties to bring forward considerations for applications on biofuels, materials and precursors. The yields of pilot-scaled fast pyrolysis process reached interesting values even if compared with optimized laboratory conditions. The results indicated highest heating values (22-27 MJ/kg) for bio-oil, char and crust material. The higher water content of aqueous extract had negative effect for its application as fuel. The lignin/carbohydrate ratio for the bio-oil (2.82) and aqueous extract (0.53) identified a higher concentration of lignin-derived compounds in the first, mainly syringyl units. Bio-oil and aqueous extract presented chemical compounds with many functionalities, such as syringaldehyde and levoglucosan, expanding their potential application for higher value-added products besides energy.

**Keywords.** up-scaling; biorefinery; thermal route; biomass valorization; bio-oil; char.

## 1. Introduction

Petroleum is the main feedstock for fuels, and its derivatives are also the basis for most engineering materials and fine chemicals. These applications are considered one of the main causes of global warming. Moreover, there are other concerns with peak oil, security supply, price instability and global equity. Thus, putting the human kind, especially the scientific community, on a trajectory toward rapid mentality change. In order to change this panorama, innumerous research groups [1] have engaged in biomass-to-fuel/chemical projects to supplement the petroleum production chain. Pyrolysis is one of the most interesting and discussed process to convert biomass into fuels or fine chemicals [2, 3]. It is defined as a thermal decomposition process of biomasses at inert atmospheres resulting in char, bio-oil and non-condensable gases which yields differently according to the processes parameters [4, 5].

Fast pyrolysis is a thermal route-based biorefinery especially designed to improve the yields of liquid products by controlling the reaction temperature near to 500 ºC, and increasing significantly the heating and heat transfer rates usually via fluidized bed. The dark brown organic liquid, referred to as bio-oil, is the main product obtained in this process and it shows potential as fuel and as a precursor for obtaining hydrocarbons. In fact, as deeply discussed by Isikgor and Becer [1], the chemical compounds usually found in fast-pyrolysis bio-oils could be used as precursors of a wide range of synthetic polymers such as poly(styrene), poly acrylates, poly(ethylene), and poly(acrylonitrile). The higher oxygen content of bio-oil compared to petroleum derivatives is still a barrier to overcome before turning it into a competitive fuel. However, some strategies to improve the fraction of hydrocarbons in bio-oils have been discussed in the last years [6, 7]. Besides the bio-oil, the fast pyrolysis conversion of biomass results in charcoal as an important coproduct. Charcoal is commonly used as source to attend the heat requirements of the fast pyrolysis process [8], but its use as char has potential for higher value-added purposes. For example: the char can be chemically modified and used as an adsorbent to remove chemicals from aqueous solutions [9].

Considering the great potential of obtaining fuels and fine chemicals from both fast pyrolysis bio-oil and char, some research groups have investigated the techno-economic assessment of their production costs [10, 11]. As the bio-oil and the char costs are strongly associated to biomass transportation, it is interesting that the fast pyrolysis plants were integrated or near to well-consolidated biomass-based industries, such as a pulp and paper plant. For instance, the wood materials rejected from a pulp process can achieve up to 200 kg/ton paper in a Kraft mill [12], and they are usually destined for low-value applications. In Brazil, the Kraft pulp lines are mostly fed by fast-growing eucalypt wood species, which had drawn especial attention over the last few years due their high productivity [13]. The wood from these species is composed by *ca.* 2-6 % of extractives, 20-30 % of lignin, and 55-70 % of holocellulose [14]. These characteristics placed it as the main raw material for the Kraft mills in Brazil; besides, it has showed interesting responses for bio-oil production [15].

This is a timely topic, given the growing socio-environmental-economical concerns that have motivated the petroleum replacement. In this sense, several scientific works have discussed the bio-oil production at lab-scale conditions; however, we understand that studies on the up-scaling of this process is paramount in the development of a sustainable bioeconomy. Thus, this study aimed at the pilot-scaled fast pyrolysis conversion of wasted eucalypt fines into several products. We present a thoroughly physical, chemical and thermal characterization of the obtained products, putting in perspective their unique characteristics in order to bring forward necessary considerations for upcoming applications on biofuels, materials and precursors.

## 2. Material and Methods

### 2.1 Pilot-scaled fast pyrolysis process and raw material characterization

Eucalypt wood fines (~ 1 mm, with 10% humidity) from a Kraft pulp line, without pretreatment, were used as start material for the coproduction of char (1), bio-oil (2), aqueous extract (3), and gas (not evaluated in this study - however, the gas is mainly composed of nitrogen ($N_2$), hydrogen ($H_2$), carbon monoxide (CO), carbon dioxide ($CO_2$) and methane ($CH_4$)). In addition, a brittle carbonaceous solid material, called crust material (4), was encrusted inside the reactor after the fast pyrolysis (Fig. 1). The pilot-scale fast pyrolysis reactor was set to operate in fluidized bed mode with nominal biomass supply of 20 kg/h, with a poor oxygen atmosphere, reaction temperature at 500 °C for 5 seconds, and 100 mm$H_2O$ of static pressure. The pyrolysis temperature was achieved by partial combustion of the biomass, with preheated atmospheric air at a flow rate of 7 $Nm^3/h$. Then, the reactor was fed with hot non-condensable gases. If the temperature difference between the bottom and top of the reactor was greater than 20 °C, automatic injection of atmospheric air would occur. In order to keep the temperature constant throughout the reaction bed. The fluidization gas flow was maintained at 15 $Nm^3/h$ during the reaction. The optimization of the process conditions, in order to obtain a higher yield of bio-oil, was performed by the equipment manufacturer according to the biomass to be used. The yield of the selected products was informed based on the total biomass fed to the reactor.

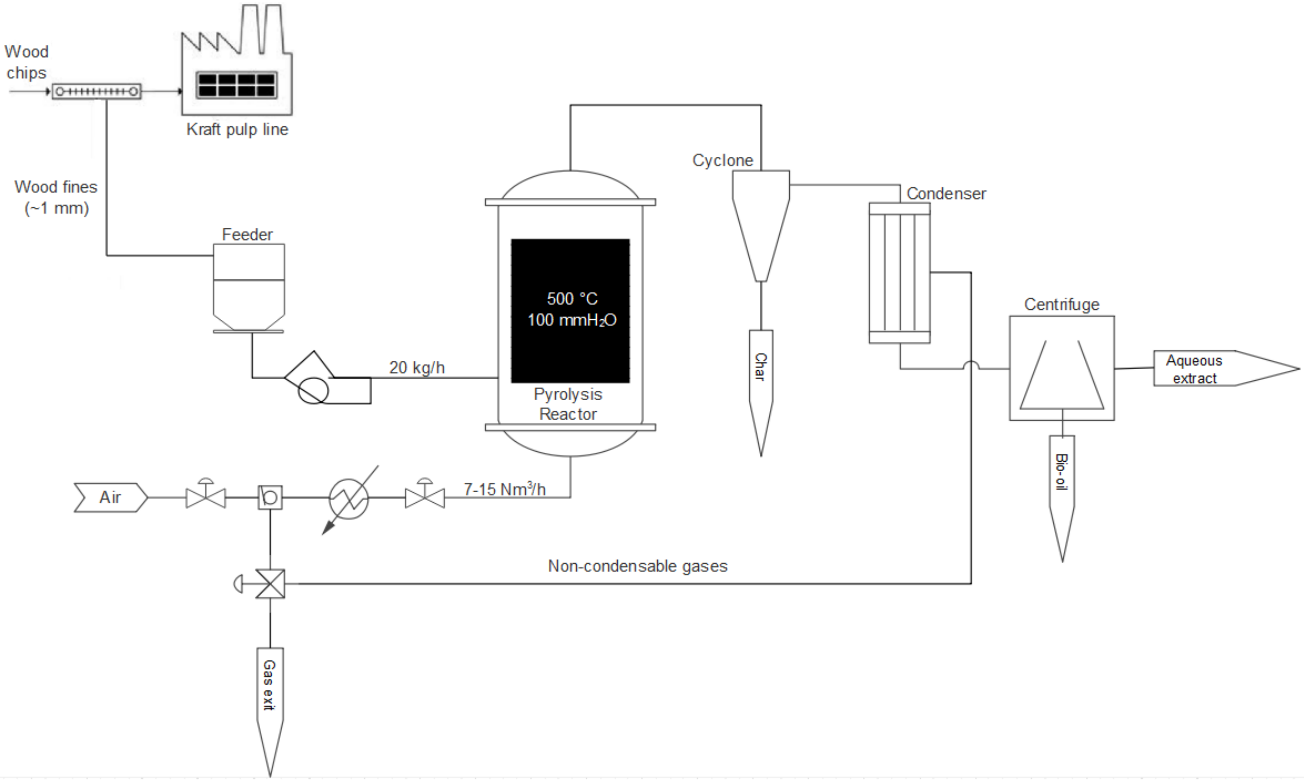

**Fig. 1.** Simplified representation of the pilot-scaled fast pyrolysis conversion of eucalypt wood fines rejected in a Kraft pulp line into several products.

The eucalypt wood fines were characterized according to their ethanol:toluene extractives, acid insoluble lignin and ash content using the procedures developed by the National Renewable Energy Laboratory (NREL) [16–18]. Their holocellulose content was quantified by using the procedure from Wise et al [19].

## 2.2 Physicochemical and elemental composition measurements

The bio-oil and aqueous extract were characterized as liquid biofuels according to the standardized specification for pyrolysis liquids (ASTM D7544 – 12). The physicochemical properties of the pyrolysis liquids for biofuels were evaluated by quantifying their total sulfur content (ASTM D4294-

10), density at 20 °C (ASTM D4052-11), pour point (ASTM D97-15), kinematic viscosity at 40 °C (ASTM D445-15) and ash content (ASTM D482-13). The volumetric Karl Fischer (Quimis, model Q349) titration method was applied to determine the water content in the samples, and the pH of the liquids was measured in a benchtop pH meter (HANNA, model HI 2214).

The higher heating value of the start material and both solids and liquids coproducts was measured in an adiabatic calorimeter (IKA®,model C5000), and the elemental analysis was performed in a CHNS analyzer (Elementar Vario Macro Cube). Solid materials were also characterized for ash content.

### 2.4 Full evaporation - headspace - gas chromatography (FE/HS – GC)

The FE/HS – GC (GC-2010 Shimadzu) was used for quantification of volatile organic compounds (VOCs) in the bio-oil and aqueous extract, following Lima et al. [20]. VOCs were introduced via a split/splitless injector (0.5 mL, 200 °C, split 1:25) and, the compounds were separated using a DB624 UI column (30 m, 0.25 mm diameter 1.40 µm thick film). Headspace equilibration temperature and time were 90 °C and 7 min respectively. The sample preparation and measurement procedures were as follow: injection of 4 µL of sample into a closed 20 mL vial using a microsyringe and immediate closure. The volatiles were converted to compound mass using a 5 points external calibration curve using a flame ionization detector (300 °C). GC oven was programmed from 40 °C (held 7 min) to 70 °C at 10 °C/min (held 6 min), then to 110 °C at 10 °C/min (held 5 min), and to 120 °C at 20 °C/min (held 5 min). Helium at a constant flux of 2.0 mL/min was used as carrier gas.

### 2.5 Thermal stability

The thermal stability and degradation behavior of the raw material, solids and liquids derived from the fast pyrolysis were investigated in a DTG-60 Shimadzu equipment. The experiments were carried out using *ca.* 10 mg in alumina pans under $N_2$ atmosphere with gas flow of 50 mL/min, temperature range from 25 to 900 ºC, and heating rate of 10ºC/min.

## 2.6 GC - mass spectrometry (GC-MS) and analytical Pyrolysis (Py) GC-MS

The GC-MS analysis was applied to investigate the potential of the liquid products as fine chemical precursors, following Lyu et al. [21]. For this, 2 mL of acetone and 20 µL of internal standard 5-iodovanillin (10 mg/ml) were added to the bio-oil or aqueous extract (100 µL). The mixture was vortexed and centrifuged (5 min, 3000 rpm), then *ca.* 1 g of anhydrous sodium sulfate was added to dehydrate, and the sample was centrifuged once again (5 min, 3000 rpm). The supernatant was collected and analyzed by GC-MS. The extract was injected (1 µL, split 1:100 at 230 °C) into gas chromatography tandem to an ion trap mass spectrometer (Thermo, Focus GC, PolarisQ), equipped with a capillary column Thermo DB5ms (30 m x 0.25mm, 25µm film thickness). The GC oven was set at 40 ºC and held for 6 min, then to 280 °C at 7°C/min and held at 280 °C for 30 min. Helium, with gas flow of 1.0 mL/min, was the carrier gas. The GC-MS interface and ion source temperatures were 250 and 200 °C, respectively. The ion trap mass spectrometer operated in the positive impact electronic mode at 70 eV, scanning *m/z* range from 40 to 650 in a 0.59 of total scan time and emission current 250 mA.

Pyrolysis (CDS 5000 pyropobe) was carried out at 700 ºC during 10 s for the solid samples (i.e. raw material and char). The pyroprobe extra conditions were: temperature interface program from 110 to 290 ºC at 100 ºC/min held for 120 s, oven at 240 ºC, transfer line at 240 ºC, coil heater at 10 ºC/ms. GC oven was programmed from 40 °C (held for 8 min) to 280°C at 7°C/min then held for 15 min. The GC-MS conditions were the same adopted in the section 2.6. This analysis was based on Kaal and Rumpel [22].

## 2.7 Ion chromatography (IC)

To quantify the amount of carbohydrates contained in the liquid products, the samples were subjected to total acid hydrolysis with sulfuric acid 12 mol $L^{-1}$ for 1 h at 37 ºC, followed by dilution from the reaction medium to 1 mol $L^{-1}$ keeping for 2 h at 100 ºC in a heating block. The hydrolysate was analyzed by ion chromatography to quantify the monomeric sugars. The separation was performed on a CarboPac PA 20 column (4 mm x 250 mm, 5 µL looping, flow rate 0.5 mL $min^{-1}$ at 30 °C).

## 3. Results

The eucalypt wood fines used as raw material in the fast pyrolysis presented 1.5 ± 0.2 % of ethanol/toluene extractives, 24 ± 1 % of acid insoluble lignin and 71 ± 2 % of holocellulose. The fast pyrolysis of this precursor at the configured pilot-scale procedure yielded 14 ± 1 % of char and 53 ± 1 % bio-oil. After centrifugation, the crude bio-oil was separated in a heavy fraction (bio-oil, 30 ± 1 %), and in a light fraction (aqueous extract, 22± 1 %). Approximately 4% of crust material has formed. Table 1 shows the product yields (liquid and coal) obtained from rapid pilot scale pyrolysis of some lignocellulosic materials. Considering all reactor types the yield ranges from 40% to 60% for liquids and from 10% to 30% for coal. These values are similar to the expected yield for biomass pyrolysis [23, 24] and the values found in this study.

**Table 1.** Char and liquid product yields from different pilot-scale pyrolysis processes of some types of biomass

| Biomass | Reactor type | Liquids yield (%) | Char yield (%) | Reference |
|---|---|---|---|---|
| Empty fruit bunch | Fluidized bed reactor | 50 | 20 | Park et al. [25] |
| Sawdust | Fluidized bed reactor | 60 | 15 | Park et al. [25] |
| Giant *Miscanthus* | Fluidized bed reactor | 50 | 20 | Park et al. [25] |
| Stem wood from spruce and pine | Cyclone reactor | 57 | 16 | Johansson et al. [26] |
| Stem wood from spruce and pine | Cyclone reactor | 56 | 16 | Sandström et al. [27] |
| Willow | Cyclone reactor | 52 | 20 | Sandström et al. [27] |
| Reed canery grass | Cyclone reactor | 51 | 11 | Sandström et al. [27] |
| Brown forest residue | Cyclone reactor | 50 | 14 | Sandström et al. [27] |
| Bark | Cyclone reactor | 41 | 17 | Sandström et al. [27] |
| Palm shell residue | Fluidized bed reactor | 60 | 19 | Ghorbannezhad et al. [28] |
| *Pinus pinaster* | Continuous fixed bed reactor | 50 to 60 | 20 to 30 | Milhé et al. [29] |
| Switch grass | Fluidized bed reactor | 55 | 20 | Greenhalf et al. [30] |
| Willow | Fluidized bed reactor | 50 | 20 | Greenhalf et al. [30] |
| Giant *Miscanthus* | Fluidized bed reactor | 45 | 30 | Greenhalf et al. [30] |
| Beech wood | Fluidized bed reactor | 60 | 15 | Greenhalf et al. [30] |

The char and crust material presented higher carbon content compared to the start material and liquid products (*i.e.* bio-oil and aqueous extract) – Table 2. The lowest carbon content was observed for the aqueous extract. The higher heating values of the obtained coproducts increased as their carbon content increased. The ash content of the liquid products was lower compared to the solid products – char presented the highest ash content. The relative amount of nitrogen was under 0.5 % for all samples, and it was concentrated mostly in solid samples. The H/C atomic ratio was notably higher for the aqueous extract compared to the other products.

**Table 2.** Ultimate analysis, higher heating value and ash content of the obtained coproducts from the pilot scale fast pyrolysis plant.

| Product | Relative % of total mass | | | Ash content | HHV[b] | H/C |
|---|---|---|---|---|---|---|
| | Nitrogen | Carbon | Hydrogen | (%) | (MJ/kg) | atomic |
| Raw material | 0.16 ± 0.06 | 43.90 ± 0.10 | 6.88 ± 0.20 | 1.12 ± 0.11 | 18.82 ± 0.10 | 1.84 |
| Char | 0.38 ± 0.09 | 67.18 ± 1.82 | 3.86 ± 0.06 | 12.25 ± 1.46 | 26.38 ± 0.91 | 0.68 |
| Crust material | 0.28 ± 0.04 | 62.24 ± 0.16 | 5.56 ± 0.06 | 2.31 ± 0.41 | 23.27 ± 0.99 | 1.06 |
| Bio-oil | 0.17 ± 0.01 | 53.63 ± 0.27 | 7.37 ± 0.22 | 1.27 ± 0.41 | 22.39 ± 0.40 | 1.63 |
| Aqueous extract[a] | 0.04 ± 0.02 | 13.18 ± 0.58 | 5.25 ± 1.64 | 0.68 ± 0.04 | - | 4.74 |

[a] Aqueous extract sample did not present ignition in the higher heating value test.

[b] Higher heating value was corrected by the ash content.

The H/C ratio of the liquid coproducts had direct relationship with their water content, and the pH was acid for both liquid products (Table 2 and Table 3). Remarkable differences were found for water content and kinematic viscosity, meanwhile density was only 10 % lower for aqueous extract (Table 3). Total sulfur content measured for both liquids could be considered equal, and they are within the limit specified by the ASTM D6751 (which is 500 mg/kg) for S500 biodiesel grade. The total sulfur of these products does not attend the EU normative (EN 590:2004 and 14214:2012), which allowed values only below 50 mg/kg. Pour point was probably affected by water content, in which aqueous extract occurred at earlier temperature.

**Table 3.** Physicochemical properties of the obtained bio-oil and aqueous extract.

| Property | Bio-oil | Aqueous extract |
|---|---|---|
| Total sulfur (mg/kg) | 85 ± 9.2 | 76 ± 9.2 |
| Density at 20 °C (kg/m$^3$) | 1 225.6 ± 0.1 | 1 101.6 ± 0.1 |
| pH | 3.3 ± 0.1 | 3.3 ± 0.1 |
| Pour point (ºC) | -24 ± 0.7 | -16 ± 0.7 |
| Water content (%) | 14.2 ± 0.55 | 65.8 ± 0.01 |
| Kinematic viscosity at 40 °C (mm$^2$/s) | 436.13 ± 9.81 | 1.16 ± 0.01 |

Bio-oil and aqueous extract presented higher mass losses at lower temperatures (Fig. 2a). Most of the mass loss of bio-oil sample occurred from 50 to 250 ºC in three overlapped events, while the mass loss of the aqueous extract took place below 100 ºC in a well-defined event (Fig. 2b). The solid materials had a small event bellow 100 °C. A discrete event at 650 °C was observed in the bio-oil and char. The thermal degradation of the eucalypt wood fines took place at 280 and 360 ºC, and a similar event at 360 °C was detected in the char (Fig. 2b). The crust material had thermal decomposition behaving intermediary to the bio-oil and char, with a long event starting at 200 °C and finishing at 650 °C.

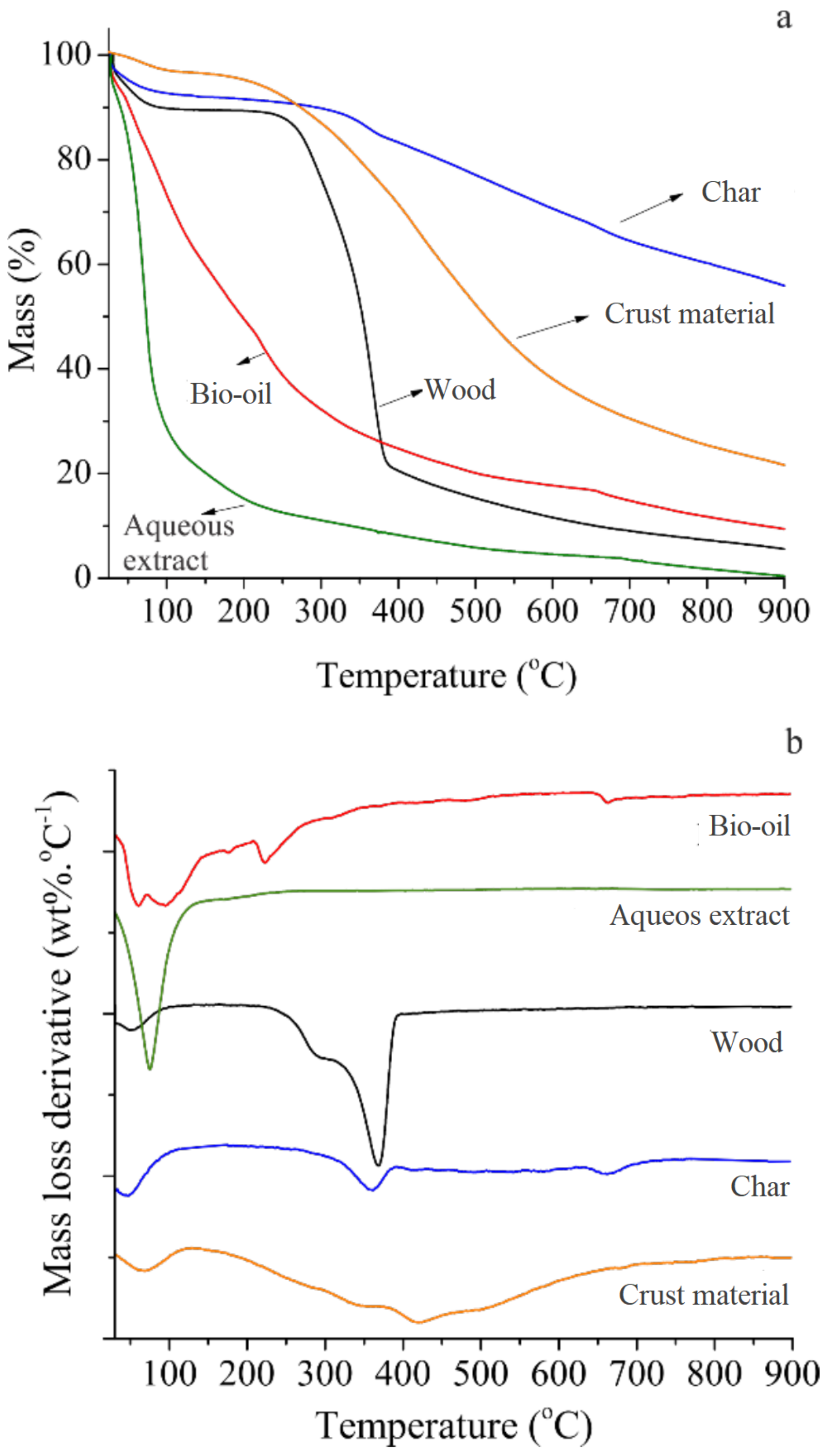

**Fig. 2.** Thermogravimetric curves (a) and their respective derivatives (b) of the raw material and the products obtained from the fast pyrolysis procedure.

Bio-oil and aqueous extract were composed by 12 and 10 % of volatile organic compounds, respectively, and the major identified compounds were acetic acid, methanol and ethanol (Table 4).

**Table 4.** Percentage of volatile organic compounds (VOCs) in the bio-oil and aqueous extract

| **Response** | **Bio-oil** | **Aqueous extract** |
|---|---|---|
| | **wt.%** | |
| Methanol | 0.40 ± 0.04 | 0.72 ± 0.01 |
| Ethanol | 0.27 ± 0.02 | 0.08 ± 0.00 |
| Acetone | 0.04 ± 0.00 | 0.05 ± 0.00 |
| Acetic acid | 11.22 ± 1.49 | 8.73 ± 1.50 |
| Furfural | 0.01 ± 0.00 | 0.03 ± 0.00 |

The bio-oil and aqueous extract composition was studied using GC-MS. The syringyl and guaiacyl-derived compounds totalized 59 and 30 % of all identified molecules in the bio-oil and aqueous extract, respectively. On contrary, the carbohydrate-derived compounds were responsible for 21 and 57 % of the compounds in the bio-oil and aqueous extract, respectively. The lignin/carbohydrate ratio of the bio-oil was 2.82 and it has decreased to 0.53 for the aqueous extract, stating a concentration of lignin-derived compounds in the oil (Table 5).

**Table 5.** Identification and quantification of bio-oil and aqueous extract compounds by GC-MS analysis.

| **Products[a]** | **m/z[b]** | **BA[c]** | **g/L** | |
|---|---|---|---|---|
| | | | **Bio-oil** | **Aqueous extract** |
| C2 - furan | **95**, 81, 67 | Carbohydrates | 2.6 | 4.2 |
| 4-hydroxy-4-methyl-2-pentanone | **43** | Carbohydrates | 2.4 | - |
| Furanone | **55,** 84 | Carbohydrates | 2.8 | 2.9 |
| Phenol | **94,** 66 | Carbohydrates, Lignin | 1.4 | 1.7 |
| C1 - pyranone | **112**, 84, 55 | Carbohydrates | 3.8 | 1.7 |
| C1-Phenol | **108**, 77, 51 | Carbohydrates, Lignin | - | 0.8 |
| C1 - phenol | **107**, 77, 51 | Carbohydrates, Lignin | 2.0 | 1.7 |
| C1 - furan | **81**, 53, 51 | Carbohydrates | 1.8 | - |
| Guaiacol | **124**, 81, 109 | Lignin | 4.7 | 3.1 |
| Catechol | **110**, 63, 81 | Carbohydrates, Lignin | 8.1 | 4.6 |
| C1 - guiacol | **138**, 123, 95 | Lignin | 4.3 | 3.4 |
| 1,4:3,6-dianhydro-α-d-glucopyranose | **69**, 57, 41 | Carbohydrates | 2.9 | 1.4 |
| C1 - catechol | **124**, 78, 106 | Carbohydrates, Lignin | 1.4 | - |
| Hydroquinone | **110**, 81, 53 | Carbohydrates, Lignin | 1.7 | 1.2 |
| Hydroxy-guaiacol | **140**, 97, 125 | Lignin | 2.3 | - |
| C1 - catechol | **124**, 78, 106 | Carbohydrates, Lignin | 2.8 | - |
| C2 - guaiacol | **137**, 152, 122 | Lignin | 4.9 | 1.0 |
| Syringol | **154**, 139, 93 | Lignin | 16.7 | 6.7 |
| Eugenol | **164**, 149, 131 | Lignin | 1.7 | - |
| Vanillin | **151**, 81, 109 | Lignin | 8.9 | 1.0 |
| C1 - syringol | **168**, 153, 125 | Lignin | 13.3 | 3.4 |
| Levoglucosan | **60**, 42, 73, 97 | Carbohydrates | 5.0 | 23.9 |
| Acetoguiacone | **151**, 166, 123 | Lignin | 3.4 | 1.4 |
| C2 - syringol | **167**, 182, 107 | Lignin | 10.0 | 1.6 |
| Guacylcetone | **137**, 137, 180 | Lignin | 4.0 | 0.8 |
| 4-allyl-syringol | **194**, 91, 133 | Lignin | 5.7 | 0.7 |
| C3 - syringol | **167**, 196 | Lignin | 2.3 | - |
| Homovanillic acid/Dihydroconyferyl alcohol[d] | **194**, 137, 182 | Lignin | 2.1 | - |
| Syringaaldehyde | **182**, 65, 139 | Lignin | 15.0 | 4.3 |
| 4-propenyl-syringol (trans) | **194**, 91, 119 | Lignin | 1.7 | - |
| Homosyringaldehyde | **167**, 196, 123 | Lignin | 2.7 | - |
| Acetosyringone | **181**, 196, 153 | Lignin | 9.2 | 2.3 |
| Conyferyl aldehyde (trans) | **178**, 147, 135 | Lignin | 2.1 | - |
| Syringyl acetone | **167**, 210, 123 | Lignin | 12.2 | 2.5 |
| Synapyl alcohol (allyl) | **167**, 182, 210 | Lignin | 1.9 | - |
| Propyosiringone | **181**, 210, 153 | Lignin | 2.8 | - |
| Homosyringic acid/Dihydrosynapyl alcohol[d] | **168**, 212, 153 | Lignin | 2.0 | - |
| Synapylaldehyde (trans) | **208**, 165, 137 | Lignin | 2.6 | - |
| **Total** | | | 175.2 | 76.3 |
| **Lignin/Carbohydrate ratio** | | | 2.82 | 0.53 |
| **S/G ratio** | | | 3.66 | 2.22 |

[a] Isomer abbreviations, C1 - methyl, C2 - dimethyl or ethyl, C3 - trimethyl, methyl – ethyl or propyl; [b] mass-to-charge ratio, bold values are the main mass fragment; [c] biological assignment

**Table 6.** Identification and relative quantification (% total) of wood and char compounds by Py/GC-MS analysis.

| **Products**[a] | **m/z**[b] | **BA**[c] | **% total** | |
|---|---|---|---|---|
| | | | **Wood** | **Char** |
| Benzene | **78**, 63, 50 | Charcoal | - | 12.2 |
| Furan | 68 | Carbohydrates | - | 1.2 |
| Cyclopentadiene | 65 | alkane | - | 1.0 |
| Cyclohexadiene | **77**, 51 | alkane | - | 5.6 |
| Toluene | **91**, 65 | Charcoal | - | 10.5 |
| Furanone | **55,** 84 | Carbohydrates | 0.2 | - |
| Furfural | **95**, 67 | Carbohydrates | 0.4 | 0.6 |
| furfuyl alcohol | **84**, 55, 42 | Carbohydrates | 0.4 | - |
| C2 – benzene | **106**, 91, 65 | Charcoal | - | 0.8 |
| C3 – benzene | **120**, 105, 91 | Charcoal | - | 0.1 |
| Styrene | **104**, 78, 51 | Charcoal | - | 0.5 |
| dihydro - methyl - furanone | **98**, 70, 41 | Carbohydrates | 1.7 | 0.4 |
| 5 - methyl - 2 - furaldehyde | **109**, 81, 53 | Carbohydrates | - | - |
| C1 – cyclopentenone | **96**, 81, 67 | Carbohydrates | - | 0.1 |
| Phenol | **94,** 66 | Carbohydrates, Lignin | - | 9.9 |
| C1 – styrene | **117**, 103, 77 | Charcoal | - | 0.3 |
| 4 - hydroxy - 5,6 dihydro-(2H)-pyran-2 one | **114**,85,58 | Carbohydrates | 8.9 | - |
| hydroxy - methyl - cyclopentenone | **112**, 84, 55 | Carbohydrates | 0.5 | - |
| Indene | **115**, 89, 43 | Charcoal | - | 0.4 |
| C1 – phenol | **107**, 77, 51 | Carbohydrates, Lignin | - | 7.5 |
| C1 – furan | **81**, 53, 51 | Carbohydrates | - | 0.2 |
| Guaiacol | **124**, 81, 109 | Lignin | 4.0 | 3.5 |
| C2 – phenol | **122**, 107, 77 | Carbohydrates, Lignin | - | 1.0 |
| dihydroxy – benzene | **110**, 63, 81 | Carbohydrates, Lignin | 1.1 | 2.9 |
| C1 – guaiacol | **138**, 123, 95 | Lignin | 4.2 | 2.0 |
| Naphthalene | **128**, 102 | Charcoal | - | 3.9 |
| C3 – phenol | **136**, 121 91 | Carbohydrates, Lignin | - | - |
| hydroxy - methyl - furaldehyde | **126**, 97, 69 | Carbohydrates | 0.1 | - |
| C1 - dihydroxy - benzene | **124**, 78, 106 | Carbohydrates, Lignin | 0.0 | 0.3 |
| Hydroxy-guaiacol | **140**, 97, 125 | Lignin | 2.2 | 1.6 |
| C2 – guaiacol | **137**, 152, 122 | Lignin | 0.7 | 0.4 |
| 4 - vinyl guaiacol | **150**, 135, 107 | Lignin | 7.6 | 1.1 |
| Syringol | **154**, 139, 93 | Lignin | 19.0 | 9.5 |
| Eugenol | **164**, 149, 131 | Lignin | 1.0 | 0.1 |
| C3 – Guaiacol | **166**, 137, 122 | Lignin | - | |
| Unidentified | **182**, 167, 139 | Lignin | - | 0.2 |
| Vanillin | **151**, 81, 109 | Lignin | 2.7 | 1.7 |
| C1 – syringol | **168**, 153, 125 | Lignin | 14.5 | 7.0 |
| isoeugenol (trans) | **164**, 149, 131 | Lignin | 4.6 | 0.5 |
| Homovanillin | **166**, 137, 122 | Lignin | 0.3 | - |
| Levoglucosan | **60**, 42, 73, 97 | Carbohydrates | 0.1 | - |
| Acetoguiacone | **151**, 166, 123 | Lignin | 0.2 | 0.4 |
| C2 – syringol | **167**, 182, 107 | Lignin | 0.6 | 1.3 |
| 4 - vinyl – syringol | **180**, 165, 137 | Lignin | 14.2 | 4.1 |
| 4-allyl-syringol | **194**, 91, 133 | Lignin | 2.1 | 0.4 |
| C3 – syringol | **167**, 196 | Lignin | - | 0.2 |
| 4-propenyl-syringol (cis) | **194**, 91, 119 | Lignin | 0.6 | - |
| Syringaaldehyde | **182**, 65, 139 | Lignin | 1.5 | 4.1 |
| 4-propenyl-syringol (trans) | **194**, 91, 119 | Lignin | 5.4 | 2.3 |
| Homosyringaldehyde | **167**, 196, 123 | Lignin | 0.1 | - |
| Acetosyringone | **181**, 196, 153 | Lignin | 0.3 | - |
| Syringyl acetone | **167**, 210, 123 | Lignin | 0.1 | 0.3 |
| Synapyl alcohol (trans) | **167**, 182, 210 | Lignin | 0.3 | - |
| S/G ratio | | | 2.37 | 3.07 |

[a] Isomer abbreviations, C1 - methyl, C2 - dimethyl or ethyl, C3 - trimethyl, methyl – ethyl or propyl; [b] mass-to-charge ratio, bold values are the main mass fragment; [c] biological assignment

The major compounds identified in the bio-oil were derived from the syringyl units of lignin. In fact, syringaldehyde, syringyl acetone and syringol represented more than 25 % of all identified compounds in the bio-oil. Other less representative compounds, but also with higher concentration, were vanillin, catechol and acetosyringone. On the other hand, the aqueous extract had levoglucosan as the only one remarkable compound, which represents over 30 % of the total (Table 5). Phenolic compounds (excluding syringyl and guaiacyl components) totalized 10.3 and 11.3 % of the bio-oil and aqueous extract composition, respectively.

Py-GC-MS gives an insight of the chemical structures of the solid materials (Table 6). The lignin derived compounds totalized over 83 and 38 % of the identified molecules after the pyrolysis of the raw material and char, respectively. It is important to emphasize that analytical pyrolysis does not represent a sensible tool for the evaluation of carbohydrates. It was easily confirmed after comparing the 12 % of carbohydrates quantified via analytical pyrolysis for the raw material, against the 70 % quantified by wet chemistry. By doing relative comparisons, it was possible to observe that the carbohydrate compounds slightly decreased in the solid products (1.3 times lower).

Syringyl derived compounds were predominant in the solid samples. The S/G ratio among the products confirm such predominance:  bio-oil (3.66) > char (3.07) > raw material (2.37) > aqueous extract (2.22). The phenolic compounds (excluding syringyl and guaiacyl components) resulted from the pyrolysis of the char (21 %) were higher than those identified in the pyrolytic products of the raw material (1.1 %). Aromatics were not identified in the raw material pyrolytic products; but it corresponded to 28 % of the compounds identified in char, resulting in an aromatic/alkyl aromatic ratio of 1.45 (Table 6).

**Table 7.** Quantification of carbohydrate percentage present in liquid products by Ion Chromatography

| **Sugar** | **wt.%** | |
|---|---|---|
| | **Bio-oil** | **Aqueous extract** |
| Arabinose | 0.30 ± 0.04 | 0.07 ± 0.01 |
| Galactose | 0.11 ± 0.01 | 0.03 ± 0.01 |
| Glucose | 6.60 ± 0.90 | 2.34 ± 0.23 |
| Xylose | 0.60 ± 0.07 | 0.12 ± 0.06 |
| Mannose | 0 | 0 |
| Cellobiose | 0.06 ± 0.01 | 0 |

Considering the fact that analytical pyrolysis is not the ideal tool for carbohydrate assessment, we evaluated the amount of carbohydrates present in liquid products (Table 7). Bio-oil and aqueous extract presented 7.7 and 2.6% of sugars, respectively, with glucose found in major amount. It is noteworthy that we performed ionic chromatography of liquid products, without the hydrolysis reaction, and no free sugars were found.

## 4. Discussion

### 4.1 Performance of the pilot-scale reactor for fast pyrolysis of eucalypt wood fines

The yield of bio-oil obtained in the pilot plant was similar to those found in the recent published works carried out at laboratory scale [31, 32], which was *ca.* 50 %. At laboratory conditions the reaction parameters are usually very well controlled, which may not be the case of larger scales. The centrifugation step at the final of the fast pyrolysis plant stands as a tool to concentrate pyrolysis products coming from carbohydrates in an aqueous extract (light fraction), and lignin-derived compounds in a bio-oil (heavy fraction).

The char is indeed a high-thermally stable carbon-rich material (Table 2) in the pyrolysis plant, but it does not is as aromatized (H/C ratio) as the traditional charcoal prepared under slow-pyrolysis [33].

The high ash content of the obtained char is a result of a not entirely efficient fluidized bed, but it is usually observed for this type of fast pyrolysis coproducts [34].

The crust material formation inside the tubes between the reactor and condensation system is a negative point of this kind of larger scale procedure (Fig. 1). As showed by Wang et al [15] it occurs due the continuous heating of the bio-oil, leading to the repolymerization of the lignin or carbohydrates monomeric compounds. The crust material formation reduces the bio-oil recovery and increases maintenance costs. Thus, by effectively controlling the reaction and vapor transporting temperatures it is possible to improve the efficiency of the pilot-plant bio-oil production.

This pilot-scale plant for bio-oil production is interesting as it operates using rejected material from a Kraft pulp line, to which it was integrated. In this case, the costs related to transportation of feedstock can be reduced to near zero. By doing so, the profitability of the bio-oil production can be improved [11] and the smart use of biomass wastes can contribute to apply the concepts of bioeconomy, especially for sustainable solutions in the replacement of fossil fuels and energy self-sufficiency.

### 4.2 Characterization of the precursor wood material and the coproducts

The first significant mass loss, event in the thermogram of the raw material (Fig. 2b) is related to the thermal decomposition of hemicelluloses and amorphous cellulose, while the second mass loss corresponds to the degradation of crystalline cellulose [35]. Thermal events related to the lignin degradation were not observed as a single peak due its degradation in a broad temperature range. The main events are related to degradation of lignin-carbohydrate complexes at 235 ºC, aliphatic side chains starting at 300 ºC up to cleavage of more stable carbon-carbon bonds at 370-400 ºC [36].

The thermal behavior of all obtained coproducts is explained by their chemical composition. The chemical composition of bio-oil and aqueous extract was similar; however, different concentrations of some specific compounds were observed. As a result, their thermogravimetric curves had similar pattern of mass loss. Nevertheless, the higher water content of the aqueous extract sample promoted a very intense mass loss at temperatures below 100ºC, which was not observed in the bio-oil curve. Besides water, the presence of VOCs in these liquid samples was also responsible for their lower thermal stability when compared with the solid products and raw material.

The char was the most thermally stable coproduct among the solids (lower H/C, Table 2); its mass loss occurred from 350 to 900 ºC in a slower rate compared with the raw material and crust material. The residual mass after 900 ºC was higher than 60 %, which was also a result of its high ash content (Table 2). The char would be even more thermal stable if all carbohydrates had been pyrolyzed during the fast pyrolysis procedure, which was not the case since a peak at around 360 ºC was observed in the DrTG curve of this sample (Fig. 2), and carbohydrate pyrolysis products were detected (Table 6). The higher carbon content, lower H/C ratio and lower amount of non-alkylated aromatic compounds (Table 6) indicates its recalcitrant character [22].

The DrTG of the crust material showed a series of overlapped mass loss events occurring from 150 to 700 ºC. Crust material can be formed by heating both carbohydrate and lignin-derived compounds (*i.e.* both pyrolytic water soluble and insoluble compounds) in a wide range of temperatures, but especially between 250-400 ºC [15]. Considering this, it is possible to infer that the observed overlapped peaks correspond to the thermal decomposition of oligomerized carbohydrate and lignin monomeric units, which is different from the thermal decomposition of the original macromolecules.

### 4.3 Coproducts from fast pyrolysis toward biofuel application

The elevated water content of the aqueous extract affected its pour point, density and kinematic viscosity as well, making it not suitable as a potential biofuel. In fact, no ignition was observed for this sample in the HHV measurement. Another aspect was its high H/C molar ratio when compared to the other samples, which means a very non aromatized structure [33].

The fast pyrolysis bio-oil obtained under pilot scale conditions is composed by a wide range of organic compounds, but most of them are phenolic and its derivatives which are oxygenated compounds. Although the bio-oil has over 20 MJ/kg of heating value, its high oxygen content limits their directly application as biofuel [32] and contributes to the chemical instability of the product. In such cases, catalytic hydrogenation strategies [37] and esterification [38] have been discussed. Besides, hydrogen-lacking characteristic of the fast pyrolysis bio-oil is the main responsible for crust material formation inside the reactor [6]. Another problem to overcome is still the high corrosiveness of the bio-oil, which is related to its acidity (low pH), mainly due to the presence of carboxylic acids such as acetic acid. The acetic acid present is mainly formed by the thermal degradation of hemicellulose [39], in this process the uronic acid ring ruptures and the acetyl group bound to xylose is eliminated [40]. Lignin also contributes to the formation of acetic acid by breaking the lignin side-chain [41]. Cellulose, when subjected to pyrolysis, depolymerizes, producing levoglucosan, then the breakdown of levoglugosan produces acetic acid [42].

The energy recovery (calculated using the HHV of the starting material and bio-oil, and the yield of the conversion of the first into the second) for the bio-oil production was *ca.* 40 %, which is below of the numbers obtained in the lab-scale catalytic bio-oil production [3]. However, the value obtained here is in agreement with the energy recovery of bio-oil production at lab-scale non catalytic process [3]. Besides, the low density of the wood decreases the energy produced by volume, which stands as one of the main drawbacks of this biofuel. In addition, wood stabilizes its moisture content according to the surroundings, usually equilibrating at 15-20 %. Thus, higher energy is lost to dry this biofuel or to evaporate this moisture during the heat production. On the other hand, the higher density of the bio-oil promotes higher heat capacity by volume, making transportation and storage easier.

The crust material and char presented the highest HHV (23 and 26 MJ/kg, respectively) and the lowest H/C (0.68 and 1.06, respectively), stating their highly aromatized structures. These results are in agreement with the observed in the thermogravimetric curves for these two solid samples. Moreover, the HHV of the char would be even higher if no carbohydrate-derivatives had remained in this sample, which was observed in its TGA curve. Even though, the char presented the most favorable characteristics to be used as a solid biofuel, *i.e.*, higher HHV and aromatized structure. In parallel there is an option to compact these char fines in order to increase the specific energy production [43]. Nevertheless, the influence of its higher ash content should be examined toward the performance and operation in the combustion stage.

### 4.4 Coproducts from fast pyrolysis as precursor for chemicals and materials

Both bio-oil and aqueous extract showed chemical compounds with many functionalities (C-H, C=O, C=C, C-C, O-H), opening a wide road of possibilities to be effectively exploited for the production of fine chemicals [2]. The obtained bio-oil presented significant concentration of interesting compounds such as syringaldehyde, which can be further converted in BTX chemicals by catalytic dehydroxylation of phenolics compounds [44], methanol and naphthalene [1]. From BTX chemicals a wide range of phenolic resins and unsaturated polyester could be synthetized [1, 45]. On the other hand, the levoglucosan-rich aqueous extract can serve as a precursor material for furan compounds, cyclopentenones and other aliphatic oxygenates by dehydration of levoglucosan [46]. Further interesting applications of levoglucosan-rich aqueous extract is the conversion of these pyrolytic sugars into ethanol by fermentation or lipids [47] as well as to manufacture surfactants, food additives, biodegradable polymers and pharmaceuticals [48]. The sugars present in the bio-oil are probably derived from higher molecular weight holocellulose fragments, which remained attached to the lignin chain after pyrolysis [49]. They may be used for the production of ethanol as well as anydrosugars [50, 51].

The higher content of phenolic compounds in the bio-oil can be useful as antifungal agent for wood preservation [52], as these compounds tend to have primary responsibility for any antimicrobial activity, mainly against brown-rot fungus [53]. The amphoteric properties of the bio-oil are interesting to increase both the dimensional stability and water repellency of wood through the blocking of its capillary microstructures.

The char from pyrolyzing biomass is recognized as a potential sorbent for aromatic contaminants. For example: char of orange peels - with similar elementary composition of char from wood - could be used as a good alternative for the sorption of naphthalene and 1-naphthol [54]; char from pine wood gasification seemed to be more attractive than activated carbon to remove toluene from water [55].

## 5. Conclusions

The yield of bio-oil obtained in a pilot plant was similar to laboratory conditions described in the literature. Bio-oil, char and crust material presented higher HHV than the raw material. The higher water content of aqueous extract and the oxygen-rich composition of the bio-oil denote the limitations for their use as fuel. The GC-MS showed a higher concentration of lignin compounds in the bio-oil, mainly syringyl monomers, whereas the aqueous extract presented higher concentration of carbohydrate-derived compounds, especially levoglucosan. Valuable phenolic compounds were identified in the bio-oil and its coproducts, highlighting their potential as antifungal agent and to produce fine chemicals. These chemical characteristics confirm the valuable application of both materials in a biorefinery system. Wood fines can be used to produce energy for industry's self-sufficiency replacing fossil fuels, generating interesting coproducts containing high added-value extractable materials.

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