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Pyrolysis of furniture wood waste: Decomposition and gases evolved.

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Highlights:

- Pyrolysis of furniture wood waste.
- Kinetic parameters of pyrolysis from TG analysis.
- Analysis of gas, volatile and semi-volatile products evolved.

Abstract

The pyrolysis of furniture wood waste was studied due to its importance as a thermochemical conversion process, and also because it is a step in the combustion process. Furniture wood contains organic additives and inorganic elements (being noteworthy the high content of Ti). These additives cause changes in the thermal processes.

A thermogravimetric analysis of the pyrolysis of furniture wood waste was carried out in a TGA apparatus using dynamic and dynamic + isothermal runs. The pyrolysis was modeled with acceptable approximation by three independent reactions, according to the decomposition of the main components of the wood (hemicellulose, cellulose and lignin).

The gaseous products evolved during the pyrolysis were measured by the TG-MS and TG-FTIR techniques. The maximum formation of gases occurs around 360 °C. The CO₂ formation remains until the end of the run, due to the wide range of lignin degradation.

In addition, runs to identify the volatile and semi-volatile compounds were also carried out in a laboratory scale tubular reactor at 500 and 850 °C and the results were compared with the pyrolysis of a cleaner wood.

Keywords:

Wood waste; Thermogravimetric analysis (TGA); TG-FTIR; TG-MS; Gases evolved.

1. Introduction

Wood is being widely used as a renewable energy and it has several advantages over other biomass, for instance, higher energy content per volume, lower amount of ash, and a very low amount of nitrogen and sulfur. Nowadays, the main thermochemical technologies are pyrolysis, gasification and combustion [1].

This paper studies the pyrolysis conversion technology. Pyrolysis is thermal decomposition in the complete absence of air or oxygen. Biomass pyrolysis is often employed in chemical synthesis or energy production [2-5]. On the other hand, pyrolysis can be a step in the combustion process and some of the pollutants emitted in the combustion process are formed during the pyrolysis step. In a TG analysis, it is possible to distinguish the different stages of the material decomposition. Wood is a complex material which essentially contains hemicelluloses, cellulose, and lignin, so any decomposition kinetic model developed must consider the degradation of these three compounds. Many authors have studied the decomposition of these components, and they concluded that the decomposition of hemicelluloses and cellulose occurs quickly, in the approximate temperature range of 200 °C – 380 °C and 250 °C – 400 °C, respectively. Lignin however, is harder to decompose and decomposes in a wide temperature range from 180 °C up to 900 °C and the generated solid residue is considerable [6-9].

Waste from furniture wood can also be considered for energy recovery, but with the inconvenience of the formation of pollutants due to the oils, adhesives, paints and varnishes used in the fabrication of the furniture [10]. This additional chemical content changes its behavior during thermal processes. For instance, some authors have studied the catalytic effect of some inorganic salts in doped wood and it was found that the temperature of degradation decreases [11-13]. On the other hand, other authors studied the thermal degradation of wood treated with urea formaldehyde (UF), melamine formaldehyde (MF) and phenol formaldehyde (PF) resins and the results were that the treated wood showed higher temperatures of degradation [14]. The gases evolved in thermal degradations have been studied using thermogravimetry/mass spectrometry (TG/MS) [15-20] and thermogravimetry/Fourier

transformed infrared (TG/FTIR) [7,21-27]. These methods offer the advantage of being simultaneous and real-time measurements of the mixture of the generated products are done. The gases evolved were also studied with the treated wood with melamine and urea additives and in thermal decomposition can produce some nitrogen compounds, such as ammonia, isocyanic acid, hydrogen cyanide and nitric oxides [28-29]. In this work, it is assumed that the furniture wood has been treated with these adhesives and other products and the presence of some inorganic compounds can also be higher than in untreated wood. Therefore, a thermogravimetric analysis of furniture wood waste can provide information on the global effect of all additives present in the furniture wood. Therefore, the objective of this work has been to obtain a kinetic model and the characterization of the products evolved during the pyrolysis of furniture wood waste. Furthermore, a characterization of a clean wood waste (solid wood) has also carried out, in order to compare the results obtained with the furniture wood waste.

2. Materials and methods

2.1. Characteristics of the materials

The furniture waste was collected from a Municipal Solid Waste Treatment Plant, after being crushed to a size less than 10 cm. Prior to experiments, a sample around 10 kg was taken from different parts of the pile with the crushed material and another sample around of 10 kg of solid wood was collected from a furniture factory. Representative samples of both kinds of wood were dried in an oven at 105 °C and grounded to a size less than 0.2 mm.

The proximate analysis of the material consists of moisture, ash, volatile matter and fixed carbon determination. The moisture and ash content were determined using the European Standards CEN-TS 14774-1:2009 and 14775:2009, respectively [30-31]. The volatile matter (VM) was determined using the method developed by García et al. [32], that shows satisfactory results according to the standard methods, mainly on moisture and volatile matter values. The fixed carbon (FC) content was calculated by difference using the following balance:

$$\%FC = 100 - (\%Ash + \%VM) \quad (1)$$

82 An elemental analysis of the major elements (C, H, N) was carried out in a Leco Micro TruSpec
83 Elemental Analyzer [33]. Determination of the content of sulfur and chlorine was carried
84 according to the European Standard CEN-TS 15289:2011 [34].

85 The Net Calorific Value (NCV) was determined using an AC-350 calorimetric bomb from Leco
86 Instruments.

87 The content of hemicelluloses, cellulose and lignin were analyzed according to Rowel et al. [35]
88 and test methods T12, T222 and T203 of the “Technical Association for the Pulp and Paper
89 Industries” [36-38].

90 Table 1 shows the characteristics of the furniture wood waste and the solid wood.

91 **Table 1.**

92 As can be seen in Table 1, the more significant differences between both samples are the ash
93 content and the nitrogen content. The difference in nitrogen content can be due to the presence
94 of additives in the furniture wood, such as melamine and nitrogenated adhesives.

95 The major and minor elements were also determined. A multi-step pressurised digestion was
96 carried out following the CEN-TS 15290:2011 Standard [39] for the determination of the major
97 elements (Al, Ca, Mg, P, K, Si, Na and Ti) and following the CEN-TS 15297:2011 Standard for
98 the minor elements (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn) [40]. Subsequently,
99 the detection of the major elements was carried out by Inductively Coupled Plasma Optical
100 Emission Spectrometry (ICP-OES) following the CEN-ISO 11885:2007 Standard [41]. The
101 detection of the minor elements was carried out by Inductively Coupled Plasma Mass
102 Spectrometry (ICP-MS) following the Standard CEN-ISO 17294-2:2003 [42]. Table 2 shows
103 the major and minor elements of the furniture wood waste, which can be compared with other
104 data of literature [43].

105 **Table 2.**

106 From Table 2, it can be observed that the concentrations of inorganic compounds in the
107 furniture wood waste are higher than those of solid wood. Nevertheless, most of the elements

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4 108 detected are within the range of those indicated in literature. In addition, Co, Mo and Sb can also
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6 109 be present in tree and waste woods. For instance, Reimann et al. [44] showed that the
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8 110 concentrations of these elements in birch and spruce wood were around 8 – 34 mg/kg d.b. for
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10 111 Co, 2.1 – 3.3 mg/kg d.b. for Mo, 2.6 – 3.1 mg/kg d.b. for Sb. On the other hand, Saqib et al. [45]
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12 112 also detected concentration values around 1.5 mg/kg d.b. for Co and 0.6 mg/kg d.b. for Sb.
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14 113 These concentration values of the wood furniture wastes are in the same order.

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17 114 The content of Ti in the furniture wood waste is much higher than those of the other woods.

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19 115 Therefore, this indicates that the sample does not correspond to clean and untreated wood.

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22 116 FTIR analyses were also carried out to qualitatively determine if there are some chemical
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24 117 substances in furniture wood waste. FTIR spectra were recorded in the wavelength range from
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26 118 4000-600 cm^{-1} with a BRUKER IFS 66/S spectrometer with a DLaTGS detector. Resolution in
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28 119 FTIR was set at 4 cm^{-1} and spectra were collected at 64 scans. The FTIR analyses were
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30 120 performed with samples of furniture wood waste, solid waste and laminate sheets from the same
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32 121 furniture waste, in order to compare the spectra obtained (Figure 1). In addition, the nitrogen
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34 122 content of the laminate sheets was also determined as being 4.9 wt. %. It is assumed that the
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36 123 laminate sheets used for this analysis are made of melamine resin and also show adhesive to fix
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38 124 the laminate sheets to the particle boards.

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42 125 Figure 1 shows the FTIR spectra whose baselines were corrected and vector normalized.

43 44 45 46 126 **Figure 1.**

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48 127 The spectrum of the laminate sheets shows more similarity to the furniture wood waste
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50 128 spectrum than to the solid wood spectrum. These similarities are mainly observed in the 1700-
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52 129 1300 cm^{-1} region. The differences between the solid wood spectrum and the spectra of the
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54 130 furniture waste and the laminate sheets can be due to the presence of additives in those treated,
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56 131 such as urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF) and phenol-
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58 132 formaldehyde (PF) resins [46-47]. Zhang et al. [46] show the FTIR spectra of the UF and MUF
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4 133 resins and they indicated that the peak at around 1650 cm^{-1} is due to C=O stretching of primary
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6 134 amides. This peak is also observed in the spectra of the furniture waste and the laminate sheets.
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8 135 The PF resin spectrum shows a peak at 1609 cm^{-1} [47], which is also observed in the spectra of
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10 136 the furniture waste and the laminate sheets.

11 12 13 137 *2.2. Thermogravimetric analysis*

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15 138 A thermogravimetric analysis was carried out in a TGA apparatus (Perkin Elmer, model TG
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17 139 STA6000) using dynamic and dynamic + isothermal runs. The sample temperature was
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19 140 measured with a sensor directly attached to the sample holder. The atmosphere used was
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21 141 nitrogen with a flow rate of 100 mL min^{-1} .

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23 142 Dynamic runs were carried out at different weights (2.5, 5 and 10 mg) and different heating
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25 143 rates ($5, 10$ and 20 °C min^{-1}), from the initial temperature up to 900 °C .

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28 144 Dynamic + isothermal runs were carried out with a constant heating rate until the required
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30 145 temperature was reached (between 280 °C and 320 °C) and this final temperature was kept
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32 146 constant for a long period of time.

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35 147 In addition, a dynamic run was also carried out with the solid wood at 10 °C min^{-1} , to compare
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37 148 the thermal behavior between treated and untreated wood.

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40 149 Furthermore, an experiment of Avicel PH-105 microcrystalline cellulose at a heating rate of 5
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42 150 °C min^{-1} was done to verify the performance of the equipment. The kinetic values obtained
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44 151 agreed well with the results presented by Grønli et al. [48] in their round-robin study of
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46 152 pyrolysis kinetics of cellulose by thermogravimetry.

47 48 49 153 *2.2. TG-MS analysis*

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51 154 The pyrolysis of furniture wood waste was also studied with a thermogravimetric analysis
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53 155 (TGA) coupled to a mass spectrometer (MS). A Mettler Toledo TGA/SDTA851e/LF/1600 (TG-
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55 156 DTA) in series with a Pfeiffer Vacuum Quadrupole Mass Spectrometer (QMS) Thermostar
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57 157 GSD301T using an electron ionization voltage at 70 eV was used. The mass of sample used in
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59 158 runs was around 3 mg . The pyrolysis analysis were performed at a heating rate of 30 °C min^{-1} up
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4 159 to a final temperature of 900 °C with a flow rate of 100 mL/min of helium (measured at room
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6 160 temperature). The detection of the 4, 13-18, 25-32, 35-46 ions was carried out in one run and the
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8 161 4, 32, 43-46, 50-52, 55-58, 60, 65, 68, 73, 78, 91, 96, 105, 106 ions in another run. The
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10 162 response of the different ions was divided by that of helium ($m/z = 4$) and subtracted from that
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12 163 corresponding to the beginning of the run.
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15 164 *2.3. TG-FTIR analysis*

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17 165 The TGA analysis was performed by TG STA6000 (Perkin Elmer) at a heating rate of 30°C
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19 166 min⁻¹ from room temperature to 900 °C, with a gas flow of 100 mL min⁻¹ of nitrogen. The mass
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21 167 of sample used was around 6 mg. The FTIR measurements were performed by a Nicolet 6700
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23 168 spectrometer coupled to the TGA to measure the gas products from the wood decomposition.
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25 169 The transfer line and gas cell were heated at 230 °C, to prevent condensation of the gases
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27 170 produced. Resolution in FTIR was set at 4 cm⁻¹ and spectra were collected at 32 scans in the
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29 171 range 400-4000 cm⁻¹.
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32 172 *2.4. Pollutant analysis*

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35 173 Runs for the identification of volatile and semi-volatile compounds from pyrolysis were carried
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37 174 out in a laboratory scale horizontal quartz reactor at 500 and 850 °C. In this reactor, the sample
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39 175 was introduced inside a crucible and a small engine introduced it inside the reactor. This
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41 176 equipment has previously been described in detail by Font et al. [49]. Runs were carried out
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43 177 with 300 mL min⁻¹ of nitrogen and with a feeding velocity of 1 mm s⁻¹. The sample mass in all
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45 178 the runs was almost 100 mg.
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48 179 Gases and volatile compounds were collected in Tedlar® bags and analyzed in three gas
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50 180 chromatographs; one with a thermal conductivity detector (TCD) to determine mainly CO and
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52 181 CO₂, another with a flame ionization detector (FID) to determine hydrocarbons and the third
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54 182 apparatus was a GC-MS with a DB-624 capillary column (30 m x 0.25 mm x 1.4 µm) to
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56 183 determine volatile compounds. Due to the N content in the furniture wood waste, it is expected
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58 184 that its pyrolysis produces nitrogen oxides, NH₃, HCN and another volatile and semi-volatile
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60 185 nitrogen compounds. Nitrogen oxides (NO and NO₂) were analyzed with a gas analyzer IM-
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2800 (Environmental Equipment Germany GmbH). Ammonia produced was collected by absorption in a 0.1 wt. % citric acid solution and analyzed by ion chromatography and hydrogen cyanide and other volatile nitrogen compounds were detected with a GC-MS with DB-624 capillary column. Semi-volatile compounds were collected in an adsorbent XAD-2 resin, extracted with solvent in accordance with the EPA Method 3545 [50] and analyzed with GC-MS by the isotope dilution method for the polycyclic aromatic hydrocarbons (PAHs). The identification of semi-volatile compounds was done comparing unknown mass spectra with NIST database reference spectra. A semiquantitative estimation of the yields was calculated with the response factors of the deuterated internal standards with the nearest retention time, according to the EPA 8270D method.

Furthermore, major elements (C, H, N, S) contained in each of the chars obtained were measured in a Leco Micro TruSpec Elemental Analyzer.

3. Results and discussion

3.1. Kinetic study

Prior to carrying out the runs for determination of the kinetics, it was verified that a variation at sample weight between 2.5 - 10 mg has no influence on the TG results. Therefore, the following TG runs were carried out with 5 mg of sample.

Figure 2 shows the experimental TG plots for furniture wood waste pyrolysis at heating rates of 5, 10, 20 °C min⁻¹. In this Figure, the weight fraction represents the weight fraction of the solid, sum of the residue formed and the non-reacted initial solid. The weight fraction is on dry basis (sample weight at 150 °C was taken as initial weight). The value of increment of temperature, corresponding to the DTA, for a run is also plotted in a convenient scale, from -10 °C, which represents a strong endothermic process, to 10 °C, corresponding to a strong exothermic process.

Figure 2.

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4 211 The decomposition of carbonates occurs between 600 – 750 °C [51]. Figure 2 shows a slight
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6 212 weight loss in this range of temperatures. The amount of carbonates can change significantly
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8 213 between samples, therefore data from more than 600 °C were omitted to carry out the kinetic
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10 214 correlation.

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13 215 Figure 3 shows the DTG curve for a pyrolysis run, in order to obtain more information about the
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15 216 fractions that can be considered in wood waste decomposition. Considering the main
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17 217 components of the wood (hemicelluloses, cellulose, and lignin) and their decomposition
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19 218 temperatures [6-9] (200 – 380 °C for the hemicelluloses, 250 – 400 °C for the cellulose, and 180
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21 219 °C up to 900 °C for the lignin) the wide band could be the sum of three peaks, the first two of
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23 220 them very close and the third one is a wide peak.

221 **Figure 3.**

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29 222 From Figure 4, the differences in the thermal degradation can be seen between treated and
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31 223 untreated wood. According to Deka et al. [14], the treatment of wood with urea formaldehyde
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33 224 (UF), melamine formaldehyde (MF) and phenol formaldehyde (PF) increases the major
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35 225 degradation temperature. However, in this study, the temperature at the maximum degradation
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37 226 rate was 356 °C for the furniture wood waste, and 366 °C for the solid wood. This decrease in
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39 227 the pyrolysis temperature is probably due to the inorganic salt content [11-13]. Another contrast
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41 228 between both types of wood is the final residue, which is due to the different ash content, 1.8 %
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43 229 for the furniture wood waste and 0.3 % for the solid wood.

230 **Figure 4.**

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233 231 The dynamic and dynamic + isothermal runs were carried out to correlate a pyrolysis kinetic
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235 232 model. The results of the two dynamic + isothermal experiments carried out in pyrolytic
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237 233 conditions are shown in Appendix A.

234 *3.2. Pyrolysis model*

235
236 235 The pyrolysis kinetic model was proposed considering the main components of the wood
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238 236 (hemicelluloses, cellulose, and lignin):

$$w_{S_{10}}Solid_1 \xrightarrow{1} (w_{S_{10}} - v_{1\infty})Char_1 + v_{1\infty}Volatiles_1 \quad (2)$$

$$w_{S_{20}}Solid_2 \xrightarrow{2} (w_{S_{20}} - v_{2\infty})Char_2 + v_{2\infty}Volatiles_2 \quad (3)$$

$$w_{S_{30}}Solid_3 \xrightarrow{3} (w_{S_{30}} - v_{3\infty})Char_3 + v_{3\infty}Volatiles_3 \quad (4)$$

where $Solid_1$ is hemicellulose, $Solid_2$ is cellulose, $Solid_3$ is lignin, “ $Volatiles_i$ ” are the gases and condensable volatiles evolved in the corresponding reactions ($i = 1-3$), and “ $Char_i$ ” is the char formed in the decomposition of each $Solid_i$. On the other hand, the small letters represent the yield coefficients representative of each reaction. Moreover, each fraction has a yield coefficient that represents the maximum mass fractions obtainable by each reaction. In this way, $v_{i\infty}$ is the yield coefficient for the $Volatiles_i$.

The conversion degree for each reaction is defined as the ratio between the weight fraction of solid reacted at any time ($w_{S_{i0}} - w_{S_i}$) and the corresponding initial fraction of this component $w_{S_{i0}}$, or the ratio between the weight fraction of volatiles obtained at any time (V_i) and the corresponding yield coefficient or the mass fraction of volatiles at infinite time, taking into account that direct relation between formation the volatiles and reacted solids is assumed for each fraction [52].

$$\alpha_i = \frac{w_{S_{i0}} - w_{S_i}}{w_{S_{i0}}} = \frac{V_i}{v_{i\infty}}, \quad i = 1 - 3 \quad (5)$$

$w_{S_{i0}}$ is the weight fraction of each $Solid_i$ that is in the original material, and consequently

$$\sum_{i=1}^3 w_{S_{i0}} = 1 \quad (6)$$

Considering the mass balance between products and reactants and the conversion degrees, the kinetic equations for the pyrolysis runs can be defined as follows:

$$\frac{d(V_i/V_{i\infty})}{dt} = \frac{d\alpha_i}{dt} = k_i(1 - \alpha_i)^{n_i} = k_i \left(1 - \frac{V_i}{v_{i\infty}}\right)^{n_i} \quad (7)$$

with the kinetic constants following the Arrhenius equation:

$$k_i = k_{i0} \exp\left(-\frac{E_i}{RT}\right), \quad i = 1 - 3 \quad (8)$$

By integration of these equations, α_i can be calculated at each time with the temperature program; the relationship between the α_i values and the weight fraction measured in the thermobalance (w) is related with the volatiles obtained (V) by

$$w = 1 - V = 1 - (v_{1\infty}\alpha_1 + v_{2\infty}\alpha_2 + v_{3\infty}\alpha_3) \quad (9)$$

3.3. Pyrolysis: kinetic parameters

The dynamic and the dynamic + isothermal runs for pyrolysis were correlated with the same set of parameters.

The calculated values were obtained by integration of the differential equations presented in the kinetic model by the Euler method considering and testing that the intervals of time were small enough to make the integration errors negligible. The optimization method of the function with Solver in a spreadsheet in Excel was used to minimize the differences between the experimental and calculated weight loss and their derivatives.

The objective function (OF) to minimize was the sum of the square differences between the experimental and calculated weight fractions and their derivatives multiplied by a factor:

$$OF = \sum_{m=1}^M \sum_{j=1}^N (w_{m,j}^{\text{exp}} - w_{m,j}^{\text{cal}})^2 + \text{factor} \sum_{m=1}^M \sum_{j=1}^N \left(\frac{dw_{m,j}^{\text{exp}}}{dt} - \frac{dw_{m,j}^{\text{cal}}}{dt} \right)^2 \quad (10)$$

where M is the number of runs and N is the number of points in each run.

In order to decrease the great interrelation existing among the pre-exponential factor, the apparent activation energy and the reaction order, the optimization is carried out in terms of a “comparable kinetic constant” k_i^* instead of optimization of k_{0i} [53].

$$K_i^* = k_i(0.64)^{n_i} = k_{0i} \exp\left(-\frac{E_i}{RT_{\text{max}}}\right)(0.64)^{n_i} \quad (11)$$

Table 3 shows the set of parameters optimized and Figure 5 shows the calculated evolution of volatiles corresponding to each fraction for a 10 °C/min run.

The first fraction decomposes at 250-450 °C, with apparent activation energy around 139 kJ/mol, and probably corresponds mainly to hemicelluloses, as this value is close to the range of

values (110-132 kJ/mol) proposed for hemicelluloses in literature [54-56]. The maximum yield of volatiles corresponding to hemicellulose (0.238) is close to the hemicellulose content (0.180) indicating that this fraction is volatilized, whereas for the other fractions, cellulose and lignin, the volatiles evolved are less than their content indicating the formation of a carbonaceous residue mainly from these fractions.

Table 3.

A second fraction decomposes at 280-380 °C with apparent activation energy around 176 kJ/mol. Other studies have found that cellulose decomposes in the range 300–400 °C with an apparent activation energy around 150–250 kJ/mol [48,55-57].

The last fraction corresponds mainly to lignin and decomposes in a wide range of temperature from 200 °C until the end of the decomposition, with an apparent activation energy around 116 kJ/mol, a value less than those of hemicelluloses and cellulose. Grønly et al. [57] also indicated that the decomposition of lignin separated from cellulose and hemicellulose takes place in a wide range of temperature and the value of activation proposed was 46 kJ/mol.

In spite of the previous comments, it must be emphasized that the kinetic parameters are those obtained from the best correlation of the data, so the first fraction corresponding to the hemicellulose can include other portions of cellulose and/or lignin, and that acceptable correlations can also be obtained with other values of activation energy and reaction orders of lignin, taking into account the great interrelation between the kinetic parameters.

Figures 3 and A.1 show the calculated values that are very close to the calculated ones according to the model presented. Small differences between experimental and calculated values were obtained with the other two runs.

Figure 5.

3.4. TG-MS analysis

Figure 6 shows the intensities of some ions in the TG-MS run, corresponding to H₂O (*m/z* 18), CO₂ (*m/z* 44), CO (*m/z* 28) and CH₄ (*m/z* 15 corresponding to CH₃⁺). At the beginning, there is a

small formation of water, due to the humidity of the sample. The formation of CO₂, CO and CH₄ starts at approximately 200 °C that means that the decomposition of the organic matter has begun. These curves have a maximum peak at 348 °C. At 650 °C, there is another peak in the CO₂ curve that is due to the decomposition of the carbonates that the wood waste contains. In addition, small peaks corresponding to some light hydrocarbons, aldehydes and alcohols have been observed in a temperature range of 200 – 600 °C. On the other hand, compounds as HCl, benzene, toluene and xylenes are below the limit of detection.

Figure 6.

3.5. TG-FTIR analysis

Figure 7 shows the spectra of gas generated at the maximum temperature of decomposition (365 °C). Nearly all peaks have been identified. The main peak corresponds to CO₂ with a wavelength between 2300-2400 cm⁻¹.

Figure 8 shows the evolution of the formation of CO₂ during the thermal degradation. The shape of CO₂ curve fitted well with the degradation of the main components, as shown in Figure 8. CO₂ formation remains until the end of the experiment, due to the wide range of lignin degradation. In addition, a small peak at 650-750 °C is observed due to the degradation of carbonates.

Peaks from 2200 to 2300 cm⁻¹ correspond to CO. The evolution of the formation of CO is plotted in Figure 9. Note that the maximum peak of CO formed occurs before that of the maximum peak of CO₂, and moreover the continuous formation of CO until the end is negligible, in contrast to the CO₂ formation. The maximum formation of CO occurs at 325 °C, as shown in Figure 9.

Peaks ranging from 3400 to 4000 cm⁻¹ of wavelengths are characteristic of water, as shown in Figure 7. The wood waste sample was previously dried, so the water formed is due to the thermal degradation of the wood waste; the formation of water occurs when the loss weight is maximal (temperature range: 200-380 °C).

336 The wavelength range 2700-3100 cm⁻¹ corresponds to compounds with a C-H bond
337 (hydrocarbon group), shown in Figure 7.

338 On the other hand, C=O bond shows its wavelength at 1660-1820 cm⁻¹. The characteristic
339 compounds are ketones, aldehydes, esters and acids; the curve of formation is very similar to the
340 C-H bond curve.

341 **Figure 7.**

342 **Figure 8.**

343 **Figure 9.**

344 3.6. Volatile and semi-volatile compounds.

345 Two experiments of pyrolysis for each wood sample, at 500 and 850 °C, were carried out in a
346 laboratory scale tubular reactor. The residence time of the gas inside the central part of the
347 reactor is around 4-6 s. Runs for the analysis of volatiles were triplicated. The mean values of
348 the yield of the volatile gases generated are shown in Appendix B (Table B.1.). Table 4 shows
349 the main volatile gases generated in the pyrolysis.

350 **Table 4.**

351 Oxygenated compound yields are due to the oxygen present in the wood in pyrolysis processes.
352 Note the high yield of CO and the yield increase of H₂ at 850 °C with respect to pyrolysis at 500
353 °C, that is probably as a consequence of the gasification of the carbonaceous residue and volatile
354 gases formed with the water formed in the pyrolysis (Equation 12).

356 On the other hand, it can be observed in the TG-FTIR analysis that the maximum CO formation
357 occurs at 325 °C (Figure 9). This difference between the TG-FTIR analysis and the experiments
358 in the laboratory scale tubular reactor is due to the difference in the heating rate. In the pyrolysis
359 run in the tubular reactor at 850 °C, the heating rate was around 300 °C min⁻¹; whereas in the
360 TG-FTIR, the heating rate was 30 °C min⁻¹. This fast heating rate produces secondary reactions

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4 361 at high temperatures, which cause the water formed to react with the carbonaceous residue and
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6 362 other volatile gases generated in the primary reactions. Instead, due to the slow heating rate,
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8 363 these secondary reactions do not occur in the TG analysis. When the first reaction products are
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10 364 formed, the temperature in the furnace chamber of the TGA apparatus is not as high as in the
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12 365 tubular reactor, therefore these products do not continue to react and leave the furnace chamber.
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14 366 The differences between the TG analysis and the experiments in the laboratory scale tubular
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16 367 reactor can also be observed in the final carbonaceous residue, being 25% and 20 % (at 850 °C),
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18 368 respectively.
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21 369 In the volatile gases evolved, the differences between the furniture wood waste and the solid
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23 370 wood are, obviously, in the nitrogen compounds.
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26 371 In the pyrolysis of furniture wood waste, NH₃ was found in a high proportion at 850 °C and the
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28 372 yield was lower at 500 °C. Meanwhile, in the pyrolysis of solid wood, NH₃ was negligible. The
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30 373 nitrogen content in the furniture wood waste can be due to the nitrogenated organic resins, such
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32 374 as MF, MUF and UF resins, and the chemical structure of these compounds promotes the
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34 375 formation of ammonia [28-29,58].
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37 376 Other nitrogen compounds appear in the furniture wood waste pyrolysis at 850 °C, such as
38
39 377 acetonitrile, 2-propenenitrile, pyrrole and pyridine, 2-methyl (Table B.1.).
40
41
42 378 NO was detected in high proportion in pyrolysis at 850 °C and the yields were similar for the
43
44 379 pyrolysis of both samples. However, NO₂ was not detected in any of the runs. HCN was found
45
46 380 in all pyrolysis runs, but their yields were very small (Table 4).
47
48 381 NH₃ shows a higher yield than HCN, which is in accordance with other studies [58-59].
49
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51 382 The main volatile organic compounds in all the runs are: methane, ethene, propene, benzene and
52
53 383 toluene.
54
55
56 384 Table 5 shows the concentration of the 16 polyaromatic hydrocarbons recognized by USEPA as
57
58 385 priority PAHs. The highest yield of PAHs is found in pyrolysis of furniture wood waste at 850
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386 °C. The formation of PAHs is very common with many materials, when operating at 850 °C.

387 The pyrolysis of solid wood show lower yields of PAHs.

388 **Table 5.**

389 Furthermore, 198 semi-volatile compounds were identified and quantified, results are shown in
390 Appendix C. Comparing the pyrolysis runs, it can be observed that the amount of semi-volatiles
391 evolved during the pyrolysis of furniture wood waste is higher than during the pyrolysis of solid
392 wood, but within the same magnitude order.

393 Table 6 lists the percentage contribution by groups of compounds of the yield of the semi-
394 volatiles obtained in pyrolysis. It can be observed that the aromatics obtained at 850 °C are
395 higher than at 500 °C. On the other hand, the oxygenated compounds predominate in pyrolysis
396 at 500 °C. Regarding the differences due to the different material pyrolyzed, a contribution of
397 nitrogen can be observed compounds in the pyrolysis of the furniture wood waste. On the other
398 hand, the yield of nitrogen compounds is negligible in the pyrolysis of solid wood.

399 **Table 6.**

400 Char and gases were collected from the laboratory scale pyrolysis; however the liquid fraction
401 was complicated to collect, due to the laboratory dimensions of the experiments.

402 The chars obtained in the experimental pyrolysis were analyzed with an Elemental Analyzer to
403 determinate the C, H, N, S content; the results are shown in Table 7. The chars obtained could
404 be used as fuel, due to their high carbon content. Furthermore, the nitrogen content has
405 decreased compared with the initial wood waste and the sulfur content is also very low,
406 therefore the emissions of NO_x and SO_x would be low.

407 **Table 7.**

408 Mass balances of C taking into account the total carbon in CO_x, total volatiles, total semi-
409 volatiles and total C in the char are shown in Appendix D.

410

411 CONCLUSIONS

412 A chemical characterization of furniture wood waste and solid wood (treated and untreated
413 wood) has been carried out to observe the possible differences. The FTIR analyses show some
414 differences between the furniture wood waste and the solid wood. The elemental analyses also
415 show an important difference in the nitrogen content, which can be due to the content of some
416 resins. On the other hand, the ICP analyses show the higher concentration of some elements in
417 furniture wood waste in comparison with solid wood. Particularly noteworthy is the high
418 concentration of Ti in the furniture wood waste sample.

419 This work has studied the global effect of all additives present in furniture wood waste.
420 Regarding the TG analyses, these reveal that the temperature at the maximum degradation rate
421 is lower for furniture wood waste compared to solid wood. Regarding the gases evolved, in the
422 pyrolysis of furniture wood waste, NH_3 was found in a high proportion, whereas meanwhile, in
423 the pyrolysis of solid wood, NH_3 was negligible. The nitrogen content in the furniture wood
424 waste can be due to nitrogenated organic resins, and the chemical structure of these compounds
425 promotes the formation of ammonia. Other nitrogen compounds were also found in the
426 pyrolysis gases evolved.

427 On the other hand, a kinetic model for the furniture wood waste was proposed and tested to
428 satisfactorily correlate the experimental results, considering the three components of wood:
429 hemicellulose, cellulose and lignin.

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Tables:

Table 1. Characterization of the furniture wood waste and the solid wood

	Furniture wood waste	Solid wood
Moisture (wt. %)	9 - 11	10 - 14
<i>Analysis on dry basis</i>		
Proximate analysis		
Ash content (wt. %)	1.8 ± 0.1	0.3 ± 0.1
Volatile matter (wt. %)	77.3 ± 0.4	80.1 ± 0.2
Fixed carbon by difference (wt. %)	20.9 ± 0.4	19.6 ± 0.2
Elemental analysis		
C (wt. %)	47.9 ± 0.03	52.7 ± 0.1
H (wt. %)	6.0 ± 0.1	6.2 ± 0.1
N (wt. %)	2.9 ± 0.6	nd
S (wt. %)	0.05 ± 0.01	0.007 ± 0.005
O estimated by difference (wt. %)	41.4 ± 0.6	40.8 ± 0.1
Cl (wt. %)	0.06 ± 0.01	0.02 ± 0.01
Net calorific value (MJ kg ⁻¹)	15.8 ± 0.1	19.5 ± 0.5
Composition		
Ethanol extracts (wt. %)	2.72 ± 0.05	-
Hemicellulose (wt. %)	18.0 ± 3.6	-
Cellulose (wt. %)	44.7 ± 2.5	-
Lignin (wt. %)	33.0 ± 1.1	-

* The standard deviations were calculated from 3 values.

nd: not detected < 0.01%

Table 2. Major and minor elements of furniture wood waste. Comparison with other types of wood [43].

	Furniture wood waste (mg/kg d.b.)	Solid wood (mg/kg d.b.)	Coniferous wood (without bark) ^a (mg/kg d.b.)	Coniferous bark wood ^a (mg/kg d.b.)
<i>Major elements</i>				
Al	480 ± 10	30 ± 20	30-400	400-1200
Ca	1590 ± 240	260 ± 5	500-1000	1000-15000
Fe	280 ± 30	25 ± 4	10-100	100-800
K	340 ± 150	160 ± 90	200-500	1000-3000
Mg	320 ± 80	100 ± 30	100-200	400-1500
Na	300 ± 120	20 ± 10	10-50	70-2000
P	100 ± 20	20 ± 10	50-100	20-600
Si	2150 ± 140	109 ± 3	100-200	500-5000
Ti	1600 ± 200	2.1 ± 0.8	< 20	n.i.
<i>Minor elements</i>				
As	0.4 ± 0.03	0.01 ± 0.004	< 0.1-1.0	0.1-4.0
Cd	1.0 ± 0.1	0.1 ± 0.02	< 0.05-0.50	0.2-1.0
Co	1.1 ± 0.1	0.05 ± 0.004	n.i.	n.i.
Cr	6.7 ± 1.4	2.0 ± 1.3	0.2-10	1-10
Cu	6.4 ± 0.7	1.4 ± 1.4	0.5-10	3-30
Hg	0.03 ± 0.04	0.01 ± 0.003	< 0.02-0.05	0.01-0.1
Mn	40.0 ± 3.6	46.8 ± 7.1	40-200	9-480
Mo	0.3 ± 0.03	0.02 ± 0.02	n.i.	n.i.
Ni	1.2 ± 0.3	0.04 ± 0.07	<0.1-10	2-20
Pb	6.3 ± 3.6	0.04 ± 0.06	<0.5-10	1-30
Sb	2.0 ± 0.4	0.01 ± 0.01	n.i.	n.i.
V	0.9 ± 0.04	0.1 ± 0.002	< 2	0.7-2.0
Zn	69.4 ± 2.0	7.7 ± 0.9	5-50	70-200

^a Variation of typical values. CEN-TS 14961-1:2010 [43]

n.i.: not indicated

* The standard deviations were calculated from 3 values.

Table 3: Kinetic parameters obtained for the pyrolysis of furniture wood waste.

Reaction	Mass fraction of volatiles, V_i	k (s^{-1})	E (kJ/mol)	n
1	0.238	$1.735 \cdot 10^{10}$	139	3.0
2	0.239	$4.894 \cdot 10^{12}$	176	1.0
3	0.211	$9.204 \cdot 10^8$	116	5.6
<i>Residue (mass fraction)</i>	<i>0.312</i>			

Table 4. Main volatile gases in wood waste pyrolysis.

Compound	Pyrolysis at 500 °C (mg/kg sample)		Pyrolysis at 850 °C (mg/kg sample)	
	Furniture wood waste	Solid wood	Furniture wood waste	Solid wood
Main gases:				
H ₂	160 ± 20	300 ± 40	7100 ± 2700	10700 ± 1200
CO ₂	63000 ± 4600	60000 ± 4600	164000 ± 15000	140000 ± 5000
CO	30000 ± 4100	39000 ± 2700	371000 ± 22000	393000 ± 27000
NO	3800 ± 400	3200 ± 500	7900 ± 1000	8400 ± 400
NO ₂	nd ^a	nd ^a	nd ^a	nd ^a
CH ₄	5400 ± 190	5900 ± 800	56800 ± 400	59600 ± 2000
Ethene	1380 ± 70	1530 ± 240	34400 ± 1100	37000 ± 1300
Propene	1360 ± 100	1541 ± 210	2860 ± 600	3440 ± 220
Benzene	340 ± 50	280 ± 40	17500 ± 2300	20600 ± 600
Toluene	460 ± 260	nd	5430 ± 2670	3680 ± 800
NH ₃	90 ± 40	5 ± 4	4000 ± 2100	8 ± 9
HCN	30 ± 10	20 ± 2	90 ± 40	90 ± 20

^a NO₂ not detected: < 100 mg NO₂/kg sample.

Table 5. Concentration of 16 priority PAHs in wood waste pyrolysis.

	Pyrolysis 500 °C (mg/kg sample)		Pyrolysis 850 °C (mg/kg sample)	
	Furniture wood waste	Solid wood	Furniture wood waste	Solid wood
Naphthalene	70	6	15700	5000
Acenaphthylene	20	2	15900	2300
Acenaphthene	nd	nd	460	80
Fluorene	nd	2	3540	820
Phenanthrene	7	1	1080	1080
Anthracene	3	1	380	440
Fluoranthene	nd	nd	260	330
Pyrene	5	nd	350	340
Benzo[a]anthracene	nd	nd	130	130
Chrysene	nd	nd	80	90
Benzo[b]fluoranthene	nd	nd	nd	60
Benzo[k]fluoranthene	nd	nd	60	70
Benzo[a]pyrene	nd	nd	50	100
Indeno[1,2,3-cd]pyrene	nd	nd	10	40
Dibenzo[a,h]anthracene	nd	nd	1	7
Benzo[g,h,i]perylene	nd	nd	10	30

nd: not detected < 1 mg/kg sample

Table 6. Total concentration of semi-volatiles and percent contributions of compounds to the total yield of semi-volatiles.

	Pyrolysis 500 °C		Pyrolysis 850 °C	
	Furniture wood waste	Solid wood	Furniture wood waste	Solid wood
Total semi-volatiles (included PAHs) Concentration (mg/kg sample)	33570	22030	57380	31350
Percent contribution, %				
Aromatics	26.6	32.6	82.6	79.7
Oxygenated compounds	43.0	49.7	9.6	15.5
Other nitrogen compounds	2.0	0.0	3.1	0.1
Hydrocarbons	9.0	0.2	0.1	0.0
Cyclic hidrocarbons	4.3	4.2	0.1	0.0
Heterocyclic compound	13.8	13.2	4.5	4.6
Terpenes	0.5	0.0	0.0	0.0
Other sulfur compounds	0.8	0.0	0.0	0.0

Table 7. Analysis elemental of char from wood waste pyrolysis.

Char		C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)
Pyrolysis at 500 °C	Furniture wood waste	68.9 ± 0.6	3.43 ± 0.02	1.52 ± 0.04	nd
	Solid wood	81.8 ± 0.3	3.37 ± 0.12	nd	nd
Pyrolysis at 850 °C	Furniture wood waste	78.6 ± 1.0	1.06 ± 0.02	1.02 ± 0.09	nd
	Solid wood	93.0 ± 0.2	0.99 ± 0.01	nd	nd

nd < 0.01%

* The standard deviations were calculated from 3 values.

Figures:

Figure 1. FTIR spectra of furniture wood waste, solid wood and laminate sheets from furniture wood waste.

Figure 2. Furniture wood waste pyrolysis at several heating rates: 5, 10, 20 °C min⁻¹ (experimental curves).

Figure 3. Weight fraction and its derivate from a pyrolysis run. Experimental and calculated curves.

Figure 4. Weight fraction and its derivate from pyrolysis of furniture wood waste and solid wood.

Figure 5. Evolution of the mass fraction of volatiles for each reaction in furniture wood waste pyrolysis: 1 (hemi-cellulose), 2 (cellulose), 3 (lignin)

Figure 6. Intensities of some ions in a TG-MS run for wood waste pyrolysis. Ions: 15 (CH_4), 18 (H_2O), 28 (CO) and 44 (CO_2).

Figure 7. FTIR spectra of gas products from wood waste pyrolysis at 365 °C.

Figure 8. Evolution of formation of CO₂ during wood waste pyrolysis.

Figure 9. Evolution of formation of CO during wood waste pyrolysis.