

Full Length Article

Combustion of furniture wood waste and solid wood: Kinetic study and evolution of pollutants

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Abstract

This work is focused on the combustion processes of wood waste. Two kinds of waste have been studied: furniture wood waste (treated and used wood) and solid wood from factories (untreated wood). A kinetic study has been carried out for each material in air and an N₂:O₂ 9:1 atmosphere with dynamic and dynamic + isothermal runs at different heating rates, considering the decomposition of the three main components of the wood and also the combustion of the char obtained. Satisfactory kinetic models were obtained for each kind of wood. Significant differences in thermal behavior were found between furniture wood waste and solid wood, probably due to the presence of additives and inorganic compounds in the furniture wood waste, which modifies the kinetic parameters of the thermal process.

Moreover, combustion runs at 850 °C of both kinds of woods were also carried out in a laboratory scale tubular reactor in order to analyze the volatile and semivolatile compounds. The main differences were found in the higher yield of nitrogenated compounds found during the combustion of the furniture wood waste.

Keywords: Wood waste; Thermogravimetric analysis (TGA); Kinetic study; Combustion; Gases evolved

1 Introduction

Nowadays, the use of biomass and wood as energy source is rapidly increasing, due to the concern about global warming and the instability in the price of the fossil fuels. The study of thermal decomposition kinetics is convenient to obtain more efficient combustion processes.

Furniture wood waste contains some additives, such as adhesives, resins, paints, varnishes and oils, which change the behavior during thermal processes. The decomposition temperature decreases due to the catalytic effect of some inorganic salts in doped wood [1-3] or can increase due to the flame retardant effect of some resins, such as urea formaldehyde (UF), melamine formaldehyde (MF) and phenol formaldehyde (PF) [4].

The global effect of the additives present in furniture wood waste during pyrolysis processes was studied and the result was the decrease in the degradation temperature due to the inorganic content and regarding the kinetic study, an acceptable model with three independent reactions (decomposition of the three main components of the wood) was proposed for the pyrolysis of furniture wood waste [5].

During combustion, the char obtained in pyrolytic conditions burns off under oxidative conditions. Some authors have found that activation energies of combustion processes of treated wood were lower than the those of untreated wood [6,7].

It is widely known that wood combustion is an important source of some toxic emissions, such as carbon monoxide (CO), volatile organic compounds (VOCs) and polycyclic aromatics hydrocarbons (PAHs). All of them are products from incomplete combustion.

PAH emissions have been widely studied since they were found to be carcinogenic compounds. Incomplete combustion also generates derivative PAHs, such as nitro-PAHs, oxy-PAHs and azaarenes [8-10]. Some of these have been also found with similar toxicity as their parent-PAHs [11,12]. The derivative PAHs show a secondary formation route that occurs in the atmosphere through reactions of PAHs with O₃, OH and

NO_x [13,14].

Treated wood shows a higher nitrogen content [5], which is due to the nitrogenated resins (UF, MF, MUF resins), melamine laminate sheets, etc. Therefore, this nitrogen content could also generate nitro-PAHs and azaarenes in thermal processes.

Therefore, the objectives of this work are the proposal of kinetic models, the characterization of the products evolved during the combustion of furniture wood waste and solid wood and the comparison of the results of both kinds of materials studied.

2 Materials and methods

2.1 Characteristics of the materials

Around 10 kg of both wood waste and solid wood were crushed and collected. The furniture wood waste was collected from a Municipal Solid Waste Treatment Plant and the solid wood from a furniture factory. Prior to the experimental runs, the samples were dried and milled to a size less than 0.2 mm.

The characterization of the materials and the methods used were presented in a previous work [5]. Comparing the characterization of the two materials, it can be observed that furniture wood waste shows higher nitrogen content, ash content and inorganic content, including chlorine, than the solid wood.

2.2 Thermogravimetric analysis

A thermogravimetric analyzer (Perkin Elmer, model TG STA6000) was used for the kinetic study of combustion corresponding to both samples. The sample mass was around 5 mg and the atmospheres used were air and N₂:O₂ 9:1 with a flow rate of 100 mL min⁻¹.

Dynamic runs were carried out at different heating rates (5, 10 and 20 °C min⁻¹), from the initial temperature up to 850 °C. In addition, dynamic + isothermal runs were also carried out with a constant heating rate until the required temperature was reached (between 300 °C and 380 °C). This final temperature was maintained constant for a long period of time (at least 215 min).

Prior to these runs, the performance of the TGA equipment was checked with a pyrolysis experiment of Avicel PH-105 microcrystalline cellulose at a heating rate of 5 °C min⁻¹. The kinetic value obtained showed good agreement with the results presented by Grønli et al. [15] in their round-robin study of pyrolysis kinetics of cellulose by thermogravimetry (Table 1).

Table 1 Comparison between the kinetic values obtained in the test run and the obtained by Grønli et al. [15] in the same experimental conditions.

| | E (kJ mol ⁻¹) Fixed value | log A (log s ⁻¹) | 100 m _f /m ₀ (% of m ₀) |
|--|---------------------------------------|------------------------------|---|
| Test run of the instrument used | 244 | 19.0 | 7.9 |
| Grønli results of a Perkin-Elmer TGA[15] | 244 | 19.0 | 8.3 |

The preexponential constant (A) is given by: $A = \frac{k}{\exp(-E/(RT_{ref}))}$ with T_{ref} = 600.1 K m₀ = initial mass; m_f = final mass.

2.3 Pollutant analysis

A laboratory scale horizontal quartz reactor was used to identify the volatile and semi-volatile compounds evolved in the incomplete combustion of the two kinds of wood studied at 850 °C under fuel-rich conditions (λ = 0.2, lambda is defined as the ratio between the real air: fuel ratio and the air: fuel stoichiometric, which equals to the real oxygen/stoichiometric oxygen ratio. The oxygen content of the wood has been also considered for the calculation of λ). This reactor has been used in previous works and a detailed description of it can be found elsewhere [16]. Runs were carried out with 300 mL min⁻¹ of air and therefore the estimated residence time was around 4 s. Around 100 mg of sample was introduced in each run with a feeding velocity of 1 mm s⁻¹.

Gases and volatile compounds were collected in Tedlar® bags and analyzed in three gas chromatographers; one with a thermal conductivity detector (TCD) to determine mainly CO and CO₂, another with a flame ionization detector (FID) to determine hydrocarbons and the third apparatus was a GC-MS with a DB-624 capillary column (30 m × 0.25 mm × 1.4 μm) to determine volatile compounds. Moreover, nitrogen oxides (NO and NO₂) were analyzed with a gas analyzer IM-2800 (Environmental Equipment Germany GmbH) and hydrogen cyanide (HCN) produced was absorbed in a NaOH solution of 1 mol/L and analyzed by ion chromatography, avoiding the possible interferences

with sulphide with an initial impinger of lead carbonate solution.

Semi-volatile compounds were collected in an adsorbent XAD-2 resin, extracted with solvent in accordance with the EPA Method 3545 [17] 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 and this identification was verified plotting the variation of the boiling point of the compounds proposed vs. their retention time and testing that they followed a regular variation. According to the EPA 8270D method, a semi-quantitative estimation of the yields was calculated with the response factors of the deuterated internal standards with the nearest retention time. Some of the semi-volatiles identified are oxy-PAHs and azaarenes.

The additives and the inorganic content in the treated wood can also increase the formation of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs). The formation of these compounds will be the subject of another work.

3 Results and discussion

3.1 Kinetic study

Fig. 1 shows the experimental TG and DTG plot for the combustion (air atmosphere) of the two kinds of wood studied at heating rates of $10\text{ }^{\circ}\text{C min}^{-1}$. In this Figure, the weight fraction represents the weight fraction of the solid, the sum of the residue formed and the non-reacted initial solid. The weight fraction is expressed on dry basis (sample weight at $150\text{ }^{\circ}\text{C}$ was taken as initial weight).

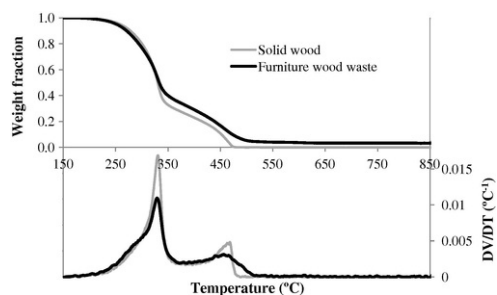


Fig. 1 Weight fraction and their derivative curves from combustion runs of furniture wood waste and solid wood at $10\text{ }^{\circ}\text{C min}^{-1}$.

From the DTG curves, in both cases, two stages are observed, the first is the wood devolatilization, corresponding to the hemicellulose, cellulose and lignin, and the second is the char combustion [18,19]. From Fig. 1, differences in the thermal degradation can be seen between treated and untreated wood. A significant difference observed in Fig. 1 is that the peaks in the DTG curves are higher for the solid wood combustion so the solid wood has a higher decomposition rate. Another contrast between both types of wood is the final residue, which is due to the different ash content, 1.8% for the furniture wood waste and 0.3% for the solid wood.

Regarding the maximum peak of temperature of degradation, Deka et al. [4] found that the pyrolysis of wood with urea formaldehyde (UF), melamine formaldehyde (MF) and phenol formaldehyde (PF) increases the major degradation temperature. However, other authors [6,7,20] studied the combustion behavior of treated wood and they found that the temperature range of the degradation for the first stage was lower with wood treated with flame-retardants than with untreated wood. They also found that the combustion of treated wood showed more quantity of char that acted as a thermal insulation barrier and as a barrier for oxygen and volatile combustible compounds with a higher burnout temperature. The furniture wood waste studied in the present work shows a relative high content of nitrogen, probably due to the nitrogenated organic resins. However, it also shows high inorganic content, and therefore the combustion behavior could be different compared with these previous studies. Table 2 shows the peak temperature of the maximum decomposition rate for the samples studied in pyrolysis [5] and combustion at $10\text{ }^{\circ}\text{C min}^{-1}$.

Table 2 Peak temperatures of thermal degradation at heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

| Sample | Combustion | | | Pyrolysis maximum peak temperature ($^{\circ}\text{C}$) (previous study) [5] |
|----------------------|---|---|---|--|
| | Maximum peak temperatures in 1st stage ($^{\circ}\text{C}$) | Maximum peak temperatures in 2nd stage (char combustion) ($^{\circ}\text{C}$) | Burnout temperatures ($^{\circ}\text{C}$) | |
| Furniture wood waste | 329 | 456 | 514 | 356 |

| | | | | |
|------------|-----|-----|-----|-----|
| Solid wood | 331 | 468 | 482 | 366 |
|------------|-----|-----|-----|-----|

From Table 2, it can be observed that the temperature of the maximum peak for the furniture wood waste is slightly lower in the first stage and that the difference is more important in the second stage. Nevertheless, the burnout temperature is higher, indicating a higher content of char that would act as barrier, as indicated by Yorulmaz and Atimtay [7] or the presence of a char showing a slower combustion rate.

Fig. 2 shows a comparison of the TG and DTG curves for the pyrolysis and combustion (in air) of the materials studied at 10 °C min⁻¹. From Table 2 and Fig. 2, it can also be concluded that the presence of oxygen anticipates the degradation peak temperature and increases the decomposition rate, as other authors have also observed [21–23].

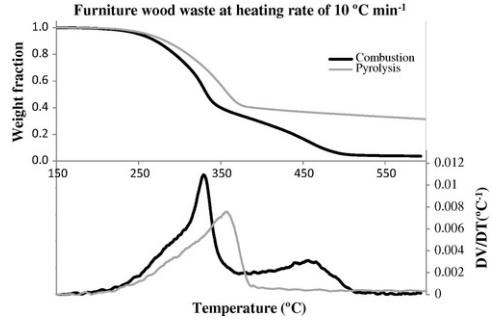


Fig. 2 Comparison of weight fractions and their derivative from furniture wood waste pyrolysis and combustion run at heating rate of 10 °C min⁻¹ (experimental curves).

3.2 Combustion model

In a previous study [5], the pyrolysis kinetic model was proposed considering the thermal decomposition of the main components of wood (hemicelluloses, cellulose, and lignin).



For the combustion, a new process is necessary taking into account that the char obtained in the reactions burns off under oxidative conditions.



In literature, it is clear that the char formed from hemicelluloses and cellulose can be considered negligible vs. the char formed from lignin (around 46 wt.%) [24]. Nevertheless, initially the yields of char₁ (from hemicellulose) and char₂ (from cellulose) were considered for the correlation of the data, but their yield obtained in the best correlation was negligible.

The conversion degree (α) is calculated as the ratio between the mass fraction of solid reacted ($w_{si0} - w_{si}$) and the corresponding initial fraction of this component (w_{si0}), or the mass fraction of volatiles at any time and the volatiles at infinite time (v_f), assuming that the yield coefficient of the formation of volatiles with respect to the non-reacted solid is constant:

$$\alpha_i = \frac{(w_{si0} - w_{si})}{w_{si0}} = \frac{v}{v_f} = \frac{1 - w}{1 - w_f} \quad (5)$$

Note the weight fraction of the solid inside the crucible is the sum of the non-reacted solid and the residue formed.

Different empirical experiments can be used for the kinetics of thermal decomposition of solid. One of the most common used is that refers to the conversion degree (α). Specially when using the potential model with order reaction different to the unity, because in this case the pre-exponential factor does not depend on the initial mass.

So following the kinetic law for solid decomposition explained elsewhere [25], the kinetic equations can be defined as follows:

$$\frac{d\alpha_i}{dt} = k_i(1 - \alpha_i)^{n_i}, \quad i = 1, 2, 3 \quad (6)$$

For the combustion of char formed by reaction 3c:

$$\frac{d\alpha_{3c}}{dt} = k_{3c}(\alpha_3 - \alpha_{3c})^{n_{3c}} \quad (7)$$

where the pre-exponential factor k_{ic} is directly proportional to the oxygen pressure:

$$k_{3c} = k_{3c}^* \left(\frac{p_{O_2}}{0.21} \right)^{n_{O_2}} (p_{O_2} \text{ in atm}) \quad (8)$$

where p_{O_2} is the partial pressure of oxygen in atm.

The kinetic constants follow the Arrhenius equation as:

$$k_i = k_{i0} \exp\left(-\frac{E_i}{RT}\right), \quad i = 1, 2, 3, 3c \quad (9)$$

By integration of these equations, α_i ($i = 1-3$) and α_{3c} can be calculated at each time with the temperature program; the relationship between the α_i and α_{3c} values and the weight fraction measured in the thermobalance (w) is related with the volatiles obtained (V) by

$$w = 1 - V = 1 - (v_{1\infty}\alpha_1 + v_{2\infty}\alpha_2 + v_{3\infty}\alpha_3 + v_{3c\infty}\alpha_{3c}) \quad (10)$$

3.3 Kinetic parameters

The thermogravimetric analysis was done with runs at two different atmospheres (air and $N_2:O_2$ 9:1), carrying out 3 dynamic runs at 5, 10, 20 °C min⁻¹ (Fig. 3a-d) and two dynamic + isothermal runs (Fig. 4a-d) for each atmosphere.

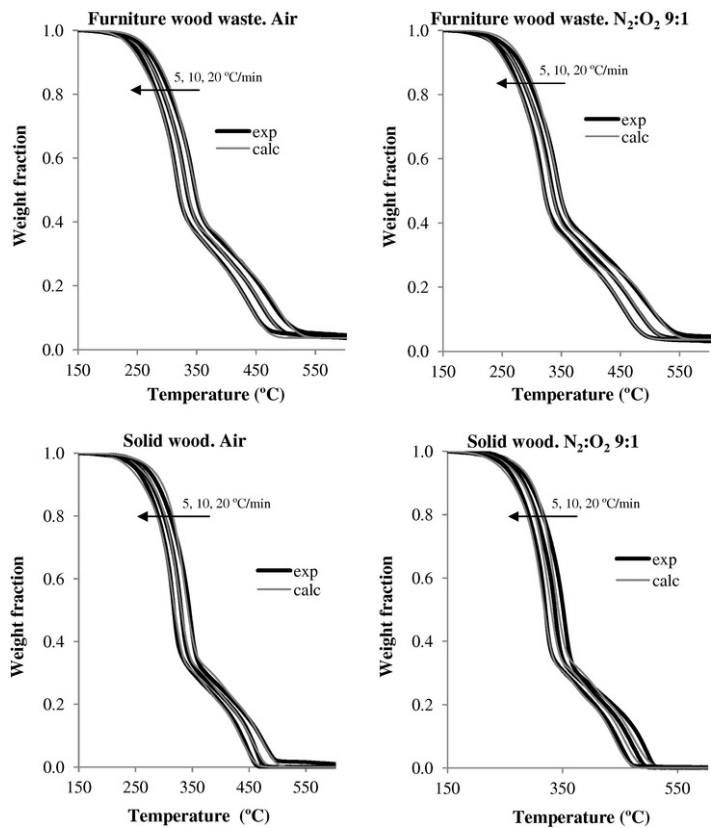


Fig. 3 Dynamic runs: (a) furniture wood waste in air atmosphere, (b) furniture wood waste in a N₂:O₂ 9:1 atmosphere, (c) solid wood in air atmosphere and (d) solid wood in a N₂:O₂ 9:1 atmosphere.

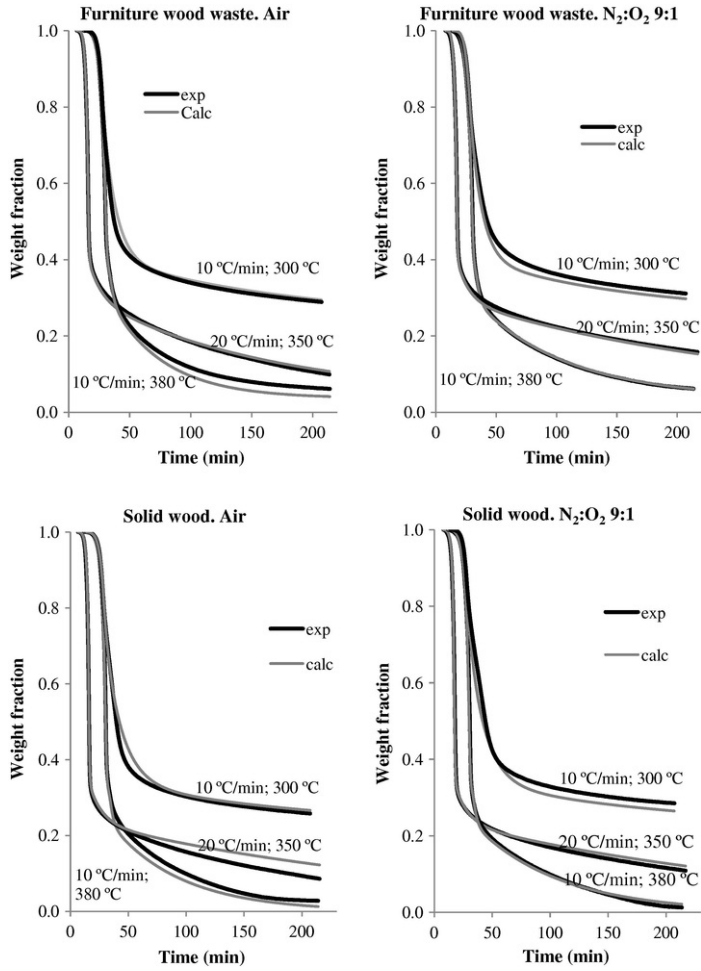


Fig. 4 Isothermal runs: (a) furniture wood waste in air atmosphere, (b) furniture wood waste in a N₂:O₂ 9:1 atmosphere, (c) solid wood in air atmosphere and (d) solid wood in a N₂:O₂ 9:1 atmosphere.

The dynamic and the dynamic + isothermal runs for combustion were correlated with the same set of parameters for each kind of wood integrating the differential equations with the Euler method (method with very small intervals of time to make the integration errors negligible). The details of this method can be found elsewhere [5].

The objective function (OF) to minimize was the sum of the square differences between the experimental and calculated weight loss values V and their derivatives with a weight factor.

$$OF = \sum_{m=1}^M \sum_{j=1}^N (w_{m,j}^{\text{exp}} - w_{m,j}^{\text{cal}})^2 + \text{factor} \sum_{m=1}^M \sum_{j=1}^N \left(\frac{dw_{m,j}^{\text{exp}}}{dt} - \frac{dw_{m,j}^{\text{cal}}}{dt} \right)^2 \quad (9)$$

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

The validity of the model has been verified calculating the variation coefficient (VC):

$$VC = \frac{\sqrt{\left(\sum_{m=1}^M \sum_{j=1}^N (w_{m,j}^{\text{exp}} - w_{m,j}^{\text{cal}})^2\right) / (N_{\text{total}} - P)}}{\bar{V}_{\text{exp}}} \times 100 \quad (10)$$

where N_{total} and P are the number of data and parameters fitted, respectively, and \bar{V}_{exp} is the average of the experimental weight fraction of volatiles evolved.

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} [26].

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

Table 3 shows the set of parameters optimized for each type of wood, together with the variation coefficients that are very small, indicating an acceptable correlation. Table 3 also shows the results obtained by other authors [19] for natural wood combustions and they are quite similar. The apparent activation energies obtained for the thermal degradation of the hemicelluloses, cellulose and for the combustion of the char formed for furniture wood waste are significantly lower than for solid wood. These lower activation energies make the reaction easier and these results are in agreement with literature [6,7,20], and are attributable to the fact that the chemical additives cause this change in the thermal degradation process of wood. In contrast, the decomposition of the hemicelluloses, cellulose and the combustion of the char for solid wood is much accelerated, according to the kinetic constants obtained.

Table 3 Kinetic parameters obtained for the combustion of furniture wood waste and solid wood (k_{iO} and k_{3C} in $s^{-1} \cdot \text{mass fraction}^{(1-n)}$ and E_i in kJ mol^{-1}). Comparison with the results with natural wood.

| | Furniture wood waste | Solid wood | Birch wood [19] | Spruce wood [19] |
|-----------------------------------|----------------------|------------|-----------------|------------------|
| <i>Devolatilization reactions</i> | | | | |
| V_1 | 0.14 | 0.20 | 0.23 | 0.15 |
| k_{1o} | 1.24E+07 | 4.20E+04 | 4.69E+11 | 2.46E+07 |
| E_1 | 96.4 | 75.5 | 144.7 | 103.8 |
| n_1 | 1.0 | 1.0 | 1.0 | 1.0 |
| V_2 | 0.45 | 0.45 | 0.48 | 0.44 |
| k_{2o} | 2.53E+11 | 2.59E+15 | 9.71E+15 | 2.46E+17 |
| E_2 | 153.9 | 199.3 | 204.7 | 221.5 |
| n_2 | 1.0 | 1.0 | 1.0 | 1.0 |
| V_3 | 0.13 | 0.12 | 0.14 | 0.21 |
| k_{3o} | 9.39E+07 | 2.21E+11 | 2.77E+04 | 1.80E+03 |
| E_3 | 127.8 | 168.1 | 83.5 | 68.4 |
| n_3 | 1.0 | 1.0 | 1.1 | 1.0 |
| <i>Combustion of char</i> | | | | |
| V_{3c} | 0.25 | 0.23 | 0.14 | 0.20 |
| k_{3c} | 5.21E+06 | 1.64E+09 | 8.87E+13 | 1.27E+11 |
| E_{3c} | 126.7 | 159.8 | 222.0 | 183.1 |

| | | | | |
|-----------|------|------|-----|-----|
| n_{3c} | 1.0 | 1.0 | 1.0 | 1.0 |
| n_{O_2} | 0.72 | 0.24 | | |
| VC (%) | 2.4 | 2.8 | | |

In the case of biomass decomposition, both in the absence (pyrolysis) and in the presence of oxygen (gasification, combustion), the reaction orders obtained have been maintained as unity, for all the fractions considered. This has been pointed out previously in different studies [19,27,28] where it is clear that using this structural model based on the chemical components (cellulose, hemicellulose and lignin) a first order approximation is valid.

The activation energies representing the pyrolytic decomposition of hemicellulose ($75\text{--}96\text{ kJ mol}^{-1}$), cellulose ($153\text{--}199\text{ kJ mol}^{-1}$) and lignin ($127\text{--}168\text{ kJ mol}^{-1}$) are close to those found in literature[27], but this can be due to the differences in the treatment given to the materials tested [28], besides the fact that the constants shown in the present work are valid for dynamic and also for isothermal runs.

From Table 3, it can also be observed that char formation increases in furniture wood waste; probably due to the presence of chemical additives, as observed by other authors [6,7,20].

Fig. 5a and b shows the total conversion rate (experimental and calculated) of furniture wood waste and solid wood, respectively. These Figures also show the decomposition rate curves corresponding to the three main components of wood and the char produced, in order to obtain more information about the wood combustion process.

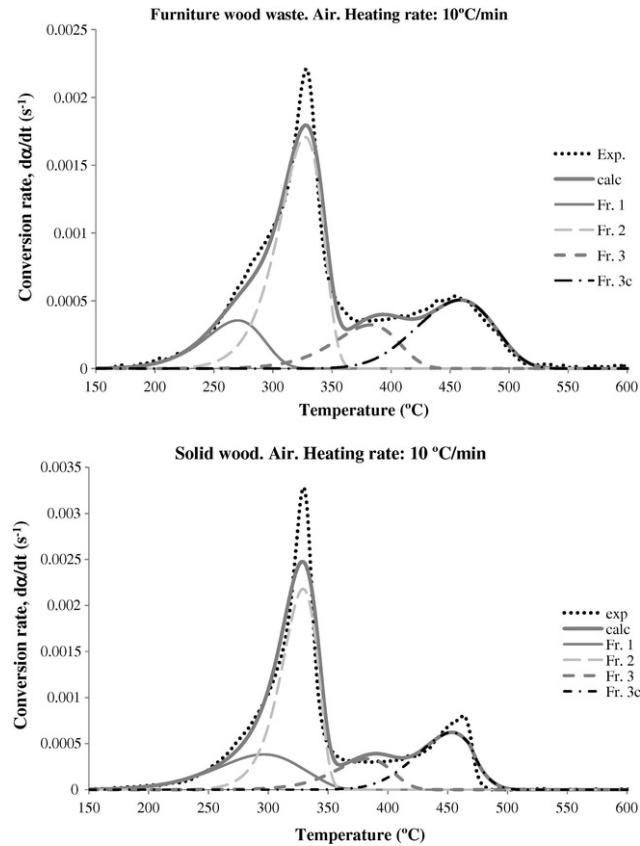


Fig. 5 Conversion rate curves of combustion run of (a) furniture wood waste (b) solid wood.

Although some slight deviations can be observed in Figs. 3 and 4, the kinetic model proposed can be considered as correct because the same set of parameters has been used to correlate the experimental results obtained in very different operating conditions, giving calculated curves very similar to the experimental ones.

In order to test the validity of the experimental results and the kinetic model obtained, three additional runs for each material were done with the following conditions: heating rate: heating rate: 10 °C/min, initial mass: 0.5 mg; 5 °C/min, initial mass: 1 mg; heating rate: 2.5 °C/min, initial mass: 2 mg. For the two first runs, the results were practically the same that those obtained with the initial mass of 5 mg, deducing that the initial mass has not an effect on the experimental variation of the weight fraction vs. temperature.

The kinetic model obtained reproduced satisfactorily the experimental results obtained with the run carried out with heating rate 2.5 °C/min and initial mass 2 mg, although there are some small differences in the first part of the decomposition.

3.4 Volatile and semi-volatile compounds

Combustion runs under fuel-rich conditions were performed and the determination of products evolved was done. This aims at simulating the bad operation of a furnace. These runs were duplicated and the mean values of the yield of the volatile gases generated are shown in [Table 4](#).

Table 4 Volatile gases evolved in wood combustion at 850 °C.

| | Furniture wood waste | Solid wood |
|---------------------------------------|----------------------|---------------------|
| <i>Carbon oxides</i> | | |
| CO ₂ (mg/kg sample) | 1,179,000 ± 128,000 | 1,433,000 ± 146,000 |
| CO (mg/kg sample) | 88,000 ± 12,000 | 117,000 ± 14,000 |
| Molar ratio CO/(CO ₂ + CO) | 0.10 ± 0.004 | 0.11 ± 0.002 |
| <i>Nitrogen oxides (mg/kg sample)</i> | | |
| NO | 1270 ± 80 | 500 ± 50 |
| NO ₂ | <10 | <10 |
| <i>Volatiles (mg/kg sample)</i> | | |
| Methane | 17,910 ± 1780 | 14,530 ± 2930 |
| Ethane | 650 ± 270 | 630 ± 40 |
| Ethene | 13,230 ± 10 | 9980 ± 1910 |
| Propene | 740 ± 410 | 680 ± 30 |
| Isobutane | 2940 ± 380 | 2490 ± 670 |
| Ethyne | 70 ± 30 | 70 ± 30 |
| Propyne | 150 ± 20 | 90 ± 20 |
| 1,3-Butadiene | 560 ± 520 | 690 ± 0 |
| Hydrogen cyanide | 105 ± 6 | 28 ± 2 |
| Acetaldehyde | 40 ± 20 | 60 ± 10 |
| 1-Buten-3-yne | 500 ± 200 | 400 ± 90 |
| 2-Butyne | nd | 150 ± 0 |
| <i>n</i> -Hexane | 270 ± 390 | 430 ± 100 |

| | | |
|---------------------------------------|---------------|---------------|
| Methanol | 250 ± 90 | 130 ± 10 |
| 1,3-Cyclopentadiene | 1380 ± 420 | 1530 ± 440 |
| Acetonitrile | 480 ± 110 | nd |
| 2-Propenenitrile | 450 ± 110 | nd |
| Benzene | 6830 ± 3320 | 7530 ± 1570 |
| Toluene | 1420 ± 220 | 2440 ± 1690 |
| Pyrrole | 90 ± 30 | nd |
| Total volatiles (mg/kg sample) | 48,880 | 41,830 |

The nitrogen content of furniture wood waste causes a higher yield of NO, as observed in Table 4. At temperatures lower than 1000 °C, NO would be expected to be produced mainly from the fuel nitrogen [29].

Small but significant yields of HCN have been detected, mainly in the combustion of furniture wood waste. It must be noted that combustions in excess oxygen or air promote the oxidation of HCN [30-32], but under fuel-rich conditions, HCN is detected.

As occurred in the pyrolysis runs [5], the differences in the volatile gases evolved between furniture wood waste and solid wood corresponds to the nitrogen compounds. None of the volatile nitrogen compounds found in the combustion of furniture wood waste were found in the combustion of solid wood. The nitrogen content in furniture wood waste can be mainly due to the nitrogenated organic resins, such as MF, MUF and UF resins.

The main volatile organic compounds in all the combustion runs are: methane, ethene, isobutane, benzene and toluene. These results are in accordance with those obtained in the combustion of pine cones and needles in the same reactor [33].

Table 5 shows the yield of the 16 polyaromatic hydrocarbons recognized by USEPA as priority PAHs.

Table 5 Concentration of 16 priority PAHs in wood waste combustion at 850 °C.

| Compounds | mg/kg sample | |
|----------------------|-----------------------------|-------------------|
| | Furniture wood waste, n = 3 | Solid wood, n = 2 |
| Naphthalene | 3140 ± 390 | 2010 ± 210 |
| Acenaphthylene | 1320 ± 140 | 950 ± 10 |
| Acenaphthene | 32 ± 10 | 22 ± 2 |
| Fluorene | 290 ± 100 | 250 ± 20 |
| Phenanthrene | 600 ± 180 | 540 ± 200 |
| Anthracene | 200 ± 70 | 170 ± 30 |
| Fluoranthene | 230 ± 50 | 200 ± 60 |
| Pyrene | 110 ± 60 | 190 ± 50 |
| Benzo(a)anthracene | 61 ± 2 | 76 ± 26 |
| Chrysene | 44 ± 4 | 48 ± 14 |
| Benzo(b)fluoranthene | 19 ± 5 | 25 ± 11 |

| | | |
|------------------------|-------------------|-------------------|
| Benzo(k)fluoranthene | 24 ± 7 | 36 ± 16 |
| Benzo(a)pyrene | 41 ± 16 | 47 ± 21 |
| Indeno(1,2,3-cd)pyrene | 17 ± 4 | 24 ± 13 |
| Dibenz(a,h)anthracene | 1 ± 2 | 3 ± 3 |
| Benzo(g,h,i)perylene | 7 ± 6 | 14 ± 9 |
| Total | 6140 ± 850 | 4590 ± 680 |

The yield of PAHs between the combustions of furniture wood waste and solid wood are quite similar, probably due to the fact that the ratio of CO/(CO₂ + CO) shows a similar value in both combustions [34–38]. Naphthalene, acenaphthylene, phenanthrene, fluoranthene and pyrene were the more abundant PAHs formed representing more than 80% of the total PAHs evolved; the most abundant was naphthalene. This is a usual trend for biomass combustions [34,36–38].

Furthermore, another 83 semi-volatile compounds were identified and quantified and the results are shown in Appendix A. Table 6 lists the percentage contribution by groups of compounds of the semi-volatiles and PAHs obtained in the combustions. The main difference between the combustion of both kinds of woods is a higher yield of organic nitrogen compounds in the combustion of furniture wood waste. The rest of the compounds and the total are quite similar for both materials, as can be observed in Table 6 and Fig. 6 (yields obtained from solid wood vs. yields obtained from furniture wood waste).

Table 6 Total concentration of semi-volatiles and percentage contribution of compounds to the total yield of semi-volatiles and PAHs.

| | Furniture wood waste | Solid wood |
|---|----------------------|------------|
| Total semi-volatiles (included PAHs) Concentration (mg/kg sample) | 13,870 | 11,420 |
| <i>Percent contribution (%)</i> | | |
| Oxygenated aromatics | 7.9 | 9.9 |
| Nitroaromatics | 3.4 | 0.1 |
| Aromatics (including PAHs) | 76.6 | 80.6 |
| Oxygenated heterocyclics | 5.3 | 6.0 |
| Nitrogenated heterocyclics | 2.4 | 0.0 |
| Not identified | 4.4 | 3.3 |

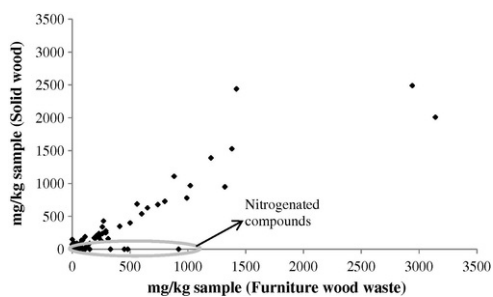


Fig. 6 Relation of compound yields between combustions of furniture wood waste and solid wood.

Nitro-PAHs such as: 1-nitronaphthalene, 2-nitronaphthalene, 3-nitrobiphenyl, 9-nitroanthracene, 2-nitrofluoranthene, 1-nitropyrene and 2-nitropyrene were also searched in the chromatogram, but they were not detected.

4 Conclusions

Kinetic models able to explain the combustion of wood waste and solid wood have been developed and tested in different conditions giving very good results. The presence of additives in furniture wood waste explains why more quantity of char is obtained. In addition, the maximum peaks of degradation temperature and activation energies are lower than the corresponding values for untreated wood.

Concerning the emissions evolved in a combustion process, the main differences are the presence of nitrogenated organic compounds (acetonitrile, 2-propenitrile, pyrrole, benzonitrile, quinoline,...) found in the experimental runs of furniture wood waste. Low but significant levels of NO and HCN have been detected.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2016.12.022>.

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Appendix A. Supplementary material

[Multimedia Component 1](#)

Supplementary data 1

Highlights

- The burnout temperature of furniture wood waste is higher than untreated wood.
 - Satisfactory combustion kinetic models are obtained from dynamic and isothermal runs.
 - More than 100 volatile and semi-volatile compounds evolved in fuel-rich combustions at 850 °C are analyzed.
 - Some nitrogenated organic compounds have been found in the combustion of furniture wood waste.
-

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