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# Coupled drying and devolatilisation of non-spherical wet pine wood particles in fluidised beds

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### Abstract

Release of volatiles of non-spherical pine wood particles was analysed by means of continuous measurements of the  $CO_2$  and  $O_2$  concentrations obtained after the complete combustion of the volatiles and from flame extinction times. The effect of the atmosphere used for devolatilisation was tested. The volatiles evolution was nearly identical using air or  $N_2$  as fluidising gas. The devolatilisation times increased with increasing the equivalent particle diameter, but there was an important scattering in the results. The data dispersion greatly decreased when the shape factor of the wood particles was considered. The devolatilisation times were fitted to a power-law relation replacing the particle diameter by the equivalent particle diameter multiplied by the shape factor. The effect of the moisture content was studied by analysis of the devolatilisation process of pine wood particles of the same size and different moisture contents (0-50%). As the moisture content of the wood particles increased the devolatilisation rate of combustible volatiles decreased and was more uniform along the devolatilisation time.

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#### **1. Introduction**

Designs of the existing fluidised bed boilers for biomass and organic wastes combustion are mainly based on experience from coal combustion [1] because the complex mechanism of combustion of these solids in fluidised beds is still not well understood.

When biomass particles are introduced into a fluidised bed combustor (750-950 °C), they first lose moisture; this is followed by devolatilisation and finally combustion of the resultant char. In some cases, moisture contents as high as 50% can be found, as a consequence the drying of the particles is very important in the global process of devolatilisation. Devolatilisation and volatile combustion are the main steps in the combustion of biomass. The volatile fraction of biomass particles a significant proportion to the total amount of heat released during combustion.

The distribution of volatiles throughout the bed will depend on the ratio between the rate of devolatilisation and the rate of particle mixing within a fluidised bed. There are many studies on coal drying and devolatilisation under fluidised bed combustion (FBC) conditions. However, the review of Agarwal and La Nauze [2] shows that the effect of the moisture on the devolatilisation of large fuel particles has received little attention. Information in the literature mainly concerns combustion characteristics of dry or relatively low-moist solid fuels. In the combustion of wet solid fuels some delay in the solid pyrolysis have been observed [3-8]. So, combustion of wet biomass may prevent an abrupt release of volatiles near the feeding point, thus enhancing the uniformity of the distribution of combustible volatiles over the cross-sectional area of fluidised beds, however, it is also widely recognised that moisture largely affects reactor efficiency.

Different experimental techniques have been involved in the study of devolatilisation rates such as determination of devolatilisation times by visual observation of flame extinction [5-9]; determination of particle weight loss in fluidised beds [10] or thermogravimetric analysers [11]; determination of particle centre temperature history [7] and continuous gas analysis [12]. Working with coal, Stubington et al. [13] compared the devolatilisation times obtained by three different methods and concluded that  $CO_2$  evolution profiles gave good agreement with flame extinction time measurements in fluidised beds, although thermogravimetric experiments gave longer devolatilisation times. Results have been typically correlated using a power-law relation in the form of

$$t_v = a d_p^{\ n} \tag{1}$$

However, there are large discrepancies in the reported values for the exponent n, with n ranging from 0.32 to 2.6, although most data fell between 1 and 2 [14]. The variability of the experimental results has been attributed to the differences in the type of apparatus employed, operating conditions, definition of devolatilisation time, etc.

Traditional methods of particle combustion analysis apply only to spherical particles, however the majority of biomass particles are highly nonspherical. Only few attempts have been made to determine the effect of shape on the burning rates. Stubington et al. [14] found no effect of the particle shape on devolatilisation times when the equivalent-mass diameter of the particle is used and the shape factor is greater than 0.7. Austin et al. [15] determined that the volatile burning times for nearly-spherical corncob particles obeyed a d-squared law. The non-spherical particles obeyed a volume to the two-thirds power law. They used several d-squared definitions to demonstrate a linear relationship between d-squared and the burning times of a particle, indicating the necessity of more research to determine the effectiveness of these correlations.

In this work, the devolatilisation process of pine wood particles of regular and irregular forms has been studied in a fluidised bed by means of continuous measurements of  $CO_2$  and  $O_2$  concentrations obtained after the complete combustion of the volatiles and from visual observation of the flame of volatiles. In addition, the effect of the particle moisture content over the devolatilisation rate has been analysed.

### 2. Experimental

The devolatilisation of biomass was studied in a fluidised bed reactor of 50 mm I.D. and 0.5 m height, with a perforated steel plate distributor, as shown in Figure 1. The fluidising gas (air or  $N_2$ ) was preheated in a ceramic fixed bed located below the distributor plate. All system was inside an electrically heated furnace. The gas flow rate and the bed temperature were measured with a mass flow controller and a thermocouple, respectively. The fluidised bed was composed of 300 g of silica sand with a particle size +0.50-0.63 mm. The superficial gas velocity inside the fluidised bed was kept constant at 40 cm/s in all experiments, and four temperatures between 650 and 950 °C were used.

The experiments were carried out with debarked pine wood chips (Pinus Sylvestris) of different sizes and irregular shapes ( $dp_{eq}=7-37 \text{ mm}$ ,  $\phi=0.4-0.75$ ). Moreover, taking into account that it is possible some small errors in the measurements of the particles because of their very irregular forms, several pine wood particles with well-defined size and shape ( $dp_{eq}=6-45 \text{ mm}$ ,  $\phi=0.5-0.8$ ) were prepared in order to better compare the experimental data. The chemical analysis of the pine wood is shown in Table 1.

The devolatilisation times were determined by two methods: (1) visual observation of volatiles flame and from (2) continuous gas analysis of  $O_2$  and  $CO_2$ . For the visual technique, the devolatilisation experiments were recorded on video through a mirror located over the reactor. The devolatilisation times ( $t_v$ ) were measured as the time elapsed between sample

addition and complete extinction of the flame of volatiles. The reproducibility of these measurements was around 5%.

The second technique consisted of measuring the combustible volatiles evolution as a function of the time by means of gas analysers. This combustible volatiles evolution was followed by means of the continuous measurement of the CO<sub>2</sub> and O<sub>2</sub> concentrations obtained after the complete combustion of the volatiles. The CO concentration was negligible in all the experiments. A non-dispersive infra-red analyser for CO<sub>2</sub> (and CO) and a paramagnetic analyser for O2 were used. The gas concentrations were logged as a function of time via a PC-based data-logging system. When N<sub>2</sub> was used as the fluidising gas, the volatiles were burned with O2 addition in a fixed bed reactor (900 °C) placed downstream from the fluidised bed. This technique allowed us to determine both the total devolatilisation times and the evolution of the devolatilisation rate with time. For better data analysis, the CO2 and O2 concentrations versus time profiles were corrected for gas flow and dispersion in the sampling line and analysers. The system dispersion was determined by adding CO<sub>2</sub> to the bed. Figure 2 shows the measured and corrected evolution of O<sub>2</sub> and CO<sub>2</sub> concentrations for a typical devolatilisation test using air as fluidising gas. The end of the devolatilisation was considered as the time when the CO<sub>2</sub> or O<sub>2</sub> concentration reached the first local minimum. After this time, the CO<sub>2</sub> and O<sub>2</sub> concentrations remained almost constant for a long time while the remaining char burnt. Figure 2 also illustrates the point for the end of devolatilisation, which was defined as the devolatilisation time, t<sub>v</sub>.

For each experiment, one particle was dropped into the hot fluidised bed. For each temperature and particle size, three to five separate experiments were performed with the well-defined particles. This was not possible with the chips because each chip had a different size and shape factor.

### 3. Results and discussion

Visual observations of flame combustion of volatiles released from pine wood particles in the fluidised bed have been carried out. From these visual tests it was observed that the release of volatiles was not uniform with time, and as a consequence it was necessary to study the volatiles evolution as a function of the time. This volatiles evolution was determined measuring the CO<sub>2</sub> produced and the O<sub>2</sub> consumed during different devolatilisation tests with further volatiles combustion. This method of determination of devolatilisation rates was developed to determinate the evolution of combustible volatiles. This kind of devolatilisation rates is useful for modelling the evolution of volatiles in combustion environments. Figures 3 and 4 show some of the results obtained with welldefined wood particles and with wood chips. It can be observed that the combustible volatile releasing rate,  $r_v$  (mmol O<sub>2</sub> consumed/g<sub>sample</sub> s), was not uniform during the devolatilisation time, confirming the visual observations. The amount of combustible volatiles released in the first moments of the reaction increased with increasing temperature and the devolatilisation time increased slightly with decreasing temperature.

Devolatilisation times have been measured by different researchers in oxidising or inert atmospheres. Due to the differences in the applied experimental technique and conditions, as well as differences in observation technique, results of fluidised bed devolatilisation did not lead to a consensus about the atmosphere effect. Jung and Stanmore [9] found that the devolatilisation was more rapid at oxidising conditions. Salam et al. [16] observed longer devolatilisation times with decreasing oxygen concentration. The decrease in devolatilisation time under oxidising conditions was attributed to the combustion of volatiles around the fuel particle which may transmit heat back to the particle [17]. Agarwal [17] proposed a devolatilisation model taking into account heat conduction from the flame front to the particle. Palchonov et al. [1] considered as unrealistic that under FBC conditions a particle could be heated by surrounding volatiles flame, unless the particle was in the bubble phase, since volatiles were found not to burn in the emulsion phase [6]. Prins et al. [6] observed that the frequency at which flames arise in the bubbles was relatively low; the combustion of volatiles occurred mainly in the freeboard region as a consequence of the fuel particles tendency to float on the bed surface during devolatilisation.

As a consequence of the above observations, the effect of the gas used for fluidisation (air or N<sub>2</sub>) was tested. It can be observed in Figure 5 that the volatiles evolution was the same using air or N<sub>2</sub> as fluidising gas, which indicates that the volatiles flame did not affect the devolatilisation process of the pine wood particles. In the visual test it was observed that most of the volatiles of the large wood particles were burnt in the freeboard region of the fluidised bed and not around the wood particle. Only at the end of the devolatilisation process was the flame observed to be formed around the particle, which was floating on the bed surface. It can be also concluded from this figure that char oxidation did not occur simultaneously with devolatilisation process maybe because, as commented by Prins et al. [6], the volatiles were released in a sufficiently continuous manner, and at sufficiently high rate, that oxygen was prevented from reaching the fuel particle surface. The oxygen around the wood particle was consumed by the volatiles combustion rather than by the combustion of the solid carboneous material. Gurgel Veras et al. [18] stated that for coal particles greater than 80 µm the two stages (volatiles and char combustion) were well separated and there was less overlap for fuels with a high initial reactivity and high amount of volatiles, since the efflux of volatile increases. Thus the devolatilisation and char combustion stages are more sequential for woods than for coals.

Figure 6 shows the devolatilisation times measured under identical operating conditions with different particle sizes at 850°C and using the two techniques above mentioned. It can

be observed that the devolatilisation times measured with both techniques were almost the same. The devolatilisation times increased with increasing the equivalent particle diameter, but there was an important dispersion in the results. However, this dispersion decreased when the devolatilisation times were plotted versus the equivalent particle diameter multiplied by the shape factor, as shown in Figure 7. Similar results were observed at other temperatures (650-950 °C) with the devolatilisation times decreasing slightly with increasing temperature.

The devolatilisation times were fitted to equation (1), replacing the particle diameter by the equivalent particle diameter multiplied by the shape factor.

$$t_{v} = a \left( dp_{eq} \phi \right)^{n} \tag{2}$$

 $dp_{eq}$  = diameter of a sphere having the same volume as the particle (3)

$$\phi = \frac{\text{surface area of a sphere having the same volume as the particle}}{\text{surface area of the particle}}$$
(4)

The values of the constants "a" and "n" at each temperature determined from linear regression of the logarithmic data are given in Table 2. As can be seen the values of "n" are between 1.5-1.6, which are in the same range as the values in literature. The "a" values decreased as the bed temperature increased which is also in good agreement with the literature data [7].

Figure 8 shows the devolatilisation profiles obtained for samples of different shape and equivalent diameter but with the same value for the product of both. It can be observed that not only identical devolatilisation times but also that the variation with time of the volatiles evolution rates was nearly identical.

One of the main problems with modelling the processes happening in wood chips is the definition of their geometry because of their irregular forms. Taking into account the findings

observed in this work, it is possible to conclude that non-spherical wood particles can be modelled as spherical particles, characterised by an equivalent particle diameter and a shape factor. In this way, the models developed for spherical particles can be applied to particles of different shapes replacing, in all of the equations of the devolatilisation model, the particle dimensions by the equivalent particle diameter multiplied by the shape factor.

### **3.1. Effect of moisture.**

Although the moisture content of the biomass has an important effect on the distribution of combustible volatiles over the cross-sectional area of fluidised beds and it is widely recognised that moisture largely affects reactor efficiency and product quality, no extensive experimental investigation is available on the drying characteristics of biomass. In this work, pine wood particles of the same size (well-defined size and shape) and different moisture content were devolatilised under oxidising conditions at the same operating conditions (650 °C and 850 °C) in the fluidised bed to analyse the effect of the moisture content over the devolatilisation rate.

To obtain particles with different moisture content, water was added to the original samples (see Table 1) and each wood particle was kept for a week in a sealed vessel to allow its stabilisation. The moisture content was determined by weighing the wood particle before water addition and after stabilisation. Some original samples were also dried in an oven at 108°C to obtain particles without moisture (moisture content = 0%).

Figure 9 shows the effect of the moisture content on the devolatilisation times as compared to the ratio of devolatilisation times for moist,  $t_v$ , and oven dried particles,  $t_{vo}$ . It can be observed that the devolatilisation times increased with increasing moisture content of the wood particles, which agrees with previous observations [3-8].

The power-law relation (equation 2) with the values reported in Table 2 underestimated the devolatilisation times for pine wood particles with significantly greater moisture content. Urkan et al. [5] determined the exponent "n" in the power-law relation of the devolatilisation times of coals with wet (up to 35%) and dried particles. They found that this exponent generally decreased with increasing moisture content of the coal, which qualitatively agrees with the results obtained in this work for wood. However, more experimental work is needed to know the effect of the moisture content on the parameters "a" and "n" of the power-law expression.

Figure 10 shows the effect of the moisture content on the variation of devolatilisation rates with time. As the moisture content of the wood particles increased, more water must be evaporated and therefore the devolatilisation rate of combustible volatiles decreased and was more uniform along the devolatilisation time.

## 4. Conclusions

Release of volatiles of pine wood particles was analysed by means of continuous measurements of  $CO_2$  and  $O_2$  concentrations obtained after the complete combustion of the volatiles and from flame extinction times. The devolatilisation times measured with both techniques were almost the same.

The volatiles evolution was nearly identical using air or  $N_2$  as fluidising gas, which indicates that the volatiles flame did not affect the devolatilisation process of the pine wood particles. Char oxidation did not occur simultaneously with devolatilisation process maybe because the volatiles were released in a sufficiently continuous manner, and at sufficiently high rate, that oxygen was prevented from reaching the fuel particle surface. The oxygen around the wood particle was consumed by the volatiles combustion rather than by the combustion of the solid carboneous material. The devolatilisation times of non-spherical pine wood particles were found to be proportional to the equivalent diameter multiplied by the shape factor. Taking into account this finding, the devolatilisation times were well predicted by a power-law relation replacing the particle diameter by the equivalent particle diameter multiplied by the shape factor. However, the power-law relation obtained with air-dried wood particles underestimated the devolatilisation times for wood particles with a significantly higher moisture content.

An increase in the moisture content of the wood particles produced an increase in the devolatilisation time and a more uniform devolatilisation rate along the devolatilisation time.

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Proximate analysis (wt%)		Ultimate analysi	Ultimate analysis (wt%) -dry basis-	
Moisture	8.3	С	52.9	
Ash	1.3	Н	6.8	
Volatiles	75.1	Ν	0.1	
Fixed carbon	15.3	O (by diff.)	38.9	

**Table 1.** Analysis of the pine wood.

T (°C)	a (s / mm <sup>n</sup> )	n
650	1.69	1.50
750	1.38	1.54
850	1.03	1.60
950	0.89	1.60

 Table 2. Constants for power-law expression.

### **Captions of the Figures**

Figure 1. Experimental set-up used for devolatilisation tests.

- Figure 2. Typical O<sub>2</sub> and CO<sub>2</sub> concentration profiles obtained during devolatilisation tests using air as fluidising gas. Measured, …….. Corrected.
- Figure 3. Experimental devolatilisation rates of wood particles with well-defined geometry and size (14.5x14.5x14.5 mm).
- Figure 4. Experimental devolatilisation rates of wood chips.
- Figure 5. Effect of fluidising gas on the devolatilisation rates. Particle dimensions: 14.5x14.5x14.5 mm. T = 850 °C. — Air, - - - - Nitrogen.
- Figure 6. Devolatilisation times measured with particles of different size and well-defined geometry. T = 850 °C.
- Figure 7. Devolatilisation times as a function of the factor  $-dp_{eq}.\phi$ -. T = 850 °C. Devolatilisation times predicted by the equation (2).
- Figure 8. Devolatilisation rates of wood particles of different size and shape but the same factor  $dp_{eq}$ . $\phi$ . T = 850 °C.
- Figure 9. Effect of particle moisture content on the devolatilisation time.

Figure 10.Effect of particle moisture content on the devolatilisation rate.



























Figure 7



Figure 8







