Oxidative Pyrolysis of a Large Wood Particle: Effects of Oxygen Concentration and of Particle Size

Elias Daouk[*a,b], Laurent Van de Steene[a], Frederic Paviet[b], Sylvain Salvador[c]

[a]CIRAD UPR114 BioWooEB, 73 avenue Jean-François Breton, 34398 Montpellier Cedex 5, France
[b]GEPEA, UMR 6144 CNRS, Université de Nantes, Ecole des Mines de Nantes, ENITIAA, DSEE, 4 rue Alfred Kastler, B.P. 20722, 44307 Nantes Cedex 3, France
[c]RAPSODEE, CNRS UMR 5203, Ecole des Mines d'Albi-Carmaux, Campus Jarlard, 81013 Albi Cedex 09, France
elias.daouk@cirad.fr

In this study, the oxidative pyrolysis of large pine wood particles was analysed using a Macro-ThermoGravimetric apparatus (Macro-TGA). The effects of the concentration of oxygen in the surrounding gas and of particle size were investigated. Three different oxygen concentrations (0 %, 10 % and 20 %) and three sizes of cylindrical pine wood samples (4 mm, 8 mm and 12 mm in diameter) were tested at a heating rate of 20 °C/min.
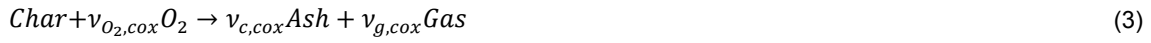
The results showed that oxygen had a strong influence on pyrolysis behaviour. We observed that the peak of wood pyrolysis was higher and appeared at a lower temperature with an increase in the oxygen concentration. When the size of the particle was increased, there was a short delay in DTG curve. But generally speaking, particle size had no significant influence on oxidative pyrolysis at this low heating rate. With the 4 mm diameter particles and at a heating rate of 20 °C/min, degradation behaviours (TG and DTG curves) were similar and resembled intrinsic degradation behaviours: heat and mass transfer phenomena did not limit the process.

1. Introduction

Today, global consumption of fossil fuels is increasing more and more with economic development and population growth. At the same time, pollution has become a concern and a major challenge in many countries. In addition, most current oil reserves are located in politically unstable areas. Consequently, the use of alternative sources, particularly of renewable energies, is increasing worldwide. Biomass is proving to be one of the most promising choices. By 2050, about half the world's current primary energy consumption could be met by biomass, and 60 % of the world's electricity market could be supplied by renewable energies, of which biomass is a significant component (McKendry, 2002) .

In this context, biomass gasification is a promising route. The gasification process involves a series of thermo-chemical transformations. A new technology was recently developed: it consists in separating the main transformation using different reactors. The pyrolysis of biomass and the gasification of char are performed in two separate reactors in a staged fixed bed gasifier. Understanding and controlling pyrolysis is crucial for process optimization. One of the main challenges of this step in process optimization is the energy supply. One solution consists in burning part of the biomass by introducing a small amount of air into the pyrolysis reactor. This type of process is called"autothermal" and this type of pyrolysis is called"oxidative pyrolysis".

Many studies have been conducted under inert atmosphere to investigate the intrinsic kinetics of pyrolysis (Di Blasi, 2008). Recently, there has been an increase in studies on oxidative pyrolysis. Oxygen was found to modify pyrolysis behaviour and to drastically increase the conversion rate. In thermogravimetric experiments, DTG curves of biomass oxidative pyrolysis showed two separate peaks instead of one under inert conditions: the first peak was attributed to simultaneous pyrolysis and oxidation of the raw materiel and the second one logically to weight loss during the oxidation of char. The kinetic mechanism of oxidative pyrolysis proposed by Ohlemiller (Leach et al., 2000) is as follows:

$$Fuel \rightarrow \nu_{c,pyr}Char + \nu_{g,pyr}Gas \tag{1}$$

$$Fuel + \nu_{O_2,oxd}O_2 \rightarrow \nu_{c,oxd}Char + \nu_{g,oxd}Gas \tag{2}$$

$$Char + \nu_{O_2,cox}O_2 \rightarrow \nu_{c,cox}Ash + \nu_{g,cox}Gas \tag{3}$$

When large particles are used, transport phenomena need to be taken into account along with the kinetics derived from molecular scale studies. Many studies have reported on the pyrolysis of mm size particle in inert atmosphere. However, to the best of our knowledge, no studies have focused on the influence of oxygen on the pyrolysis of large biomass particles.

The objective of this work was to study the influence of oxygen on biomass pyrolysis kinetics at the particle scale.

2. Experimental

2.1 Samples

The samples consisted of a single cylindrical pine wood particle. Cylindrical samples make it possible to obtain more repeatable results during experiments than wood chips as they are homogeneous in size and composition. Our samples were all 15 mm long. The influence of particle size on the pyrolysis process was studied using particles with three different diameters: 4, 8 and 12 mm. The proximate and ultimate properties of the pine wood are listed in Table 1.

Table 1: Proximate and ultimate analysis in dry basis of biomass pine wood sample

Parameters	
Moisture content (%)	10.5 ± 0.2
Proximate analysis (wt. %)	
Volatile matter	83.3 ± 0.5
Fixed carbon	15.4 ± 0.7
Ash	1.3 ± 0.2
Ultimate analysis (wt. %)	
C	52.2 ± 0.5
H	6 ± 0.25
N	0.1 ± 0.05
O (by difference)	41.7 ± 0.75
LHV (MJ/Kg)	19.6 ± 0.12

2.2 Experimental device

The study was carried out using a macro-thermo-gravimetric apparatus (macro-TGA) at CIRAD-Montpellier. Figure 1 is schematic diagram of the experimental setup. The mass loss of a sample (TG) and temperature were simultaneously recorded over time. Temperature was measured using a thermocouple installed directly below the crucible.

The equipment consisted of a micro-balance, a furnace, and a thermocouple. Nitrogen 4.5 (99.995% purity) and synthetic air 80:20 (80 % nitrogen, 20 % oxygen) were each connected to a Brooks Mass Flow Meter Controller with a range of 0-400 NmL/min enabling exact control of flow rates of the incoming gas and hence the desired oxygen content in the flowing gas. Three oxygen concentrations (0 %, 10 % and 20 %) were tested. Several tests were carried out to determine the minimum flow rate needed to prevent stoichiometric limitation. A total gas flow rate of 400 NmL/min was selected. All measurements of mass loss, temperatures and flow rates were performed using a slow acquisition system (0.2 Hz). Thermocouples and flow-meters were connected to an ISK 200 converter/amplifier located upstream from the computer. If the samples are placed directly in the crucible, the degradation of the samples can be influenced by heat transfer from the crucible, and in addition, the sweeping gas cannot attack the entire sample. To avoid the effect of the crucible on degradation, the samples were placed in a basket suspended above the crucible, as shown in Figure 1. The crucible was kept to serve as ballast. In the experiments, the samples were heated from room temperature to 120 °C with a plateau of 30 min (drying phase), and from this temperature to 800 °C with a plateau of 30 min (degradation phase). All the experiments were carried out under a constant heating rate of 20 °C/min.

Testing demonstrated good reproducibility of the TG curves with a maximum error of around 3 % between the three experiments.

In the second stage, two 0.5 mm thermocouples were imbedded in a particle 12 mm particle to record the internal temperature at the centre and at 2 mm from the particle surface in an oxidative atmosphere with 10 % of oxygen concentration.
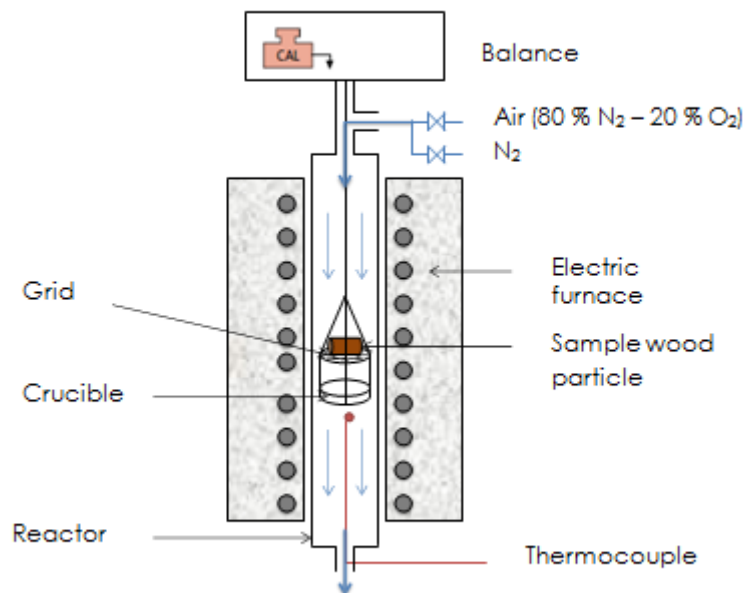

Figure 1: Schematic diagram of the experimental setup

3. Results and discussion

For each experiment, TG and DTG curves were drawn as a function of temperature. TG curves represent the ratio of the weight of the sample (w) to the initial weight (w_i) after drying phenomena. To clearly analyse and compare the results, DTG curves were obtained by taking the time derivative of TG curves (the time difference between two recorded mass is 5s). As the noise of the mass loss signal is amplified by derivation, DTG curves were numerically smoothed using the 10-point moving average technique.

3.1 Effect of oxygen on thermal degradation

Figure 2 shows that in an oxidative environment, three stages can be distinguished in the mass loss curves, as already reported in literature (Amutio et al., 2012). These stages have been defined as dehydration, oxidative pyrolysis, and char oxidation. The differences between the curves obtained during the dehydration phase are due to variations in the initial moisture content between the particles.

Figure 2 shows the mass loss (TG) and conversion rate (DTG) under different atmospheres (inert, 10 % and 20 % vol. % O_2), for the 4 mm diameter particles, as a function of temperature. It can be seen that oxygen greatly affected pyrolysis. Oxidative pyrolysis (2nd stage) occurred at a lower temperature range when the oxygen concentration in the sweeping gas was increased. Moreover, the peak in the oxidative pyrolysis stage was higher and appeared at a lower temperature when the oxygen concentration in the atmosphere was increased. In an atmosphere with 20 % oxygen, the peak was about 1.5 times higher than in an inert atmosphere. These results are in a good agreement with those obtained by Anca-Couce (Anca-Couce et al., 2012) at the molecular scale. Generally the presence of oxygen enhances the pyrolysis phase. In the kinetic scheme proposed by Ohlimiller (Leach et al., 2000), oxidative pyrolysis consists of the two first equations Eq (1) and Eq (2): wood pyrolysis and wood oxidation. The wood oxidation reaction speeds up pyrolysis.

Many authors consider that woody biomass has three main components (hemicellulose, cellulose and lignin) and smaller amounts of extractives and ash. Branca (Branca and Di Blasi, 2004) associate the shoulder that appears at the beginning of the DTG curve with, hemicellulose degradation and the peak with cellulose degradation. In an oxidative atmosphere (10 % and 20 % oxygen), our results showed that the hemicelluloses shoulder was less clear than in an inert atmosphere, as can be seen in figure 2. Anca-

Couce (Anca-Couce et al., 2012) puts this down to an overlap of the cellulose and hemicellulose peak, responsible for a higher maximum reaction rate in presence of oxygen.
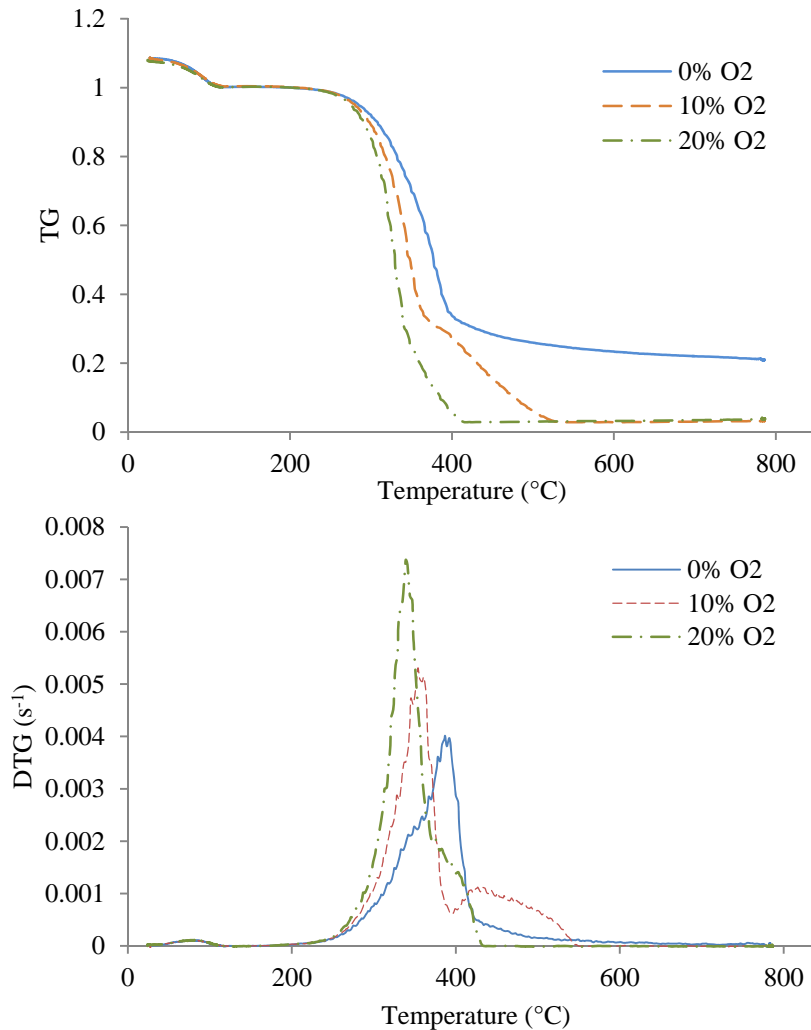

Figure 2: TG and DTG curves for the different atmospheric components (0 %, 10 % and 20 % vol. % O_2) for the 4 mm diameter wood particle

3.2 Effect of particle size on thermal degradation

Figure 3 shows TG and DTG curves for the different particle diameters (4, 8 and 12 mm) in the two atmospheres (0 % and 20 % oxygen concentration). In the inert atmosphere, the same peak in DTG curves was obtained with the three particle sizes. In the oxidative environment, a smaller peak was obtained with particles of 8 and 12 mm in diameters than with particles 4 mm in diameter. The differences between the TG and DTG curves among the three particle sizes can be attributed to the effect of transfer phenomena on degradation behaviour.

The biggest difference in the TG and DTG curves was obtained between the 4 mm particle and the two other particle diameters (8 and 12 mm). The curves obtained for the 4 mm particle are similar to those reported by Su (Su et al., 2012). In this case, the degradation behavior of the whole 4 mm particle resembled degradation behavior at molecular scale and transfer phenemona can be considered to be neglegible. For a 4 mm particle, the temperature field can be considered as uniform within the particle.

In the oxidative environment, the DTG curve peak was greater for the 12 mm particle than for the 8 mm particle. This can be explained by the fact that the energy released from the biomass oxidation reaction Eq (2) is higher in the case of the bigger particle since the particle mass is higher. As reported in the literature, at molecular scale, in the oxidative environment, two peaks appeared in the DTG curves: the two stages of pyrolysis (char forming and char oxidation) were separated over time. Contrary to results reported in the literature, in our study. , the second peak did not appear in DTG curves in the case of large wood particles

as shown in Figure 3. This can be attributed to char oxidation beginning before the end of oxidative pyrolysis. The particle size thus clearly affected the char oxidation stage: an interaction between oxidative pyrolysis (2nd step) and char oxidation (3rd step) can occur. Moreover, the char oxidation phase was clearly less pronounced and became slower with an increase in the size of the particle. This can be explained by the fact that at particle scale, the effect of heat and mass transfer can not be neglected in the char oxidation phase.
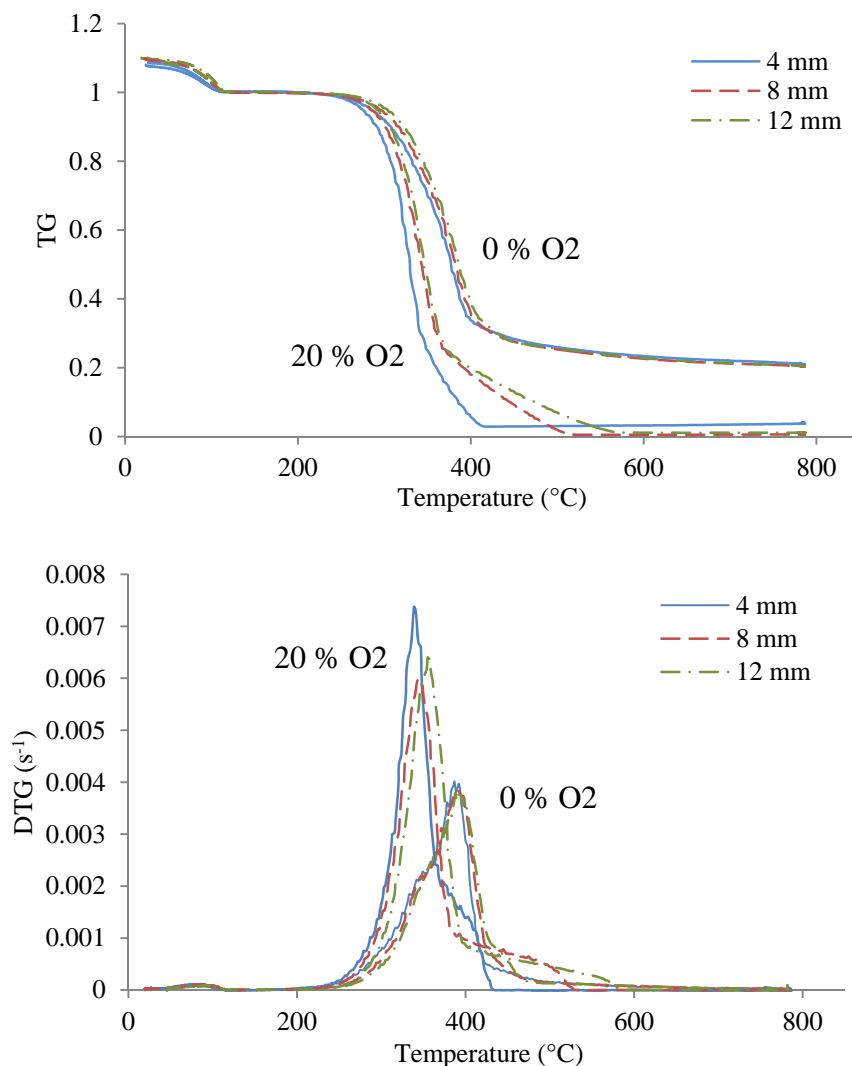

Figure 3: DT and DTG curves for the different particle diameter (4, 8 and 12 mm) for the two atmospheres with 0 % and 20 % of oxygen concentration

3.3 Temperature inside a thick particle

Figure 4 shows the temperature measured inside the particle at the centre and at 2 mm from the particle surface. The temperature first increased until it reached the inflexion point, then increased strongly during oxidative pyrolysis until reaching a small plateau. Two thermal regimes during wood pyrolysis have also been noticed by Gauthier *(Gauthier et al., 2013)*. Subsequently the temperature increased linearly throughout the char oxidation phase.

Similar temperatures were observed during particle heating and at the beginning of oxidative pyrolysis. At the end of oxidative pyrolysis, a difference between the two temperatures appeared: the temperature at the centre of the particle was always 30 to 40 °C higher than the temperature 2 mm from the surface during the 20 °C/min heating rate phase. This was due to the source term linked to exothermic char oxidation. Differences between the two temperatures were only observed after the exothermic reaction began.
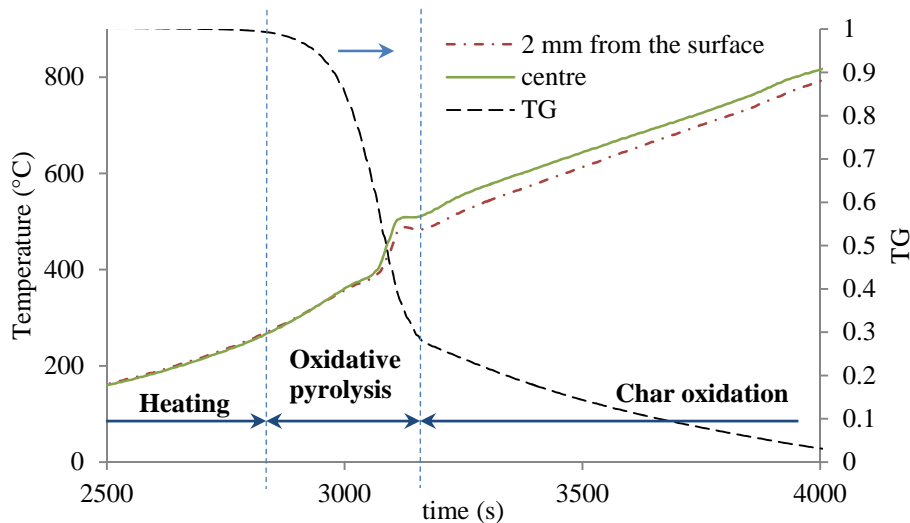
Figure 4: Temperatures profiles inside the particle with a diameter of 12 mm (at the centre and 2 mm from the particle surface) and the TG curve for an atmosphere containing 10 % O_2 at a heating rate of 20 °C/min

4. Conclusions

Oxidative pyrolysis of large wood particle was performed in a macro-thermogravimetric apparatus.

The results showed that oxygen had a strong influence on pyrolysis, even in the case of large particles. The peak oxidative pyrolysis phase was higher and appeared at a lower temperature when the oxygen concentration in the atmosphere was increased. The hemicellulose shoulder in the DTG curves was less clear when the oxygen concentration in the atmosphere was increased.

When the size of the particle was increased, a short delay was observed in TG and DTG curves. In the oxidative environment, a smaller peak appeared with the 8 and 12 mm particles than with the 4 mm particles. This was due to transfer phenomena involved in large wood particles. With the 4 mm particles and a heating rate of 20 °C/min, TG curves resembled intrinsic degradation behaviours reported in the literature. In this case, we can say that transfer phenomena can be ignored.

The temperature measurements inside the particle revealed an inflexion point and a marked increase in temperature at the end of the oxidative pyrolysis stage. A difference of 30 to 40 °C was observed between the temperature measured at the centre and 2 mm from the surface.

Particle size had no significant influence on the oxidative pyrolysis stage at this low heating rate. Transfer limitations only appeared when exothermic reactions began. To clearly demonstrate the effect of particle size on oxidative pyrolysis, experiments with high heating rate will be conducted in another device that can achieve heating rates of up to 900 °C/min.

References

Amutio, M., Lopez, G., Aguado, R., Artetxe, M., Bilbao, J., Olazar, M., 2012. Kinetic study of lignocellulosic biomass oxidative pyrolysis. Fuel 95, 305–311.

Anca-Couce, A., Zobel, N., Berger, A., Behrendt, F., 2012. Smouldering of pine wood: Kinetics and reaction heats. Combust. Flame 159, 1708–1719.

Branca, C., Di Blasi, C., 2004. Global interinsic kinetics of wood oxidation. Fuel 83, 81–87.

Di Blasi, C., 2008. Modeling chemical and physical processes of wood and biomass pyrolysis. Prog. Energy Combust. Sci. 34, 47–90.

Gauthier, G., Melkior, T., Salvador, S., Corbetta, M., Frassoldati, A., Pierucci, S., Ranzi, E., Bennadji, H., Fisher, E., 2013. Pyrolysis of Thick Biomass Particles: Experimental and Kinetic Modelling. Chemical Engineering Transaction, 32.

Leach, S.V., Rein, G., Ellzey, J.L., Ezekoye, O.A., Torero, J.L., 2000. Kinetic and fuel property effects on forward smoldering combustion. Combust. Flame 120, 346–358.

McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. Rev. Issue 83, 37–46.

Su, Y., Luo, Y., Wu, W., Zhang, Y., Zhao, S., 2012. Characteristics of pine wood oxidative pyrolysis: Degradation behavior, carbon oxide production and heat properties. J. Anal. Appl. Pyrolysis 98, 137–143.