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Thick wood particle pyrolysis in an oxidative atmosphere

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Particle
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Thermo-gravimetric analysis

HIGHLIGHTS

- The oxidative pyrolysis was studied in thermally thin and thick regimes.
- The oxygen has a significant influence on oxidative pyrolysis.
- The effect of particle size was studied in thermally thick regime conditions.
- The temperatures inside a particle highlighted the exothermicity of the process.

ABSTRACT

Oxidative pyrolysis of pine wood particles was analysed thermo-gravimetrically. 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% v/v) and three different sized cylindrical pine wood samples (4 mm, 8 mm and 12 mm in diameter and 15 mm long) were tested. Two types of Macro-TG apparatuses were used; the first was non-isothermal and was used at a heating rate of 20 °C/min, and the second was isothermal used at two temperatures, 400 °C and 600 °C. In the low heating rate non-isothermal apparatus, results showed that oxygen had a strong influence on pyrolysis behaviour, but particle size did not. In the high heating rate isothermal apparatus, particle size had a significant influence on conversion: transfer phenomena limit oxidative pyrolysis.

1. Introduction

Biomass for energy production is of growing importance worldwide due to its potentially influence on greenhouse gas effect reduction if substituted to fossil fuels. Biomass is one of the few renewable sources which can be stored and consequently does not suffer from intermittency, unlike wind or sun. In addition, biomass can be trans-ported over long distances, unlike hydro and geothermal power. The main challenge today is using renewable biomass fuels with much higher efficiencies than achieved in their traditional uses. Thermo-chemical conversion of biomass has been the subject increasing attention, particularly gasification, which enables conversion of biomass into combustible gas, mechanical and electrical power and synthetic fuels and chemicals (Di Blasi, 2000).

Fixed bed technologies are particularly suitable for gasification in small power plants because of their high efficiency (< 5 MWth). The gasification process involves a series of thermo-chemical transformations: biomass drying and pyrolysis, oxidation of volatile matter and char gasification. Staged fixed bed technologies were recently developed to optimize the process by limiting tar content. The NOTAR® gasifier sold by XyloWatt is one example of this technology. The two main steps, pyrolysis of the biomass and gasification of the char are performed in two separate reactors inside the staged fixed bed gasifier. Understanding and controlling pyrolysis is crucial for process optimisation as the yields and the quality of the different pyrolysis products – gas, tar and char – have a major impact on the process as a whole. One of the main challenges of this step in process optimisation is supplying the necessary energy. One solution is burning part of the biomass by introducing a small amount of air into the pyrolysis reactor to provide the energy needed for the process. This solution is pro table with respect to both the efficiency of the thermal process and gas quality. This type of process is called “auto-thermal” and this type of pyrolysis is called “oxidative pyrolysis”. In the literature, it is reported that the presence of oxygen greatly affects the behaviour of the pyrolysis (Amutio et al., 2012; Chaos et al., 2012; Chen et al., 2011; Su et al., 2012).

This study focuses on the oxidative pyrolysis of a thick wood particle. It should be noted that the fixed bed process operation is

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limited by the size of the particle, which has to be more than a few millimetres to avoid too high pressure drop through the char bed when the conversion progresses. In addition, the use of thick wood particles as a feedstock reduces grinding costs.

Many studies have been conducted under inert atmosphere to investigate the intrinsic kinetics of pyrolysis (Di Blasi, 2008; Gu et al., 2013; Lu et al., 2013; Ranzi et al., 2008). This is the case of thermally thin regime. Recently, there has been an increase in studies on oxidative pyrolysis (Amutio et al., 2012; Anca-Couce et al., 2012; Branca and Di Blasi, 2004; Lautenberger and Fernandez-Pello, 2009; Shen et al., 2009; Su et al., 2012; Takashi and Hidesaburo, 1992). The studies have been carried out in thermo-balance with different oxygen concentrations in the inlet gas stream to study the effect of oxygen on the biomass pyrolysis process. Other authors compared these results with those obtained under inert atmosphere (Amutio et al., 2012; Branca and Di Blasi, 2004; Takashi and Hidesaburo, 1992). In oxidative atmosphere, the pyrolysis start at lower temperature and the degradation is faster than in inert atmosphere. In thermo-gravimetric experiments, DTG curves of biomass oxidative pyrolysis showed two separate peaks versus one peak in inert conditions: the first peak was attributed to simultaneous pyrolysis and oxidation of the raw material and the second peak logically to weight loss during oxidation of the char. Shen et al. (2009)reported that the DTG curves were separated into two stages, with the first stage (low temperature region) in the range of 200–370 °C and the second stage (high temperature region) in the range of 370–490 °C. According to Branca and Di Blasi (2004), for the low temperature region, degradation characteristics were qualitatively similar to those observed in pure nitrogen. From a quantitative point of view, the presence of oxygen has been reported to predict and increase the devolatilization peaks: the DTG peaks were about 1.5 times higher than without oxygen. These results have been confirmed by other authors (Amutio et al., 2012; Su et al., 2012). In all these studies of oxidative pyrolysis, small milled samples of biomass were used for the experiments in order to reduce the effects of heat and mass transfer limitations.

At the particle scale, the internal temperature and mass gradients can be significant and transport phenomena need to be taken into account along with kinetics derived from the thermally thin regime studies. The Biot number as defined in Eq. (1) can determine whether or not the temperature inside the wood particle will vary significantly:

$$Bi = \frac{hd}{\lambda} \tag{1}$$

where h is the external heat transfer coefficient, is the thermal conductivity of wood and d is the wood particle diameter.

Bryden and Hagge (2003) defined three regimes of wood pyrolysis using Biot number:

- $Bi < 0.2$, thermally thin regime, the particle temperature is nearly uniform,
- $0.2 < Bi < 10$, thermally thick regime, the internal and external rates of heat transfer are of comparable magnitude,
- $Bi > 10$, thermal wave regime, the internal rate of heat transfer is slow relative to the external rate of heat transfer.

Many studies have reported on the pyrolysis of mm size particle under inert atmosphere (Haydary et al., 2012; Johansson et al., 2007; Larfeldt et al., 2000; Peters and Bruch, 2003; Sadhukhan et al., 2008). The objective of this study was to investigate the effect of oxygen during oxidative pyrolysis of a thick wood particle. As a consequence, we paid particular attention to the influence of the size of the particle, the concentration of oxygen, the heating rate and temperature on oxidative pyrolysis. The second objective of this study was to create a database which can be used to validate a comprehensive model of oxidative pyrolysis or to determine apparent reactivities. Experimental determination of apparent reactivities, which take both intrinsic kinetics and heat and mass transfer into account, offers an appropriate solution to the problem of integrating phenomena at particle scale in a complex reactor model at fixed bed scale (Blondeau and Jeanmart, 2011; Teixeira et al., 2014). Consequently, the research work presented in this paper is also the first step in modelling auto-thermal pyrolysis reactors.

2. Experimental devices and procedures

The samples consisted of cylindrical pine wood particles. Because cylindrical samples are homogeneous in size and composition, they make it easier to obtain repeatable results during experiments than wood chips. Our samples were all 15 mm long. We used three different diameters: 4, 8 and 12 mm to study the influence of particle size on pyrolysis. The orientation of the fibres is parallel to the sample axis. The particle diameter selected was representative of the thickness of wood chips, which has previously been shown to be a characteristic dimension for gasification (Van de steene et al., 2011). The range of diameters was large enough to study the influence of particle size on oxidative pyrolysis. The results of proximate and ultimate analyses of the pine wood used are listed in Table 1.

Two different types of experiments were carried out in this study. For the first, we used a low heating rate thermo-gravimetric (TG) analyser at CIRAD, France. A thermally thin regime occurs during these experiments. For the second type, we used a high heating rate macro-TG apparatus at Mines-Albi, France, making it possible to reach thermally thick regime with $0.2 < Bi < 10$. From additional experiments, we can estimate a Biot number $0.3 < Bi < 7$ for the 400 °C experiments and $0.3 < Bi < 10$ for the 600 °C experiments. Conducting the experiments in a TG apparatus allows us to compare the effect of oxygen on a thick particle with results obtained in the literature at a micro scale, i.e. with milled samples.

2.1. Thermally thin regime experiments

Fig. 1 shows the experimental setup used for the experiments. The mass loss of the sample and the temperature were simultaneously recorded as a function of time. The temperature of the surrounding particle atmosphere was measured a few millimetres below the crucible. The equipment consisted of a micro-balance (Rubotherm), a reactor, a furnace and a thermocouple. The diameter of the reactor was 25 mm. This device made it possible to reach a maximum heating rate of 20 °C/min. Nitrogen 4.5 (99.995% purity) and a mixture 80:20 (80% nitrogen, 20% oxygen) were each connected to a mass flow meter-controller with a range of 0–400 N ml/min enabling control of flow rates of the incoming gas and hence the desired oxygen content in the owing gas. Three oxygen concentrations (0%, 10% and 20%) were

Table 1
Proximate and ultimate analysis of biomass pine wood sample on a dry basis.

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

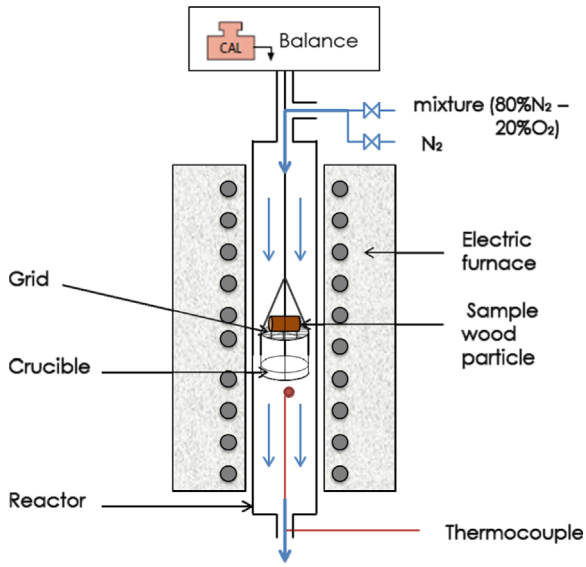

Fig. 1. Schematic diagram of the experimental setup.

tested. The choice of the gas flow rate of 400 N ml/min is discussed below in Section 3.2.2. All measurement of mass loss, temperatures and flow rates were performed by an acquisition system with 0.2 Hz frequency. Thermocouples and flow-meters were connected to an ISK 200 converter/amplifier located upstream from the computer.

Samples were suspended in a grid basket above a crucible in the reactor (see Section 3.2.1). The sample axis is perpendicular to the furnace axis. The crucible had a dual role: it allowed recovery of small fragments that may break away from the particle during conversion and it served as ballast. In the experiments, the samples were heated from room temperature to 120 °C followed by a plateau of 30 min (drying phase), and from this temperature to 800 °C (degradation phase). All the experiments were carried out under a constant heating rate of 20 °C/min.

2.2. Thermally thick regime experiments

The main drawback of the previously described equipment is the low heating rate compared to that used in industrial reactors. Milhé et al. (2013) found a heating rate in the order of 120–180 °C/min in their continuous fixed bed reactor (CFiBR). The apparatus, whose principle is similar to the one depicted in Fig. 1 is described in detail in a previous work (Guizani et al., 2013). In this device, transfer phenomena are more limiting and can affect the pyrolysis conversion.

The macro-TG apparatus consists of three major parts – the heating system including a gas preheater and an electrically-heated reactor, the gas flow control system consisted of two mass-flow meters/controllers and the weighing system that comprises an electronic scale with an accuracy of ±0.1 mg, a stand and a basket to hold the samples. The diameter of the reactor was 75 mm. The temperature was controlled to ensure good temperature homogeneity throughout the furnace. The mass loss was performed by an acquisition system with 10 Hz frequency.

Here, after heating the reactor to the desired temperature (400 °C or 600 °C), the grid basket with the dried sample was rapidly placed in the hot furnace, in less than 15 s, and the sample was pyrolysed. Oxygen content in the reactive gas was adjusted to 0%, 10% or 20%.

A repeatability test was conducted before each apparatus was used. These tests confirmed the good repeatability of the TG curves needed to make this study.

Additional experiments were carried out to measure changes in the temperature inside a thick particle at different radii during the oxidative pyrolysis in both apparatus. Two thin thermocouples of 0.5 mm diameter were inserted 7 mm in the axial direction of a 12 mm particle. One is at the centre of the particle. The second is 2 mm from the lateral surface. Mass loss was not measured at the same time as changes in temperature, because the thermocouples may disturb the mass loss measurement.

3. Results and discussion

3.1. TG and DTG curves

3.1.1. Thermally thin regime experiments

For each experiment, TG and DTG curves were drawn as a function of temperature. TG curves represent the ratio of the sample weight (m) to the initial weight (m_i) after drying. To analyse and to compare the results, DTG curves were numerically obtained using the time derivative of the TG curves. As the noise of the mass signal is amplified by derivation, DTG curves were numerically smoothed using the moving average technique with a filter width $n=10$. Typical examples of TG and DTG for oxidative pyrolysis are shown in Fig. 2. In an oxidative environment, three steps were identified in the TG and DTG curves, as reported in the literature (Amutio et al., 2012; Shen et al., 2009; Su et al., 2012). These were defined as dehydration, oxidative pyrolysis and char oxidation.

To compare experimental results concerning the oxidative pyrolysis step, Su et al. (2012) defined several temperature indexes as shown in Fig. 2. "T_s" is the start temperature, "T_e" is the end temperature and "T_p" is the peak temperature of the oxidative pyrolysis phase. Two other indexes were defined as the pyrolysis reactivity index "$R_p=(d(m/m_i)/dt)_{max}$" and the average reaction rate "R_e" defined as the ratio of mass loss fraction to time with respect to the temperature range [T_s–T_e].

3.1.2. Thermally thick regime experiments

TG and DTG curves were drawn as a function of time. In this case, the noise in the TG curves is higher because of the discontinuities observed in the experimental mass loss curves, which are discussed in detail in Guizani et al. (2013). These discontinuities are one consequence of the balance. In our case, TG and DTG curves were numerically smoothed using the polynomial smoothing technique in a least-squares sense. For the TG curves, a filter width $n=150$ was used. The derivative of the TG curves was calculated using the smoothed TG curves and then DTG curves are smoothed with a filter width $n=50$.

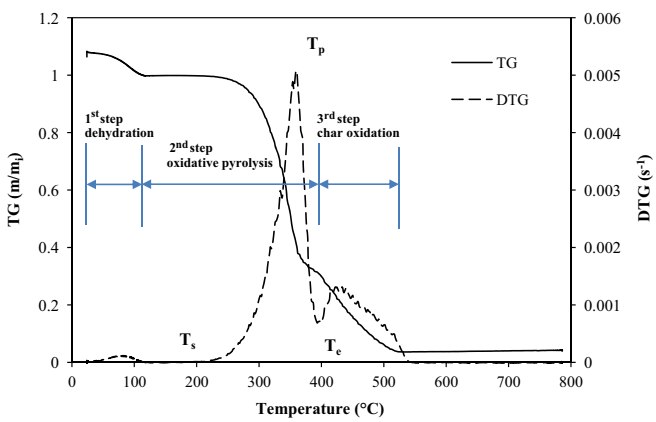

Fig. 2. TG and DTG of oxidative pyrolysis.

3.2. Experimental calibrations

3.2.1. Effect of the crucible

The presence of a crucible can influence the degradation of samples in TGA experiments. Indeed, if the particle is placed directly in the crucible, the sweeping gas cannot reach the entire surface of the particle. With respect to heat and mass transfer, there is thus a risk that the thermochemical situation is not that of the isolated particle. So, to observe the effect of the crucible on pyrolysis, a grid basket was designed and installed in each apparatus.

Thermally thin regime experiments. Two experiments were carried out with a particle diameter of 4 mm in an atmosphere with 10% O_2 v/v. In the first experiment, the sample wood particle was placed in the crucible, and in the second experiment, the wood particle was placed on the grid basket. The results are shown in Fig. 3. It can be seen that the difference between the two experiments was not negligible: the curves shifted to the low temperature range, and oxidative pyrolysis reactivity (first peak of DTG) increased when the grid basket was used. In this case, we can say that degradation of the biomass sample was limited by external transfer phenomena due to crucible.

Thermally thick regime experiments. Similar tests were performed in the apparatus in which the particle was placed on a grid basket above the crucible. The same effect was observed as in the thermally thin regime experiments. As a consequence, a grid basket was used for both devices.

3.2.2. Determination of the sweeping gas flow

In experiments under inert atmosphere, the gas flow rate has no influence on the degradation process. However, in an oxidative atmosphere, the sweeping gas flow rate has to be high enough to avoid limiting oxygen transfer to the particle surface.

To determine the minimum flow rate in the thermally thin regime macro-TG apparatus, four tests were carried out with a varying gas flow rate: 50, 250, 400 and 800 N ml/min. A particle diameter of 12 mm and an oxygen concentration of 10% were used. The results in Fig. 4 show that above 400 ml/min, varying the gas flow rate had no influence on the TG and DTG curves. We can thus consider that above this value, the gas flow rate does not affect degradation. This justified the choice of a sweeping gas flow rate of 400 ml/min for the tests. Additional tests were carried out to determine the flow rate in the thermally thick regime apparatus and a gas flow rate of 10 N l/min was chosen for this type of tests.

3.3. Effect of oxygen on conversion

The oxygen fraction had a significant influence on pyrolysis kinetics of wood particles. Fig. 5 shows the thermogravimetric

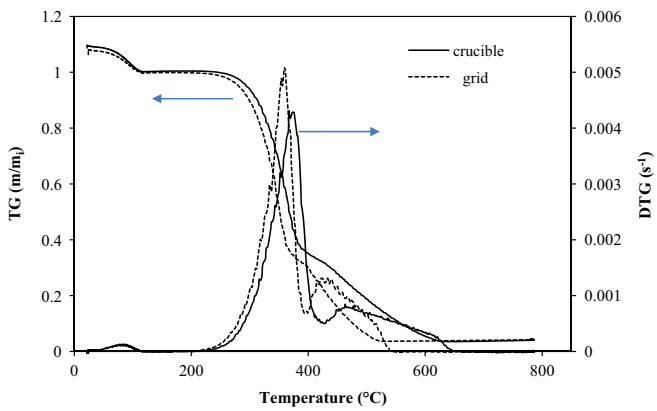

Fig. 3. Effect of the crucible on pyrolysis.

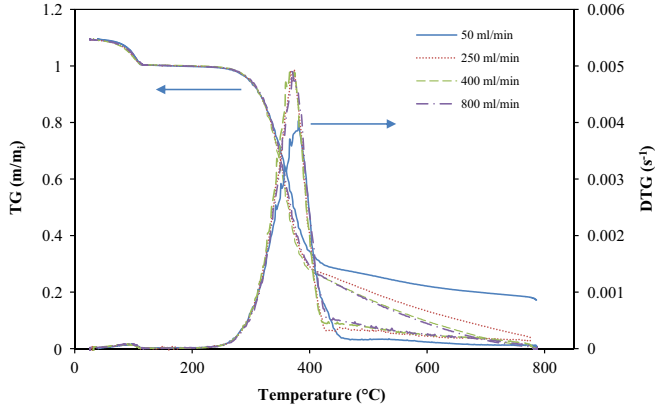

Fig. 4. Influence of sweeping gas flow rate with an oxygen concentration of 10%.

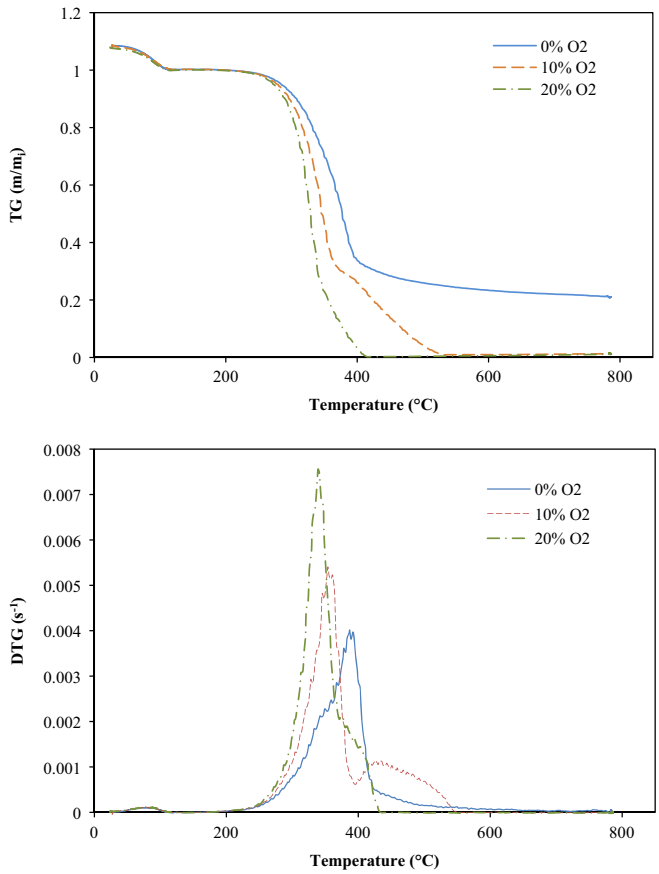

Fig. 5. Influence of oxygen concentration on conversion of 4 mm particles at low HR.

mass change curve (TG) and the derivative thermogravimetric curve (DTG) under different atmospheres (inert, 10% and 20% vol% O_2), for the 4 mm diameter particles, as a function of temperature, from thermally thin regime experiments. Characteristic pyrolysis parameters, as described in Section 3.1, are summarized in Table 2 for all particle sizes and atmospheres. We observed that the oxidative pyrolysis phase occurred in a lower temperature range when the oxygen concentration in the sweeping gas was increased, as shown by the decrease in T_s, T_p and T_e. For example, for the 4 mm particles, T_e was about 421 °C under inert atmosphere and about 374 °C in a 20%O_2 atmosphere, i.e. 47 °C lower. This difference increased with an increase in the size of the particle. For example, for the 12 mm particles, T_e was about

Table 2
Characteristic parameters of pyrolysis under different conditions, in the low HR experiments.

Parameters		T_s (°C)	T_e (°C)	T_p (°C)	R_p (s^{-1})	R_e (s^{-1})
4 mm	Inert	218	421	392	0.004	0.00113
	10%O_2	209	396	354	0.0053	0.00166
	20%O_2	208	374	339	0.0074	0.00171
8 mm	Inert	216	463	391	0.0038	0.00098
	10%O_2	213	412	363	0.0048	0.00123
	20%O_2	209	391	350	0.006	0.00146
12 mm	Inert	221	472	394	0.0037	0.00097
	10%O_2	221	421	368	0.005	0.00123
	20%O_2	221	399	356	0.0065	0.00149

472 °C under inert atmosphere and 399 °C in a 20%O_2 atmosphere, i.e. 73 °C lower.

Moreover, the DTG peak of the oxidative pyrolysis phase, which represents the maximum reaction rate, was higher when the oxygen concentration increased. In a 20%O_2 atmosphere, the maximum reaction rate was about 1.5 times higher than under inert atmosphere as can be seen by comparing the R_p values in Table 2. Our results are in a good agreement with those in the literature (Amutio et al., 2012; Anca-Couce et al., 2012; Branca and Di Blasi, 2004; Chen et al., 2011; Su et al., 2012), where the same effect of increased DTG peak was observed which an increase in the oxygen concentration. Ohlemiller, cited in Carvalho et al. (2002), explained that the oxidative pyrolysis phase consists of two reactions: wood pyrolysis and wood oxidation, as wood oxidation is exothermic, it speeds up pyrolysis.

Woody biomass has three main components, hemicellulose, cellulose, lignin and smaller amounts of extractives and ash (Burhenne et al., 2013; Carrier et al., 2011; Gao et al., 2013; Ranzi et al., 2008). Branca and Di Blasi (2004) and Grønli (1996) linked the shoulder that appears at the beginning of the DTG curve with hemicellulose degradation and the peak with cellulose degradation. Under inert atmosphere, our results (Fig. 5) show that the pyrolysis of hemicellulose mainly occurred between 220 °C and 340 °C and the pyrolysis of cellulose between 340 °C and 410 °C. These results are in good agreement with those of Yang et al. (2007). In an oxidative atmosphere, our results revealed a less clear hemicellulose shoulder than under inert atmosphere. Anca-Couce et al. (2012) put this down to an overlap of the cellulose and hemicellulose peaks, causing a higher maximum reaction rate in presence of oxygen.

3.4. *Effect of particle size on conversion*

Fig. 6 shows TG and DTG curves for the different particle diameters in the two atmospheres, 0% and 20% O_2, for the thermally thin regime experiments. Generally, particle size had no significant influence on the oxidative pyrolysis phase at a heating rate of 20 °C/min in this range of diameters. This can be explained by a slow heating rate and the particle temperature is nearly uniform. Fig. 6 shows a short delay in the TG and DTG curves with an increase in the diameter of the particle. For example, T_e increased from 374 °C to 391 °C and 399 °C for the particle sizes 4 mm, 8 mm and 12 mm, respectively, in an atmosphere with 20% O_2. When R_p and R_e are compared between the results obtained with 4 mm and 12 mm particles, the differences are more significant. In the case of a 4 mm particle, two peaks appeared in DTG curve revealing the oxidative pyrolysis and char oxidation. The characteristic parameters are similar to those reported by Su et al. (2012) for intrinsic kinetics. Table 2 also shows that, under the same atmosphere, the maximum reaction rate (R_p) was the same for the three particle sizes. In the oxidative environments, smaller R_p were obtained.

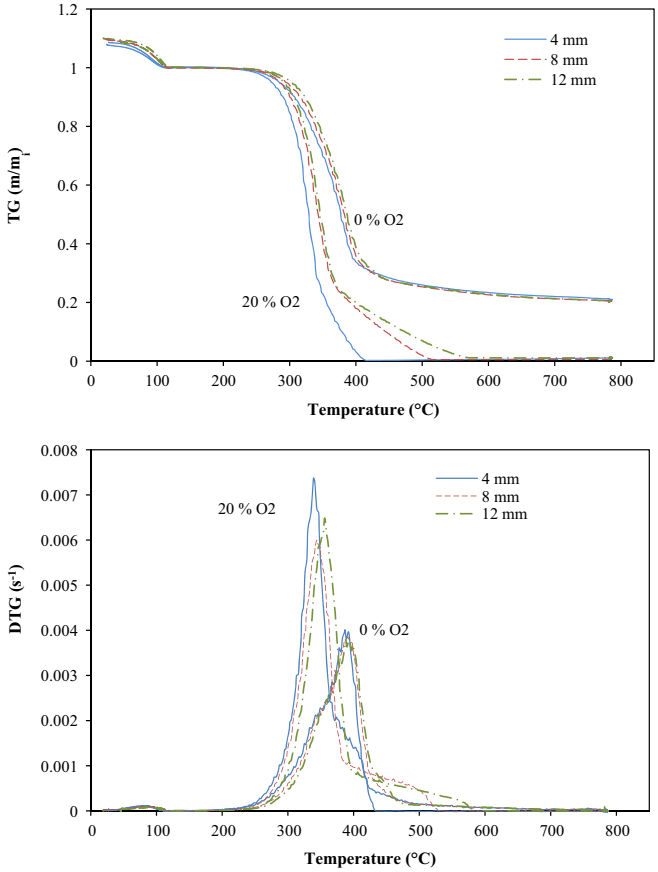

Fig. 6. Influence of particle size on conversion under inert atmosphere and in an atmosphere with 20% O_2 at low HR.

From the literature, we can deduce, that particle size has a significant effect on thermo degradation behaviour at high heating temperatures (Di Blasi, 2008) corresponding to a higher Biot number greater than 0.2. In order to demonstrate the effect of particle size on oxidative pyrolysis, thermally thick regime experiments were performed using the Mines-Albi Macro-TG apparatus with $0.2 < Bi < 10$. Figs. 7 and 8 show the results obtained at furnace temperature of 600 °C and 400 °C in the different atmospheres and with the 4 and 12 mm diameter particles, respectively. In contrast to previous experiments, the particle size had a significant effect on conversion. At a furnace temperature of 600 °C, the reaction kinetics slowed down with an increase in the particle diameter. Conversion time for 12 mm particles was around twice that of that required for 4 mm particles. The same qualitative results were obtained by Haydary et al. (2012) with tire particles with diameters ranging between 4 and 8 mm. In the experiments at 400 °C, the conversion time was twice longer than at 600 °C. In addition, the DTG curves show that the peak was smaller when the particle size was increased. In the experiments at 600 °C, the peaks were about three times smaller for 12 mm particles than for 4 mm particles. At 400 °C, DTG peaks were obtained that were about 2–3 times smaller than those obtained at 600 °C, and the peaks for 12 mm particles were about 1.5 times smaller than for 4 mm particles. When the thermally thick regime occurs, heat and mass transfer limitations have a significant impact on conversion and logically, the impact is higher when the particle size is increased and the Biot number increased. Also the oxidation could lead to a higher porosity and thus a better mass transfer.

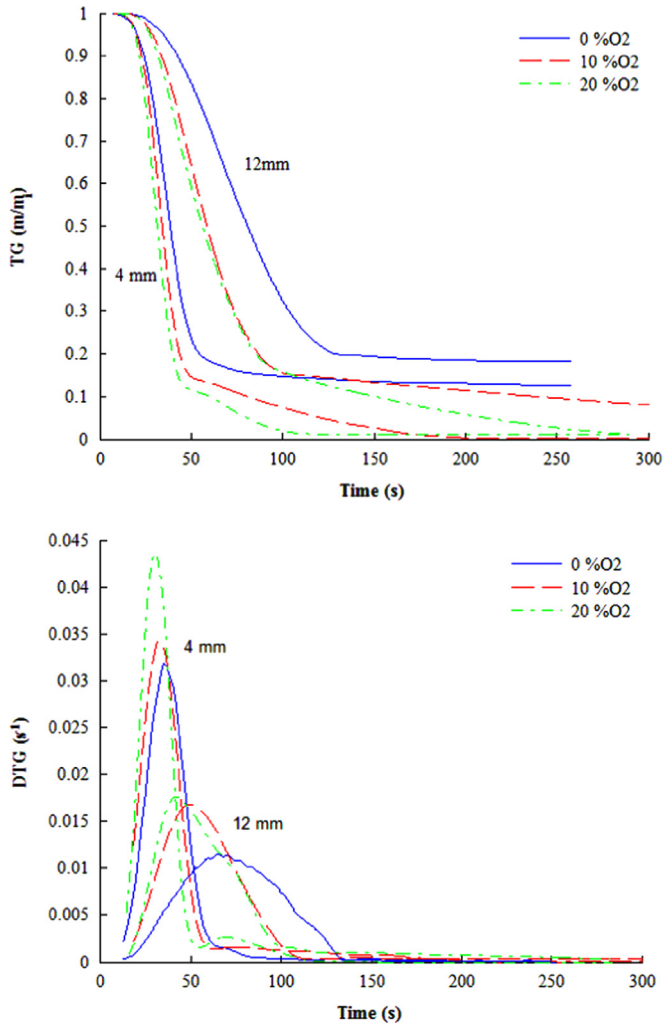

Fig. 7. High HR results at a furnace temperature of 600 °C: influence of particle size on thermal degradation in different atmospheres.

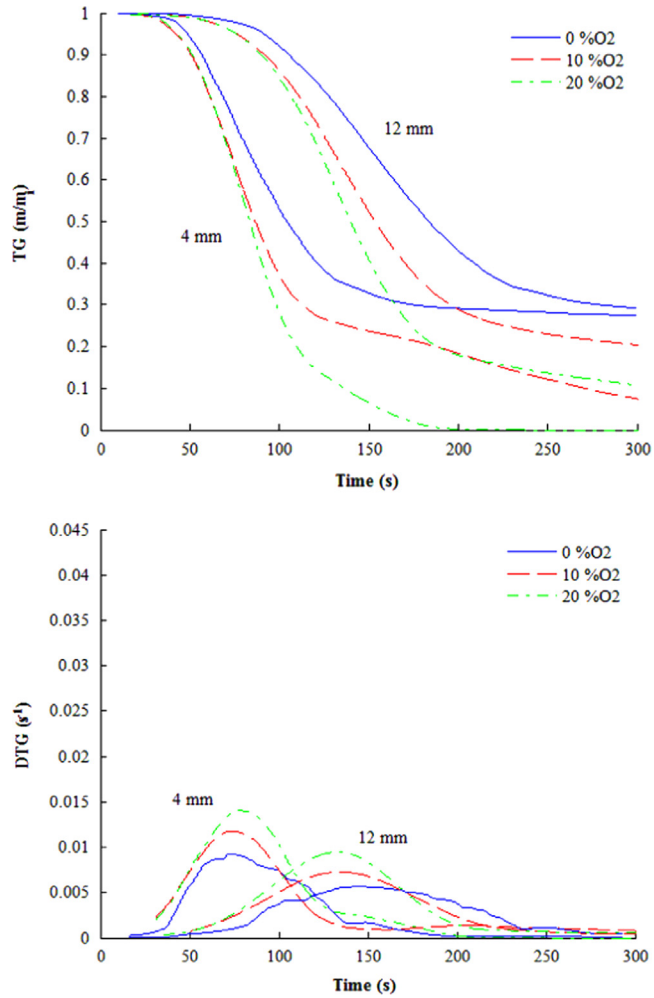

Fig. 8. High HR results at a furnace temperature of 400 °C: influence of particle size on thermal degradation in different atmospheres.

3.5. *Temperature changes inside a thick particle*

In this section, we present the results of temperature measurements inside a 12 mm thick particle in the two types of experiments, thermally thick and thermally thin regimes. Figs. 9 and 10 show the measured temperature profiles at the centre of the particle and at a distance of 2 mm from the lateral surface of the particle in an atmosphere with 10% O_2: Fig. 9 shows the thermally thin regime experiment with a heating rate of 20 °C/min and Fig. 10 shows the thermally thick regime experiment at 600 °C.

For the thermally thin regime experiment, the temperature first increased until it reached an inflexion point at the end of oxidative pyrolysis phase, then increased strongly until it reached a small plateau. Subsequently, the temperature increased linearly throughout the char oxidation phase. During the oxidative pyrolysis phase, the particle was isothermal. At the end of oxidative pyrolysis a difference between the two temperatures appeared, and a difference of 30–40 °C was observed during char oxidation. In Fig. 9, the centre temperature exceeds the surrounding temperature at a certain time during the final phase of oxidative pyrolysis. This can be explained by the exothermic reactions from the pyrolysis degradation contribution (Larsen et al., 2006; Park et al., 2010) or from the oxidative reactions contribution.

Park et al. (2010) showed that the temperature profiles during pyrolysis in inert atmosphere, inside a spherical wood particle, can be divided in two distinct sequential thermal regimes. The first

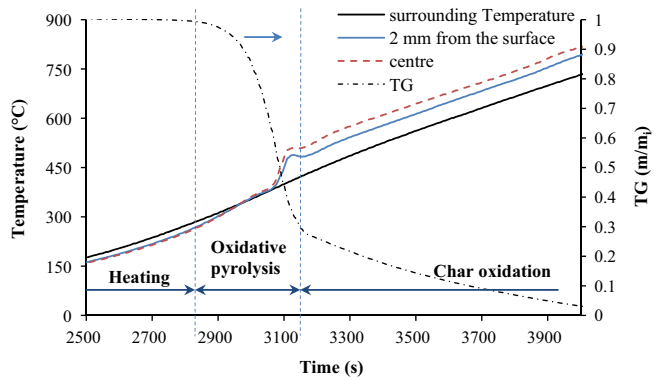

Fig. 9. Temperature profile inside a particle with a diameter of 12 mm and TG curve for an atmosphere containing 10% O_2 in the low HR apparatus.

one is an endothermic reaction that causes a plateau of temperature at the particle centre. The second is exothermic reaction that causes a steep temperature increase after the plateau. The exothermic period corresponds to the conversion of the intermediate solid to final char. Solid mass show a weak decrease during this "exothermic period". Larsen et al. (2006) confirmed this point, by saying that the observed rise in temperature can be a consequence of an exothermic reaction during the pyrolysis phase. Figs. 11 and 12, for the thermally thin and thick regimes respectively,

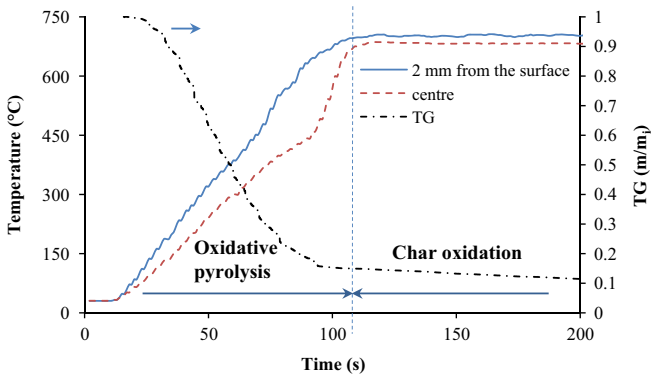

Fig. 10. Temperature profile inside a particle with a diameter of 12 mm and TG curve in an atmosphere containing 10% O_2 at 600 °C in the high HR apparatus.

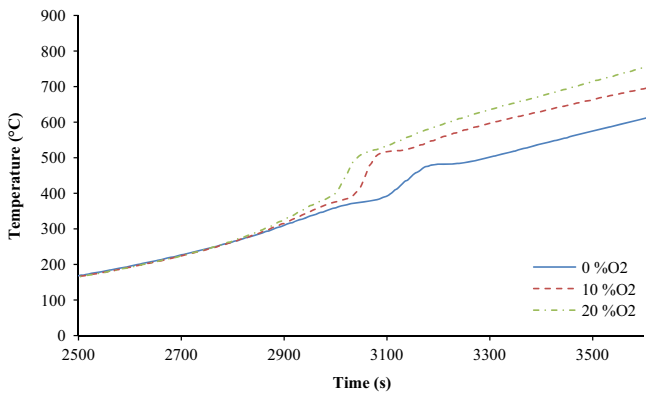

Fig. 11. The centre temperature in the three different atmospheres for a 12 mm particle in thermally thin regime.

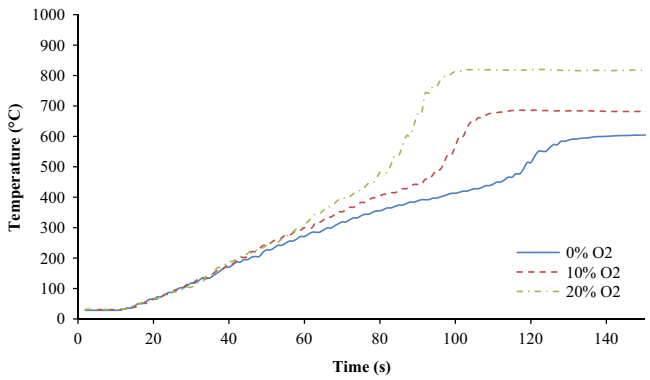

Fig. 12. The centre temperature in the three different atmospheres for a 12 mm particle in thermally thick regime at 600 °C.

show the contribution of the oxygen to the exothermic reactions, by comparing temperatures at the centre in inert and oxidative atmospheres. Oxygen has a major contribution to the exothermic reaction period. The maximum temperature at the centre, at the end of the oxidative pyrolysis phase, is about 480 °C for inert atmosphere, 520 °C for 10% O_2 and 530 °C for 20% O_2, for the thermally thin regime experiments.

For the thermally thick regime experiment, the temperature first increased until it reached an inflexion point around $t = 70$ s, then increased strongly until it was higher than the furnace temperature: overheating of the particle was also observed for the thermally thick regime experiments. The oxygen had also, in this case, a major role on the exothermic reactions. As we can see from Fig. 12, the maximum temperature is about 590 °C in an inert atmosphere, and 685 °C and 820 °C when respectively 10% and 20% of O_2 are injected. The heating rates at the centre of the particle were estimated to be 350 °C/min, and at a distance of 2 mm from the lateral surface of the particle, to be around 400 °C/min. Significant differences between the two thermocouples were recorded. This confirms the strong transfer limiting phenomena in the case of the thermally thick regime when $Bi > 0.2$ from the beginning of the experiment. The rise in temperature at the end of oxidative pyrolysis phase appears clearly in the centre of the particle and less at 2 mm from the lateral surface. It could be observed inside the particle thanks to the limitation of internal heat transfer of the particle which delayed the temperature increase caused by external heat transfers, below the ambient temperature.

4. Conclusions

The aim of this work was to analyse the influence of oxygen concentration, particle size and temperature on oxidative pyrolysis of wood, using two different Macro-TG apparatuses capable of operating with thermally thin and thick regime.

Preliminary experiments showed that placing the particle in a crucible influenced the degradation of the sample as it limited by heat/mass transfer, so a grid basket was used to hold the particle instead. In an oxidative atmosphere, a minimum sweeping gas flow was determined to prevent O_2 availability limiting the conversion.

At a heating rate of 20 °C/min, thermally thin regime can be assumed even for particle until 12 mm diameter.

Thermally thin regime experiments revealed that oxygen has a significant influence on oxidative pyrolysis. We observed that the peak of wood pyrolysis was higher and appeared at a lower temperature when the oxygen concentration was increased. In oxidative pyrolysis, the hemicellulose degradation shoulder was less clear than under inert atmosphere.

Thermally thick regime experiments, with $0.2 < Bi < 10$ highlighted the effect of particle size on oxidative pyrolysis. The oxidative pyrolysis phase was slower with bigger particles. For example, at a furnace temperature of 600 °C, the 12 mm particle took twice as long to complete the oxidative pyrolysis phase than the 4 mm particle. In addition, the peak in the DTG curve was about 3 times smaller for the 12 mm particles than for the 4 mm particles. At a furnace temperature of 400 °C, the effect of particle size was qualitatively the same as at 600 °C.

The temperature measurements at the centre of a thick particle and close to the lateral surface of the particle showed that heat transfer was only limited when thermally thick regime occurs. In addition, we highlighted the high exothermicity of the wood oxidative pyrolysis in both thermally thin and thick regimes.

These experimental results on the evolution of the conversion rate and of the temperature inside the particle are original and should facilitate the development of numerical models of the oxidative pyrolysis of biomass particles.

Nomenclature and units

λ	sample conductivity (W/m K)
d	sample diameter (m)
h	heat transfer coefficient (W/m^2 K)
LHV	lower heating value (MJ/kg)
m	sample weight (kg)
m_i	initial sample weight after drying (kg)
R_e	average reaction rate (s^{-1})
R_p	pyrolysis reactivity index (s^{-1})
t	time (s)

T_e	end temperature (°C)
T_p	peak temperature (°C)
T_s	start temperature (°C)
Bi	Biot number
TG	thermogravimetric mass change curve
DTG	derivative thermogravimetric curve
HR	heating rate

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