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Thick wood particle pyrolysis in an oxidative atmosphere

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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.

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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 thermogravimetric 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 autothermal 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