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Experimental investigation on the smouldering of pine bark

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HIGHLIGHTS

- Heat dissipation is the key to trigger and support smouldering.
- Air permeation through the biomass bed controls the smouldering.
- Study on tens of grams of biomass.
- The geometry of the biomass bed is crucial.
- Tests under flow, to control the O_2 content and measure emission.

ARTICLE INFO

ABSTRACT

We investigated the pine bark spontaneous reactivity in oxidant atmosphere, and its self-heating development in laboratory tests on samples in the tens of grams range. Smouldering has been triggered and sustained by limiting the biomass heat dissipation. Tests in an oven (uncontrolled ambient composition, imposed ambient temperature) were first carried out to screen the effect of different parameters, including particle size, amount of material, moisture content, material compaction, heating rate, and storage geometry, on the onset and development of smouldering. The thermal ignition of pine bark was observed starting from 190 °C. Experiments carried out in a flow tubular reactor (imposed ambient temperature and composition) were also carried out. The main produced gases analyzed under different ignition conditions, and concentrations of CO, CO_2, H_2 and O_2 were measured and discussed. The flow results indicated that pine bark evolves into smouldering supported by a minimum oxygen concentration, at low enough fluxes to limit the material cooling due to convection. Finally, the ratio CO/CO_2 monitored identifies different oxidation stages during the smouldering process.

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1. Introduction

The environmental and strategic issues associated with an energy based on fossil fuels require their substitution with renewable sources in the power generation processes. Among all renewable energy sources, biomass can be the largest contributor to the primary global energy supply. Lignocellulose-based biomass is one of the most abundant biomass resources on earth. It is available in a number of different forms, but wood is the largest family. The wood transformation industry produces several wastes, useful for energy production. Beyond saw-dust, bark is a controversial waste, because of its composition and mechanical properties. Here we focus on pine bark as a common and representative type of bark. It is a lumber transformation by-product. Because of its mechanical structure, pine bark's use as a construction material is limited. Spain is 4th in Europe for forest surface, being 29% of the total surface (5.2 million hectares), dominated by conifers, mainly pine. *Pinus pinaster* is also the tree occupying the most extended area in Europe and Asia, and it is the species with the most extended dissemination in the West of the Iberian Peninsula, where it covers more than 28% of the whole forest surface, and the timber industry is largely (82%) based on pine wood transformation. Others Mediterranean subspecies extend all over Spain and in all the countries located in the Mediterranean area as well [1]. Due to large availability of pine bark on a global scale, there is an increasing interest in its use [2–6]. Transportation, storage and use of biomass require some knowledge of its spontaneous reactivity [7]. A burning rate higher than coal has been reported [8], likely explaining the onset of fires (even explosions) during storage, milling or conveying [7]. That can be even more critical for bark, where the higher ash content may bear catalytically active inorganic species.

Reactivity of a biomass often shows in a subtle form, i.e. the spontaneous smouldering [9]. Smouldering is a slow, low-temperature, flameless combustion, sustained by the heat evolved when oxygen directly reacts on the surface of a condensed-phase fuel (solid or liquid) [10]. Uncontrolled smouldering processes can produce severe damages, mainly when flaming occurs. However, smouldering can be profitably used if carefully controlled. A self-sustaining low temperature combustion could be used to obtain bio-char from biomass plants, to be used as more stable and efficient fuel or in agriculture. Additionally, smouldering has the important advantage of not requiring additional energy because it can be self-sustained by the heat released during biomass oxidation [12]. Recently, the smouldering combustion process has been suggested as a new method potentially useful in the treatment of biosolids [13], and liquid organic contaminants, such as tars, especially as an alternative disposal option or environmental remediation [14].

The smouldering onset and propagation are still poorly understood. It occurs within a solid porous medium which can be a permeable aggregate of particles, grains, or fibers where the fuel is either a combustible component of the porous matrix or a separate substance embedded. The reaction can be self-sustaining in the presence of a sufficient amount of fuel, enough oxygen and limited heat losses. The characterization of smouldering activation is complicated, since the ignition temperature is not a fundamental parameter of the fuel, but it depends on several factors including the sample mass, heating rate of the material, surrounding gas atmosphere, bed porosity, and others [15]. Chen et al. [16] investigated the role of other parameters on the self-sustained propagation of smouldering, in the critical conditions, such as the moisture content, inorganic content, bulk density and the heat of smouldering combustion. The effect of oxygen concentration on biomass smouldering is critical but still poorly investigated [17]. The literature about the role of parameters that certainly affect the smouldering process, including the gaseous atmosphere and produced gases, appears limited [18]. Most experimental investigation are also limited to TGA analysis [7,8], severely simplifying the crucial role of oxygen and heat transport across the bed. The present study aims at investigating the low-temperature ignition of the pine bark and its spontaneous smouldering using laboratory-scale tests at a larger scale (10^1 to 10^2 g), in static or flowing atmosphere. The increase of scale is a need given that the smouldering process is the result of chemical and transport mechanism, where the latter are determined by the geometry. This is a first experimental investigation to explore factors like particle size, amount of material, moisture content, material packing, heating rate, geometry of the storage, air feed flow and oxygen concentration. Flow experiments add information about the gases produced during and after the ignition, under different atmospheres and operating conditions.

2. Materials and methods

2.1. Pine bark

In this work, the material used as reference biomass was a commercial pine bark (PB). Its composition, characterized by high carbon and higher ash content compared to the core wood [19], makes its combustion to differ, because of the special reactivity conferred by inorganics in the ashes. This is also the motivation to focus on bark.

2.2. Characterization of pine bark

The commercial pine bark initially provided in the form of chips (mean size of a few cm) was preliminary milled and sieved in order to collect samples with sufficiently narrow particle size ranges. Specifically, different fractions were collected, with mean particle size <2 mm, between 2 and 4 mm and >4 mm. Pine bark was then physically and chemically characterized: elemental analyses was carried (Fison EA 1108 CHNS) following standard procedures suggested by European technical committees [20]. Composition analysis of pine bark was performed according to TAPPI and Wise methods [21,22]. The determination of the gross calorific value was performed by using a calorimeter pump Phywe LEC-02 model and by following the procedure described in the standard UNE-EN 14918:2011. The proximate analysis was carried out in a thermobalance with an amount of about 50 mg, through a sequence of two steps. A first stage is run in a N_2 atmosphere, from ambient temperature to 800 °C, at a heating rate (HR) of 5 °C/min, to evaluate the moisture and volatile matter. A second stage was under an oxidative atmosphere (air), keeping a constant temperature of 800 °C until total combustion of any organics, to determine the amount of fixed carbon and ashes. Differential scanning calorimetry (DSC) has been carried out to identify the range of temperature where the exothermic reaction should be expected. Test were performed under an oxidative atmosphere (air), from ambient temperature up to 150 °C at HR of 2 °C/min, 1 h isothermal, further heating at the same HR up to a final temperature of 500 °C.

2.3. Experimental set-up

In the present work two experimental techniques have been used to investigate the onset of pine bark smouldering. Specifically, they involved (i) a standard laboratory oven and (ii) a flow tubular reactor. The two experimental configurations are sketched in Fig. 1.

With the former, pine bark samples were loaded in gas-permeable containers and arranged inside an oven (Fig. 1, above). It is known that smouldering phenomena, even those ones triggered by an external heat source, are the result of a thermal balance between the heat provided to the sample, or generated by the biomass combustion, and the amount of heat lost, because of thermal dispersions. Therefore, the oven allowed to keep the ambient around the sample at a fixed temperature, initially controlling the heat transferred to the biomass, and required to activate the onset of smouldering; afterwards, the oven limits the heat losses from the biomass when the sample temperature increased as a result of the smouldering ignition.

We carried out a variety of tests using the oven, specifically analyzing the temperature of a stagnant air atmosphere required to activate the pine bark smouldering. The standard conditions in the oven experiments are: 45 g (approx.) of sample, with a particle size <2 mm and a heating rate of 2 °C/min. Modifications of these conditions to investigate the effect of individual variables are specified in the following. Basically, these tests allowed to study the onset of smouldering under conditions comparable with a large scale biomass storage, assuming to reproduce the thermal inertia of a large amount of biomass by means of the oven. The gas-permeable containers were square or cylindrical in shape, made with an aluminum net having mesh size equal to 0.5 mm. Two thermocouples (TCs) were used to record both sample temperature and gas temperature inside the oven. The gas temperature in the oven was regulated by a third TC, placed below the container, quite close to the oven wall. Note that the oven atmosphere could not be controlled, since it is not gastight. Different thermal policies were applied to heat up the biomass sample, increasing the oven temperature at different heating rates, from room temperature up to 250 °C. When the sample temperature increased above 250 °C, the oven was automatically switched off. The onset of smouldering was conventionally defined as the point where the temperature of the sample overcomes that of the gas atmosphere in the oven.
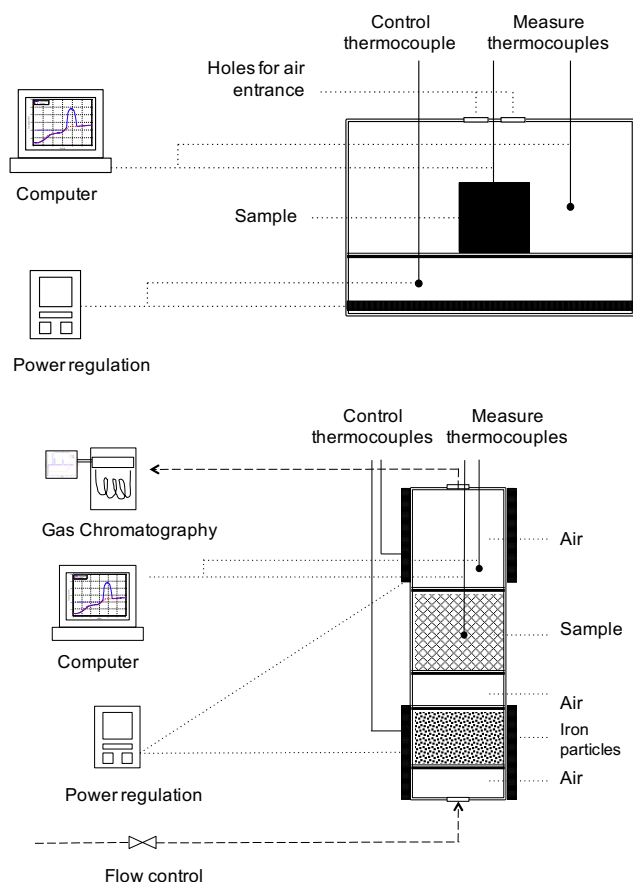
Fig. 1. Schematic representation of oven (above) and flow tubular reactor (below) arrangements.

The second configuration is a flow tubular reactor, with a controlled gas flow passing through a packed bed of biomass as a powder. The height of the reactor was 360 mm with an inner diameter of 40 mm. The biomass was arranged in the middle. The sweeping gas, typically carrying oxygen, was fed from the bottom side of the reactor. A metal grid was used to held the sample within the reactor, preserving the gas flow permeability through the biomass. The reactor was externally heated by two belt-type heating resistances, both upstream and downstream to the bed. An additional packed bed of iron particles was arranged upstream (i.e. below) the biomass sample in order to prevent both gas composition and thermal gradients along the radial direction in front of the biomass sample. The flow configuration allowed to perform experiments with different gas feed composition, and to monitor the gas composition at the exit of the reactor.

The weight of samples used for all tests in the flow reactor was approximately 10 g. Temperatures of sample mass and of the gas downstream the packed bed were monitored with thermocouples positioned within the core of the biomass powder, and in close proximity of the gas stream exit, as shown in Fig. 1 (below). The thermal policy was similar to the one used during the experiments in the oven, applying a single ramp up stage up to 250 °C at different heating rates, varying from 2°/min up to 10°/min. Gas products have been analyzed by gas chromatography (Agilent 6890), with both thermal conductivity (TCD) and flame ionization (FID) detectors, using a PoroPakQ and a Molsieve 5A column in series, to simultaneously measure hydrocarbons and permanent gases (e.g. CO). The carrier gas for the analysis was He. A condenser and two fiber filters were placed after the reactor to obtain a clean

and dry gas stream entering the GC. In this procedure, the onset of smouldering was defined by means of the significant change in the slope of the pine bark temperature curves.

Reproducibility of the temperature measurements in the smouldering tests proved to be excellent, both in the oven and in the reactor (see Supplementary Material, Fig. SM-1).

3. Results

3.1. Characterization of pine bark

Raw pine bark was analyzed in order to evaluate its main physical-chemical properties. Elemental and composition analysis and the heating value were obtained, as reported in Table 1. The proximate analysis of raw pine bark was obtained in a thermobalance, through a two steps-method: during a first stage, in inert (N_2) atmosphere, the moisture and volatile matter were quantified; then, the percentage of ashes and fixed carbon was measured, concluding the same test under an oxidative atmosphere (air). The weight loss profile is reported in Fig. 2; the four proximate analysis components and the temperature at which the gas has been switched are highlighted.

The major loss occurs between approx. 200 and 800 °C, corresponding to the volatile matter decomposition, whose amounts is approximately 58.8%, in agreement with Literature [23,3]. This value is very important in the material ignition, as the volatiles release supports their combustion, thus increase the particle surface temperature. Switching to air at 800 °C causes the fixed carbon to burn completely (slightly increasing the Set temperature).

The onset of pine bark oxidation was analyzed by DSC, now in a constant air atmosphere, up to 500 °C. Results are shown in Fig. 3.

Three consecutive stages can be observed, indicated by numbers in Fig. 3. First, the endothermic stage, of about $\Delta H = 0.31$ MJ/kg$_{initial\ biomass}$, consistent with an estimate of 13% of moisture, slightly higher the 11.3% measured by TGA. Two exothermic steps follow, due to combustion of cellulose first, and less reactive components (e.g. lignin) later. In oxidative atmosphere, it is likely that also char oxidation could trigger at approx. 400 °C [11]. The combustion enthalpy measured, 10.3 MJ/kg$_{initial\ biomass}$ is comparable to similar measurements (6.1 and 6.5 MJ/kg reported) for pine wood [12,24]. The value remains much lower than the heating values measured by calorimetric pump, and reported in Table 1, suggesting that total oxidation was not achieved below 500 °C. The exothermic processes begin at approximately 150 °C, within the DSC (i.e. mg samples), at 2°/min of HR. It suggests that the spontaneous ignition of pine bark cannot be lower than 150 °C, at comparable HR and expected appreciable

Table 1
Characterization of pine bark.

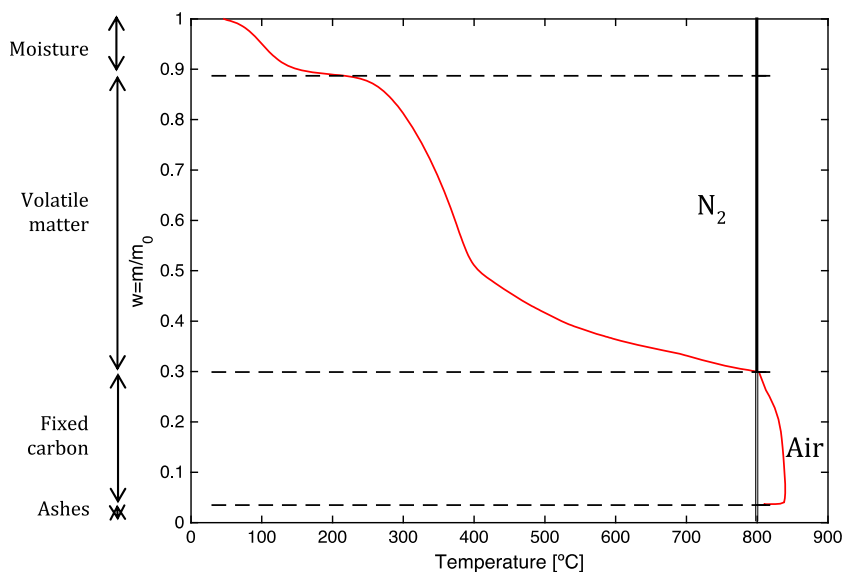| Parameters		Results
Elemental analysis	Carbon, %	42.06
	Hydrogen, %	6.88
	Nitrogen, %	0.37
	Sulfur, %	0.00
	Oxygen, %	50.69
Fibers analysis	Hot water soluble compounds, %	15.95
	Ethanol-benzene extractives compounds, %	2.47
	Lignin, %	37.52
	Holocellulose, %	48.06
Heating value	Gross calorific value, MJ/kg	18.98
Proximate analysis	Moisture, %	11.30
	Volatile matter, %	58.80
	Fixed carbon, %	26.40
	Ashes, %	3.50

Fig. 2. Proximate analysis of pine bark from a two-stages TGA; the switch between N_2 and air is identified by the vertical line and the four component fractions are identified by horizontal.
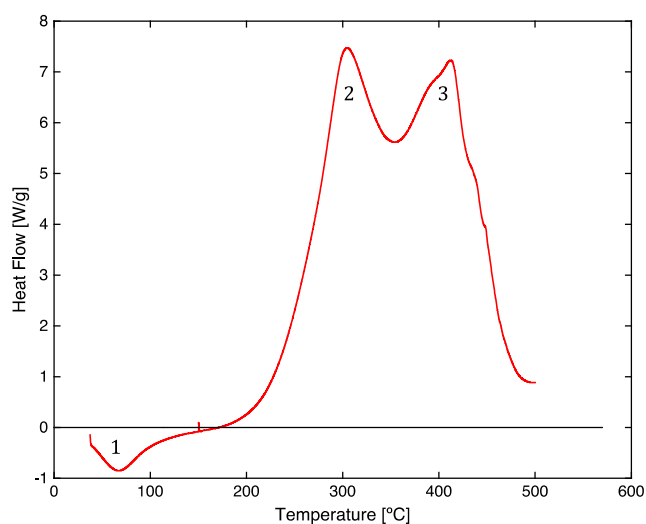

Fig. 3. Low to medium temperature DSC of pine bark in air.

above 200 °C. This result has been confirmed by the experiments in the following, on much larger amounts. The result agrees with [12], where a higher heating rate and pine wood were used, and with [15] where they measured the ignition temperature at 220 °C for wheat straw, 235 °C for poplar wood, and 285 °C for eucalyptus wood, in TGA at 5°/min. DSC shows residual oxidation activity at 500 °C, because of a low heating rate, too weak to self-support that temperature in smouldering experiments. Summarizing, the pine bark has properties comparable to similar woody biomass [12,15,25], but shows a higher propensity to oxidation, possibly due to the higher ash content, that may act catalytically to reduce the activation energy of the oxidation.

3.2. Uncontrolled gas atmosphere (oven) experiments

The first set of experiments was carried out in a standard oven, not gastight enough to control the composition of the atmosphere surrounding the biomass samples (Fig. 1, above). In this configuration, the air (i.e. the O_2 carrier) flows through the packed bed of

pine bark was driven only by natural convection. Therefore, when the smouldering starts, the consequent increase of the sample temperature causes the entrapped air to escape because of the lower density; in turn, that induces a depression in the porous matrix that calls for an influx of gas from the surrounding atmosphere, that permeates through the packed bed porosity. A number of parameters are known to affect the smouldering process as well as the temperature at which this phenomenon triggers. Factors include the sample mass, particle size, volatile matter yield, bed geometry and porosity, oxygen concentration [12,26,27]. Moreover, these variables are closely interrelated so that their interactions affect the smouldering behavior of the biomass in a complex way, as well as the experimental conditions at which smouldering is investigated. The effect of several parameters was studied to clarify the onset and progress of the smouldering process. Specifically, ignition temperature and the biomass thermal behavior after the ignition were analyzed and correlated with the above mentioned factors. All the experiments in the oven were carried out in a square box (sides = 6 cm) with approx. 45 g of biomass, unless otherwise specified.

3.2.1. Particle size

In determining the activation temperature of pine bark smouldering, the particle size is expected to be an important factor. In heterogeneous, gas-solid reactions the rate depends on the accessible solid surface per unit volume (of the solid particles or of the porous bed) involved in the reaction. Therefore, in the oxidation of pine bark powder it is expected that the lower the particle size, the higher the reaction rate. That may affect the onset of smouldering and the following rate of increase in the sample temperature. Fig. 4 (left) shows the pine bark temperature profile as a function of time compared with the temperature evolution of the gas atmosphere inside the oven.

Note that the solid temperature is referred to the core of the biomass bed. During the first heating phase, the material temperature is lower than the one in the oven, because moisture evaporates absorbing the required heat of vaporization. Once the pine bark has stably reached 150 °C down to its bed core, and moisture has been completely released, the oven temperature is raised further, at a constant HR, until triggering the pine bark smouldering, as clearly identified by the temperature of packed bed that raises
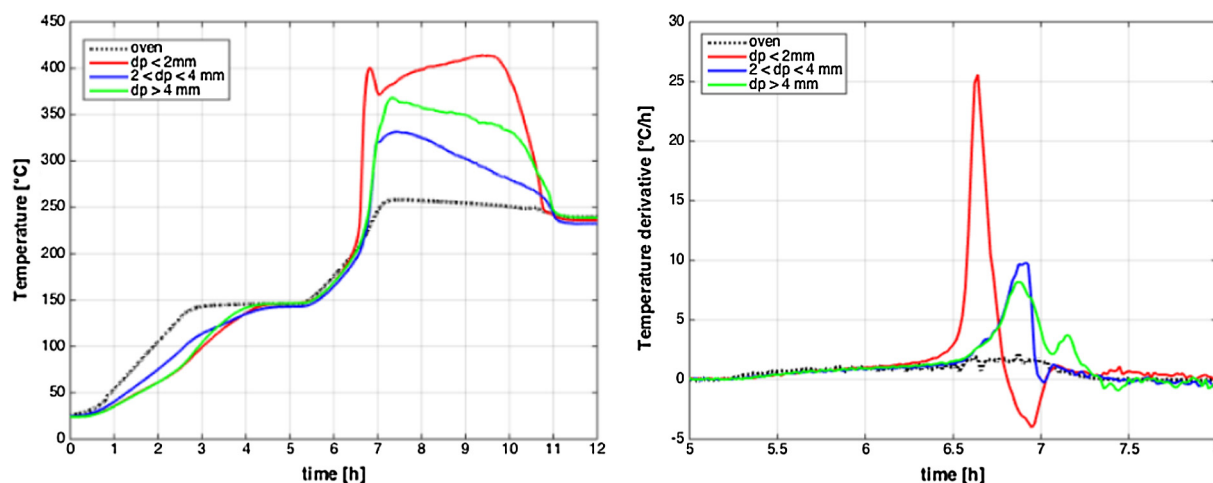
Fig. 4. Temperature evolution (left) and its time derivative (right). Pine bark samples with different particle size in a static atmosphere (oven).

above the set point temperature of the oven. Derivatives reported in Fig. 4 (right) point out that the spontaneous ignition of pine bark with smallest particle size (average dp < 2 mm) occurs at a significantly higher rate compared to samples having larger particle size. Considering the maximum in the derivatives, we estimate a doubling in smouldering rate by halving the average particle size. We also observe that with sample at dp < 2 mm, smouldering clearly activates at lower temperatures, approx. 20 °C less compared to the larger particle size samples. However, the difference is not so large, because the small, medium and large particle size ranges used were not differing by orders of magnitude. To check how representative are the measurements, these tests were duplicated, proving an excellent reproducibility (see Supplementary Material, Fig. SM-1).

Results are consistent with Literature. He et al. [26] reported that the maximum temperature in the fuel (corn stalk, pine trunk, pyrolysis char and activated char from corn stalk) increases with decreasing particle size, apparently thanks to a better thermal insulation of the fuel (ash) bed for finer particles. They also noticed that the velocity of the char oxidation front is not affected by the particle size. Also Torrent et al. [28] observed in TGA and DSC a strong correlation between ignition temperature and particle size as well, confirming that the smaller the size, the higher the specific surface and the lower ignition temperature, so that more reactive the material appears. Nevertheless, our original contribution is a larger scale demonstration, which goes beyond concerns of representativeness of TGA, typically based on mg samples. Additionally, it is closer to real scale processes which are more reasonably affected by heat and mass transfer mechanisms similar to those ones occurring in our experimental configurations.

The correlation between particle size and ignition temperature for pine bark smouldering appears nonlinear. It suggests that other factors may affect the triggering of smouldering much more significantly. The sample size may be one of these factors. It is investigated in the next section.

3.2.2. Sample amount

The sample amount affects the heat transfer mechanisms that, beyond the smouldering ignition, may support or suppress the self-sustaining phenomenon. In a larger sample, the heat conduction inside the bed can be the main heat transfer mechanism; a poor thermal conductivity limits the heat dispersions from the core of the sample, supporting the progress of smouldering. In Fig. 5, temperature evolution for three different sample amounts inside the oven is shown. In this case, three different boxes were used:

small (3 cm × 3 cm × 3 cm), with 5.8 g of sample; medium (6 cm × 6 cm × 6 cm), with 43.8 g of sample; large (10 cm × 10 cm × 10 cm) with 254.8 g of sample.

During the initial isothermal oven step, Fig. 5 (left), at 150 °C, the larger sample takes a longer time to reach the oven temperature and hence large temperature gradients between the solid and the oven atmosphere persist for longer times. It could be argued that the larger sample has a relative larger thermal inertia, due to the bigger amount of material, which affects the heating phase, keeping the heating rate of the material lower. However, a larger sample has also a higher moisture content to be removed. Hence, we conclude that the observed result is a clear indication that it is the moisture removal that is responsible of keeping the solids cooler. Moisture release is also slower in larger sample, because of the longer diffusion path. In other words, the flow of vapors out of the porous bed appears limited by the internal diffusion. Symmetrically, that also anticipates that the inwards flow of air could be limited by the bed porosity.

Once all the samples have reached 150 °C, we observed that a further increase of the oven temperature brings the larger samples to stronger ignition. They also terminate the activity more rapidly. The amount of fuel supports the smouldering process for longer time, as expected, without clear damping effects. But the role of the sample amount on the rate of increase (and decrease) of temperature is not so obvious. As mentioned, larger samples determine a larger thermal inertia, i.e. slower heating and cooling. The low thermal conductivity of pine bark bed, reducing heat dissipations towards the surrounding, further supports the thermal inertia of the sample, during the smouldering evolution. Again, that is not consistent with the fast rate of heating and cooling reported for larger samples during smouldering, and deserves further investigations.

However, it has to be noted that oxidation of pine bark determines the consumption of the organic matter contained in the solid particles and hence, as long as the smouldering evolves, a large fraction of volatile compounds leave the solids, leading to a significant reduction of the volume contained in each sample holder (in turn replaced by ashes). As a consequence, the thermocouple positioned in the center of the sample container, and used to monitor the solid phase temperature, is progressively exposed to the atmosphere, failing to record the actual temperature of the inner solid phase.

Finally, analyzing the oxidation rate by means of the temperature time derivatives (Fig. 5, right) it can be claimed that the larger the sample mass, the faster the oxidation rate of pine bark
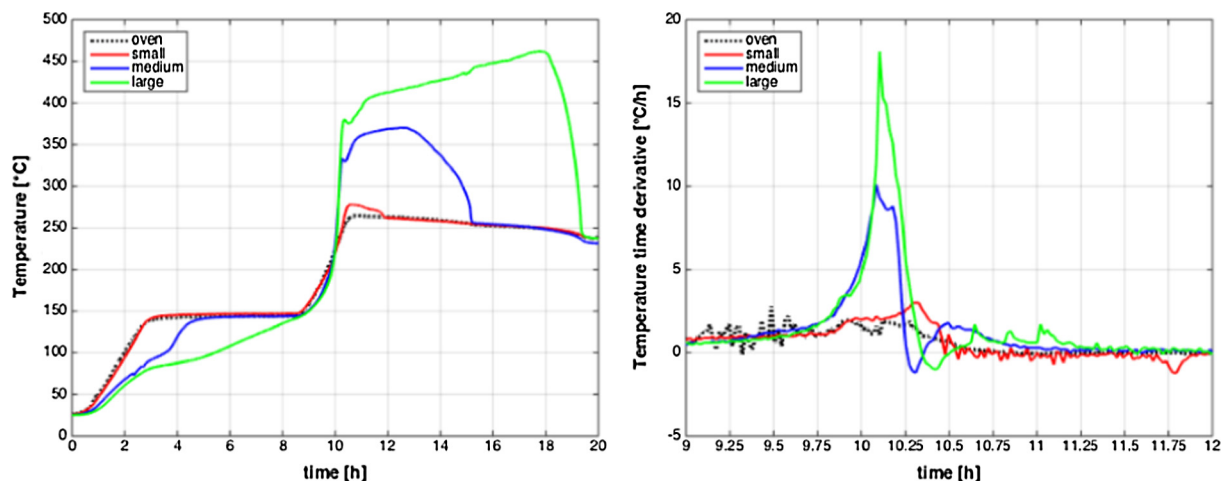
Fig. 5. Temperature evolution (left) and its time derivative (right). Pine bark at different sample amounts, in a static atmosphere (oven).

particles. However, this result is not directly related to the sample amount but rather it depends on the ability of smouldering to self-sustain: when it activates, the larger sample mass contributes to keep the material at high temperatures that, in turn, promote the smouldering process development.

3.2.3. Moisture content

To analyze the effect of moisture content, pine bark was preliminary dried, to compare its smouldering behavior with a standard sample. Specifically, a powder sample of 100 g of pine bark was kept in an oven at 105 °C for 24 h, before testing. The resulting temperature profiles as a function of time are shown in Fig. 6. The most significant differences are limited to the first part of the $T(t)$ curves: the temperature of the dried sample closely matches that one imposed to the oven, while the temperature of the standard (i.e. not-dried) sample of pine bark remains significantly lower because of the moisture evaporation, which absorbs the latent heat of vaporization from the solid particles. After the isothermal stage at 150 °C, the behavior of both samples proceeds quite similarly, with a slightly lower ignition temperature (approximately 10 °C) for dried pine bark. However, no significant differences can be observed during the smouldering process, as

justified by the shape of $T(t)$ profiles as well. The comparison indirectly provides an indication of the reproducibility of our procedure, once moisture is removed.

Finally, these results confirm that moisture content delays the onset of smouldering, being an intrinsic temperature limiting process, but it does not affect the ignition temperature which remains close to 200 °C.

3.2.4. Material packing

Particle size and sample amount are two factors clearly interconnected. Both affect the apparent density of a packed bed of solid particles. Bulk density of a powder reflects its porosity and its permeability. In turn, permeability has been observed to affect the strength of smouldering, since it controls the flow of the oxidant (i.e. air/O_2) across the biomass particles [29–31]. We experimentally explored the correlation between bed density (then permeability) and smouldering activation. A set of experiments compared the smouldering behavior of a standard (poorly packed) pine bark sample, with a bulk density of about 0.231 g/cm^3, with a sample whose compaction was forced to increase the bulk density of the pine bark mass up to roughly 0.347 g/cm^3, i.e. increasing the amount of mass by +50%, given that the same volume has been filled. Fig. 7 shows the results. $T(t)$ profiles are quite similar in shape for both samples (Fig. 7, left). Clearly, the area below the curve after the onset of smouldering is larger with higher density, because of the larger amount of mass loaded in the same volume. During the first stage, the moisture evaporation in the less packed sample apparently is easier, as proved by its completion earlier than the sample with higher degree of compaction. However, it has to be noted that less mass also means less moisture to evaporate and hence, a straightforward comparison on moisture evaporation and density could not be done because of the different sample masses used.

As emphasized from the time derivatives (Fig. 7, right), at lower compaction the trigger of smouldering appears anticipated as well, even if there is not a significant difference in the ignition temperatures, both close to 230 °C. More important, the initial oxidation rate, right after ignition, is higher in the poorly packed pine bark sample and, if the maximum values of dT/dt curves are taken as reference, it can be observed that a bulk density increase of approx. 50% leads to a decrease in the oxidation rate of about 1/3. Two mechanisms can explain the difference. First, when the sample amount is characterized by a higher permeability (i.e. lower bulk density or, in other words, by a lower degree of compaction) the gas passing through a packed bed by means of buoyancy effect is
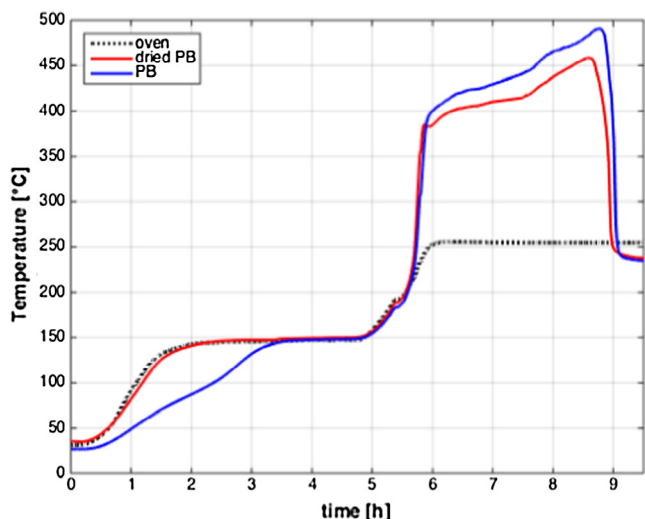

Fig. 6. Temperature evolution. Pine bark with different initial moisture content, in a static atmosphere (oven).
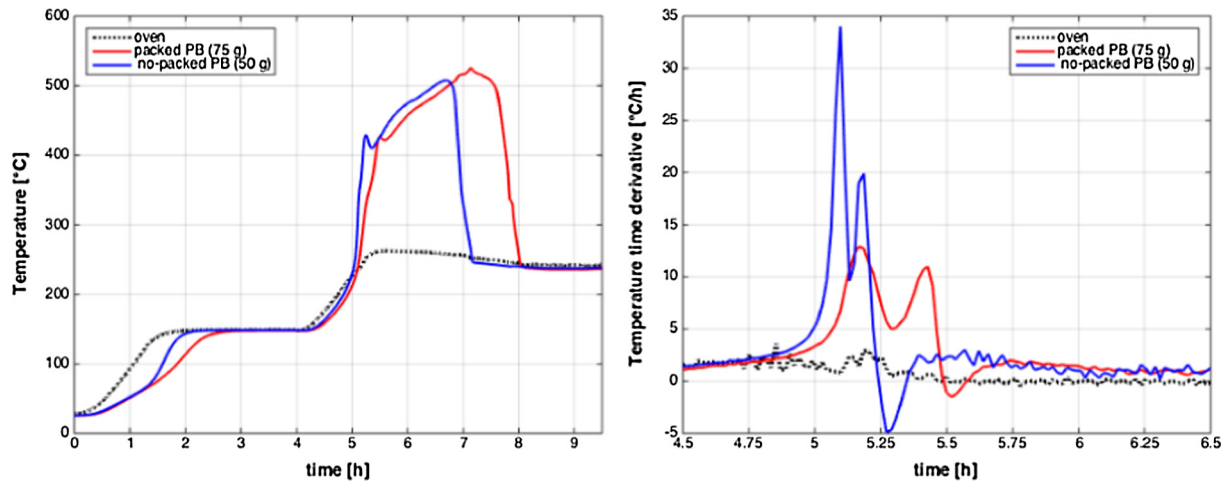
Fig. 7. Temperature evolution (left) and its time derivative (right). Pine bark at different degree of compaction (standard and +50%), in a static atmosphere (oven).

facilitated, resulting in a higher O_2 concentration at the biomass surface that determines a faster reaction. But the more compacted material has both a larger mass per unit volume then a higher mean heat capacity, being the fraction of solids per unit volume larger and the heat capacity of air much lower than the solid. At the same time, the mean thermal conductivity of the bed does not vary significantly increasing the solids fraction, given the poor conductivity of the solids. Thus, a higher c_p makes the thermal inertia to grow, slowing any rate of temperature variation. In addition, the same sample volume, thus also the same A/V, imply that the heat dissipation is the same in both cases, while the mass has a larger thermal inertia at higher density.

3.2.5. Heating policy

So far, experimental results have pointed out that the temperature at which smouldering of pine bark particle triggers is approx. 200 °C. However, the experiments mentioned were carried out with the same thermal policy. We speculate that the thermal history before the smouldering onset may affect it. We modified the heating rates and the final temperature applied during the isothermal stage. Single experiments were conducted using two heating rates, namely 2 °C/min and 10 °C/min, up to 200 °C, and a third test, loading the samples in the pre-heated oven, skipping the HR. Results are compared in Fig. 8.

The ignition profiles after ignition in the three cases were similar; differences appear during the heating stage, which is obviously slower for smaller heating rates. Experimentally it was observed that, during a first stage, the pine bark apparently pyrolyzed. That was proven both by the charring of the particles observed by stopping a test before the onset of smouldering, and by intense smoke production, consistent with a flameless thermal degradation This first stage of pyrolysis was characterized as a delay period in the smouldering ignition, where the temperature of samples was slightly higher than the ambient temperature, but no evidences of the smouldering process were actually monitored. Between 150 and 200 °C, we observed a significant emission of smoke, clearly reflecting the internal pyrolysis process that takes place up to a point when a sharp change in the slope of $T(t)$ profile marks the smouldering activation. Aligning each profile to the corresponding ignition point, it appears that the three tests yields a very similar temperature rise after ignition, and quite comparable evolution later on (Fig. 8, middle). The similar reactivity after ignition is confirmed by the maxima in the temperature time derivatives (Fig. 8, bottom). It can be concluded that the heating rate of the oven does not affect significantly the onset of smouldering

activation, neither its evolution. The amount of residuals measured at the end of any of these experiments is comparable, independently from the heating rates. The residuals ranged between 10.70 and 12.20%, much more than the ashes (3.5%) determined by the proximate analysis. Beside the important observation that experiments on a larger scale may depart significantly from the TGA measurements, these data suggested that the smouldering progresses quite unevenly in a larger mass, likely affected by the geometry of the sample, the amount of external surface and its access to the oxidant, limiting the total consumption of all the combustible material. The difference between solids residue and ashes suggests that unburned carbon is in the residue, although it appearance is very similar to ashes. Also, the lack of oxygen around the sample (within the oven) and its declining temperature (compared to the heat dissipation) may be responsible for a drop of reactivity, preventing the total combustion.

Since the heating rate apparently did not affect the temperature of smouldering onset and the thermal behavior of each sample tested was similar, independently from the preliminary heating stage, further experiments were carried out in isothermal mode. A set temperature was achieved in the oven almost immediately (at its maximum heating rate), and kept constant during all the test. Assuming that the oven temperature achieved reproduces the environmental temperatures in case of accidents, we studied its effect on the thermal stability of the material, trying to spot the actual auto-ignition temperatures [32].

Fig. 9 shows the change in $T(t)$ of the pine bark at different, fixed ambient temperature. When the ambient temperature was 175 °C, the sample heated up gradually to this value, without any indication of smouldering. Increasing the ambient temperature at 185 °C, the heated sample slightly exceeded the ambient, reflecting faint exothermic activity, that extinguishes quite rapidly. The heat generated by the biomass oxidation was slightly greater than the heat losses from the packed bed; the heat released by the reaction was not enough to support the smouldering development. Finally, for a further increase of the ambient temperature up to 195 °C, we see that a sudden smouldering activation occurs as soon as the sample temperature reaches the ambient T.

Moreover, it appears that the delay in the smouldering ignition increases as the ambient temperature decreases, as expected and already reported by Jones et al. [7], where an ignition delay was observed to increase exponentially as the isothermal temperature decreased. The Authors also suggest to defined the critical temperature as the lowest temperature at which self-heating occurs and self-sustains in a biomass pile. However, this temperature is not

Fig. 9. Temperature profiles as a function of time: effect of ambient temperature on the onset of smouldering.
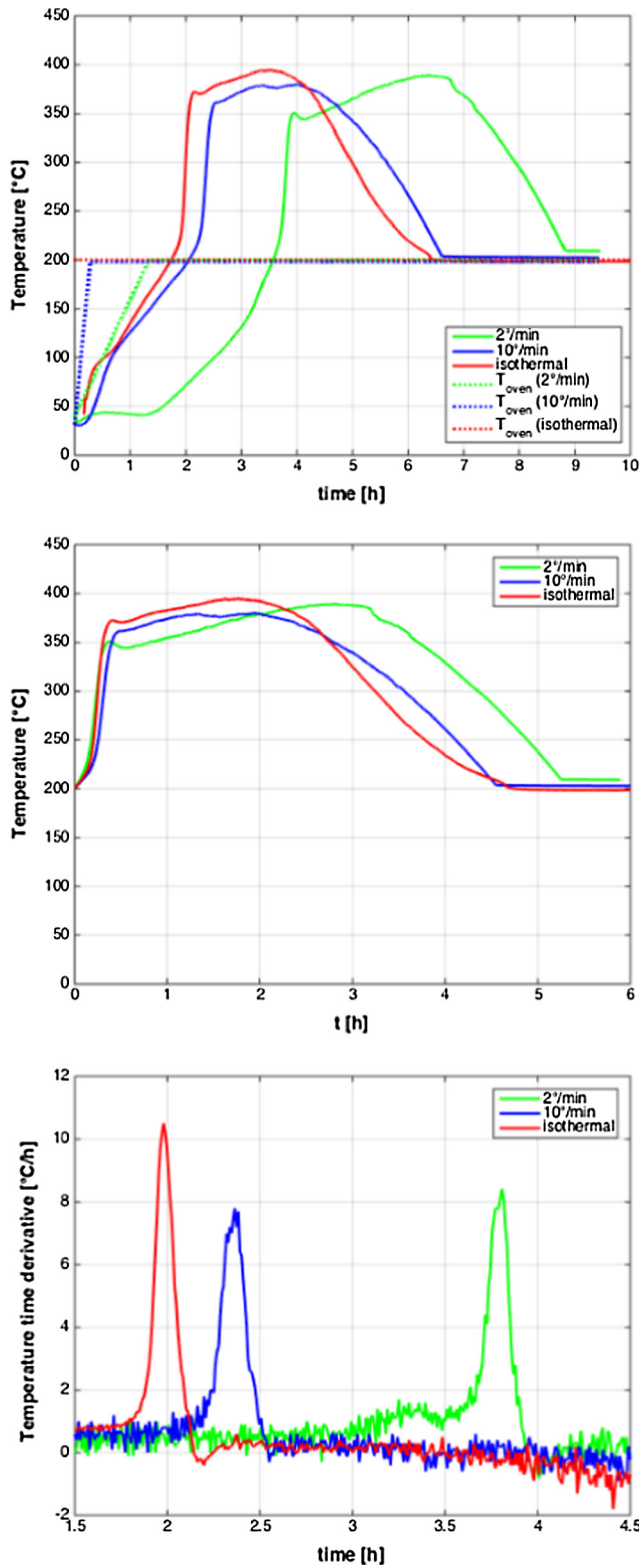

Fig. 8. Effect of the heating rate: complete temperature versus time profiles (top), comparison after the onset of smouldering (middle) and temperature time derivatives (bottom).

the ignition temperature of smouldering can be identified at 190 °C. Also the measured final mass losses, 14.68, 23.34 and 89.80% for the ambient temperature of 175, 185 and 195 °C respectively, confirm that only above 195 °C there was a clear smouldering. They also tell us that at 185 °C some more degradation took place, compared to the 175 °C case, where the weight loss is slightly more than just moisture.

3.2.6. Sample geometry

Since the smouldering process involves an oxidation, its rate of development depends on the amount of oxygen available to react with the biomass. In practice, the local oxygen is a major controlling factor, that contributes to determine a slow oxidation rate, compared to open fires. Some authors reported that smouldering also occurs with low oxygen concentrations, when the oxygen content inside the packed bed is depleted or ambient oxygen concentration is low [12]. Beyond the specific surface area that characterize the porous solid particles, the external surface of its bed, exposed to the surrounding atmosphere, also determines the ease of oxidant supply to the particles. Particularly in the case of inflow driven by natural convection through a porous bed, the rate of oxidant intake of the bed can be the limiting factor of the whole process. Therefore, the geometry of the particles bed during the biomass storage and handling becomes a crucial variable, because it determines the external surface and, specifically, the ratio between this area and the total volume of the material bed (A/V). It also affects the mean diffusion path from the external surface to the smouldering front. We carried out several experiments, similar to those ones described so far, modifying the geometry of the sample holders, varying the A/V ratio, to investigate its effect on the smouldering activation, at the same operating conditions.

Fig. 10 shows the results for 7 A/V ratios, using different geometries of the container. Geometry #1 has a cylindrical hole in a rectangular box (A/V = 2.1 cm^{-1}); #2 is a slender, rectangular box (A/V = 2 cm^{-1}); #3 is a perfectly square box, having a side of 3 cm (A/V = 2 cm^{-1}); #4 is again rectangular, with a different aspect ratio (A/V = 1.9 cm^{-1}); #5 is cylindrical with permeable walls (A/V = 1.8 cm^{-1}); #6 is a larger square box, with a side of 6 cm (A/V = 1 cm^{-1}); #7 is a pipe, thus permeable only through the planar faces (A/V = 0.5 cm^{-1}). All the bounding walls were permeable (a grid), except for geometry #7. The sketch of the sample configurations applied in these experiments is reported in Fig. 10 (above). It has to be noted that in configurations #7,

easy to be obtained and hence Ramírez et al. [32] suggested to define the ignition temperature as the mean of the lowest temperature at which self-ignition occurs and the highest at which ignition does not occur. According to this definition, in this study,
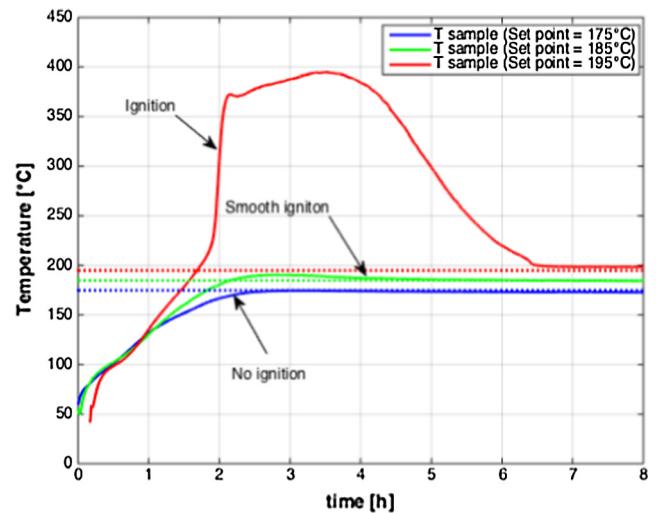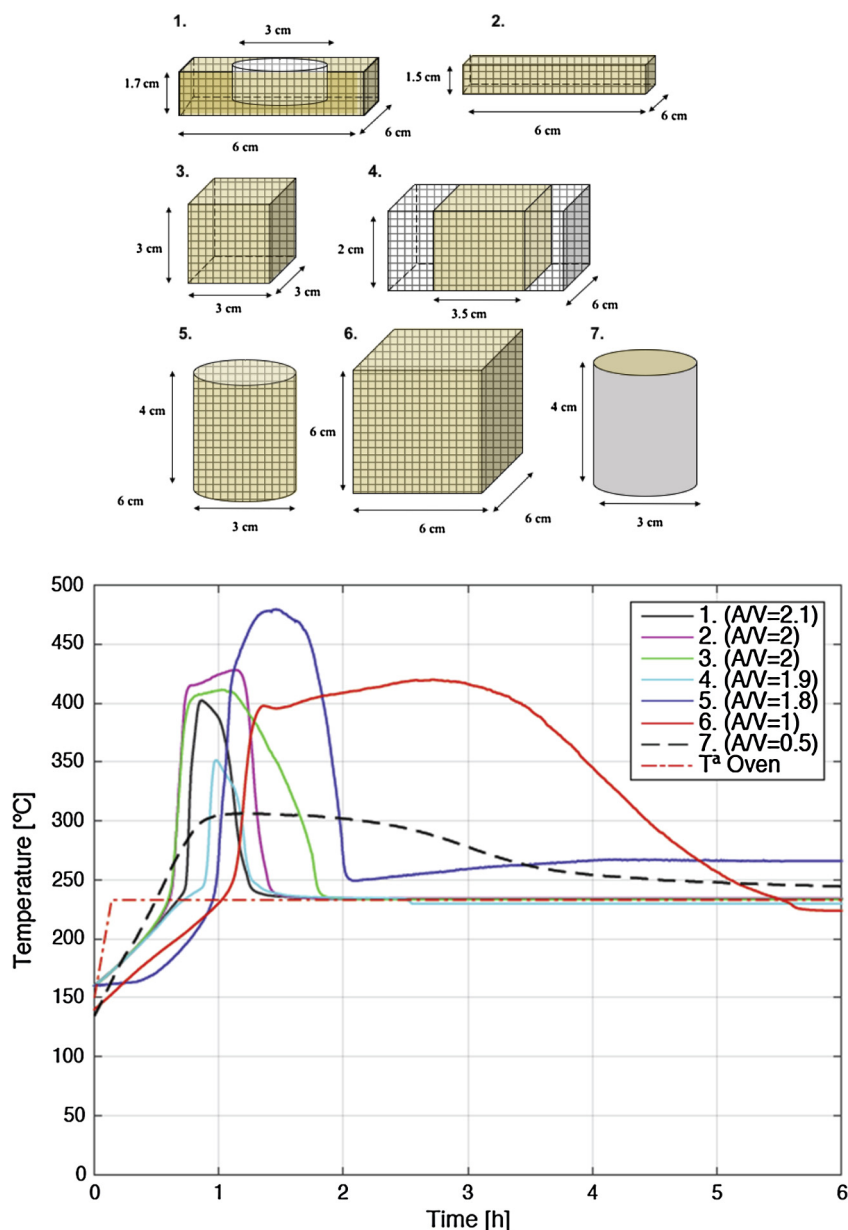
Fig. 10. Sketch of different sample geometries (above): (1) cylindrical hole in a rectangular box (A/V = 2.1 cm^{-1}), (2) rectangular (A/V = 2 cm^{-1}), (3) square (A/V = 2 cm^{-1}), (4) rectangular (A/V = 1.9 cm^{-1}), (5) cylindrical (A/V = 1.8 cm^{-1}), (6) square (A/V = 1 cm^{-1}) and (7) cylindrical (A/V = 0.5 cm^{-1}). Effect of A/V on the smouldering development (below).

the total, lateral surface of the cylindrical sample holder was closed to force the air flow through the upper and lower surfaces. The ambient temperature was set at 230 °C, using the maximum heating rate the oven can withstand.

Analyzing the $T(t)$ profiles, the temperature of the smouldering onset is always about 235 °C. On the contrary, there is a larger variability concerning the times at which smouldering triggers and how sharp is the transition. Assuming the ignition time as the one at which the pine bark temperature overcomes the oven temperature, it varies in a quite large range, between 0.5 and 1.2 h. As previously observed, the process shows clearly an initial, slow temperature increase, followed by a sharp temperature rise. That would be consistent with an initial flameless combustion, largely substoichiometric, forming an active char that later ignites faster, as suggested by Literature [12]. We speculate that both phases and the transition between them is affected by the easy of oxidant intake, in turn determined by the geometry of the sample.

In Fig. 11, left, we reported the maximum oxidation rates of the pine bark (the maximum in the $T(t)$ derivative from Fig. 10 profiles) as a function of the A/V ratio. It can be clearly seen that the larger the A/V ratio, the faster the progress of smouldering, after its onset. Consistently, the time of ignition, Fig. 11 (right) shows an inverse law; the larger the A/V ratio, the earlier the self-heating phenomena occurs. The case of A/V = 0.5 is quite singular. It is a geometry approximating a pipe, where chimney effect is expected. Here the smouldering process did not show the typical two phases that are apparent from the other cases (Fig. 10) nor a sudden activation. We speculate that the inflow of air was larger than in the other cases, just because of the enhanced chimney effect. That leads to an earlier oxidation, spreading over a large interval of time, keeping the temperature lower than the other cases, where the heat dissipation was more difficult.

In conclusion, the ratio between external surface and volume of pine bark samples certainly affects the oxidation rate of the
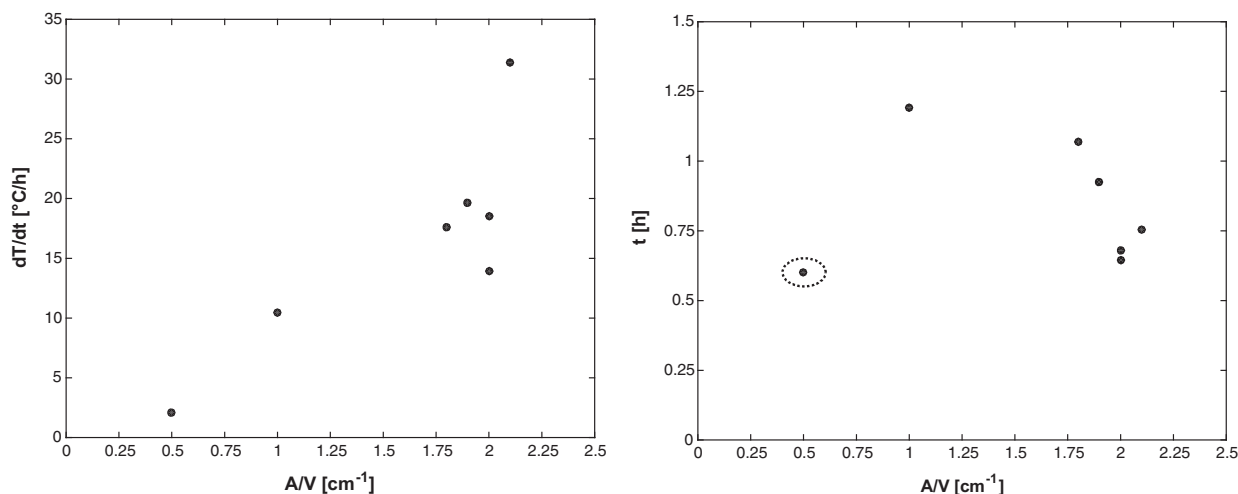
Fig. 11. Maximum oxidation rate of the pine bark (left) and ignition times (right) as a function of the ratio between external sample surface and its total volume.

biomass. An integral analysis, i.e. the evaluation of the amount of energy released and not its rate of release, suggests that the energy released, expected proportional to the sample amount, it is not uniquely determined by the integral of the $T(t)$ curves. The actual temperature achieved is the result of a competition between heat generation and dissipation. The energy released is proportional to the volume. The energy dissipated depends on the external surface and the sample geometry, that may inhibit the convective cooling by air intake. A likely model of the smouldering evolution suggests that smouldering triggers on one external surface, where the oxidant concentration is higher, but thermal dispersions at the boundaries are also higher, damping its development. As long as the front moves inwards, it provides heat in the inner part of the biomass where the heat losses are much less. The temperature can increase, promoting the smouldering development up to the thermal degradation of the biomass. If the geometry of the sample container enhances the heat losses, the smouldering process may not trigger or stop earlier, as observed by Carvalho et al. [18].

3.3. Forced flow tests

As proved by the tests discussed so far, the flow of air through the porous packed bed of pine bark supports the oxygen required for the biomass oxidation and self-heating. However, it also promotes the heat losses by means of convective heat transfer mechanisms that may prevent the process to self-sustain. In the previous experimental configuration, based on the oven, the flow of the oxidant through the solid particles was determined uniquely by buoyancy and hence, it was directly related to the temperature gradients between the sample and the ambient surrounding it. Differently, a forced flow arrangement allows to partially decouple the temperature and the velocity distribution within the sample. We carried out experiments similar to the previous ones in the oven, using a flow tubular reactor in which the gas velocity entering to the packed bed was externally imposed.

3.3.1. Flow rate

The first parameter investigated in the flow reactor was the effect of air flow rate. In the previous experiments in the oven we observed that ignition can be obtained even at very small flow rates of combustion gas, as given by the natural convection in the porous matrix, once sufficient oxygen is provided to the biomass. On the other hand, high flow rates promote convective cooling up to the point of preventing the occurrence of smouldering

[15,24,33]. To systematically investigate the effect of flow rate on the onset of smouldering, three different gas flow rate, (100, 250 and 400 mL/min) have been compared. The reactor was heated at 2 °C/min until 250 °C followed by an isothermal step of several hours. Results are shown Fig. 12.

The smouldering activation is well defined only at the lower flow rates (<250 mL/min), where the self-heating started at approx. 230 °C. On the contrary, with the larger flow rate (400 mL/min) ignition is not well defined. That is evident in the derivatives, reflecting the biomass oxidation rate, Fig. 12, right. It shows that the maximum of the reaction rate (i.e. maximum values of dT/dt) achieved with flow rates in the order of 100–200 mL/min is slightly higher than the one measured in a static atmosphere.

Even though at 400 mL/min smouldering was not so evident from $T(t)$ measurements, its reaction rate shows a progressive increase approximately one hour earlier compared with the cases at lower inlet gas flow rate. And that occurs when the biomass temperature is as low as 100 °C when the dT/dt of the biomass exceeds the 2 °C/min of the reactor. The quite surprising result could be explained assuming that a larger amount of oxidant can promote the oxidation processes even when the material has a low temperature. However, with a high gas flow rate, the biomass temperature increase due to the larger amount of heat released by the reaction is balanced by the convective cooling effect caused by the air flux passing through the bed. As a consequence, even if smouldering took place (as proved by pine bark temperature above the one of the inlet gas), the biomass temperature did not increase significantly during the test.

3.3.2. Inlet gas composition

To further examine the smouldering behavior of pine bark in the flow reactor, experiments with different inlet gas compositions were carried out, modifying the oxygen concentration in the gas fed to the smouldering reactor. The gas compositions used are: (a) 100% O_2, (b) 50% O_2 + 50% N_2, (c) 21% O_2 + 79% N_2 (synthetic air), (d) air until the smouldering ignition, and 100% N_2 afterwards, (e) 100% N_2. Inlet gas flow rate was set at 250 mL/min. The reactor was heated at 2 °C/min until 250 °C and kept isothermal. Results are shown in Fig. 13. The temperature profiles appear very different depending on the inlet gas composition. In a pure inert flow (100% of N_2), the pine bark smouldering never occurred, as expected. In a flow of air, the material starts self-heating at 224 °C. The ignition temperature lowers when the content of oxygen increases, leading to ignition points at 204 and 170 °C for inlet
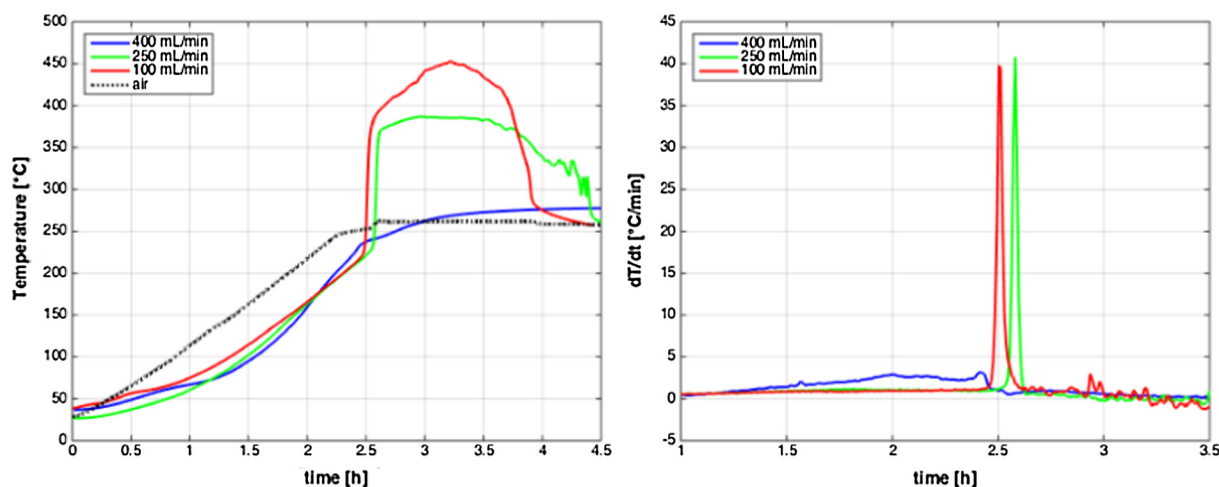
Fig. 12. Temperature evolution (left) and its time derivative (right). Pine bark. Effect of air flow rate on the smouldering onset, in a flow reactor.

gas composition of 50 and 100% O_2, respectively. Ignition temperatures as a function of oxygen concentration are shown Fig. 14. Results follow a well-defined linear trend, i.e. T_{ign} = 238–0.68%O_2.

Results of Figs. 13 and 14 confirm once more that the smouldering process is regulated by the concentration of oxidant, both to trigger and to develop the self-heating processes. They also prove that the oxidation stage is mandatory to support the pyrolysis phase. As a further confirmation of the O_2 requirement for smouldering, in the experiment (d), the O_2 feed was stopped after the onset of smouldering; the process immediately ceased. Ignition temperatures under a gas flow of air are in the range of those ones obtained by other Authors with similar materials. Grotkjær et al. [15] obtained an ignition temperature of about 220 and 230 °C for straw and wood respectively. García et al. [34] reported a temperature of smouldering activation of roughly 212 °C for wood chip, while for different biomasses [28] they mentioned ignition temperatures between 230–250 °C.

3.3.3. Outlet gas composition

Ignition temperature was also related with volatile matter content, according to Grotkjær et al. [15]. However, the effect of atmosphere in the process and the composition of exit gases were not
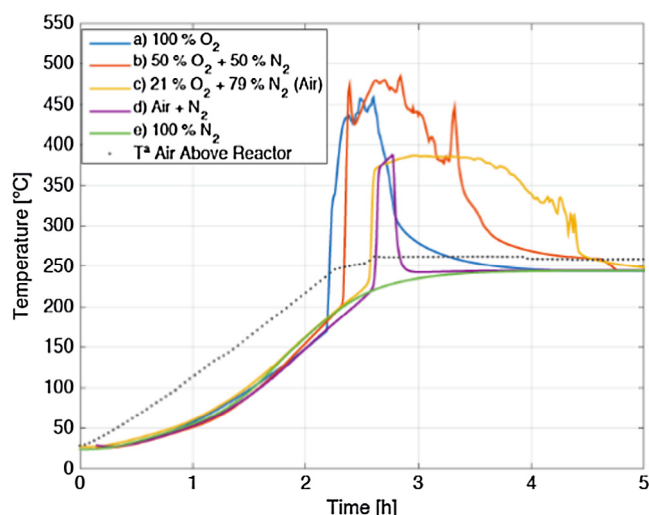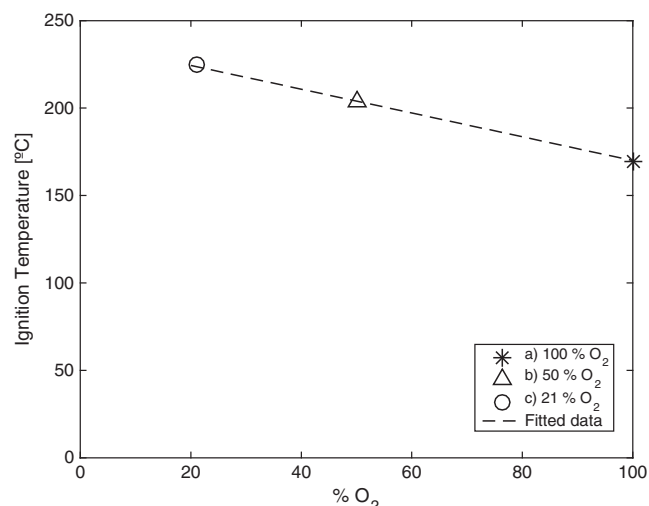

Fig. 14. Ignition temperature as a function of O_2 concentration in the gas fed to the flow reactor.

deeply investigated in the Literature. Thanks to the forced flow reactor, we could analyze the composition of the exiting gases and try to correlate them with the oxygen content in the inlet. We tracked the gas products by GC in several tests carried out in the flow reactor, varying the inlet gas composition. Results of the comparison between temperature evolution and the composition of gas products are shown in Fig. 15. Inlet composition in each test is specified in its caption.

Note that the frequency of gas analysis is much lower (1 measurement each 6 min at the higher sampling rate) than the temperature measurements (almost continuous), so that correspondences in time may be slightly falsified. GC analysis have been already simplified to increase the sampling rate, thus loosing information about possible higher hydrocarbons that may result from partial combustion. Even higher molecular weight hydrocarbons have been trapped before GC analysis, in the condenser and on the filters, thus impossible to quantify as a function of time. The first observation is the drop of O_2 in the outlet as soon as smouldering begins. Conversely, the restoration of its inlet concentration indicated the completion of the process. Correspondence with the $T(t)$ profiles is always very timely. The production CO_2 also mirrors the $T(t)$ profiles very closely. CO emissions are typically observed in the first phase of the smouldering, when partial

Fig. 13. Temperature evolution of pine bark in a flow reactor. Effect of the inlet O_2 concentration on the smouldering onset.
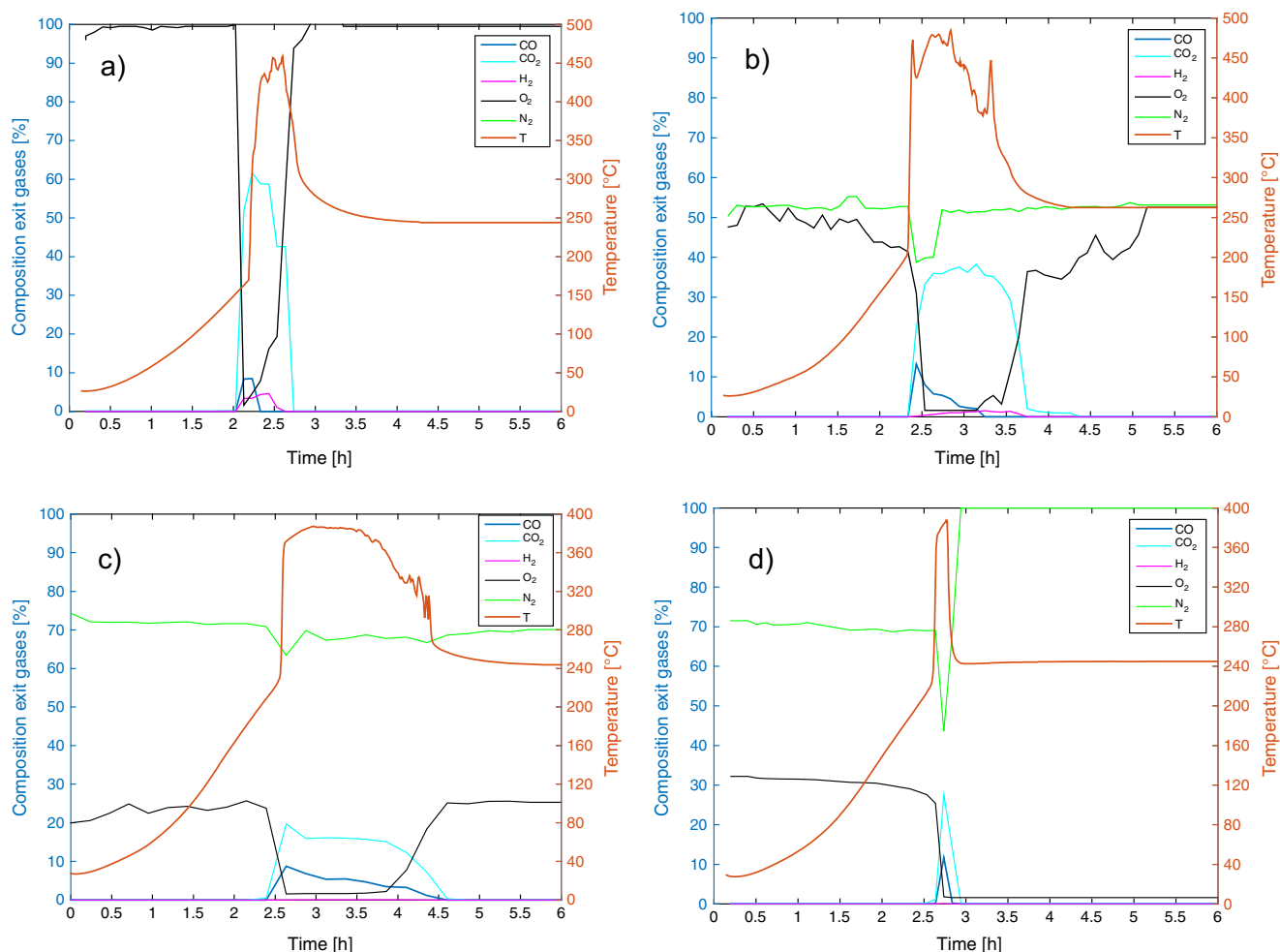
Fig. 15. Temperature evolution and the composition of gas stream exiting from the reactor. Smouldering of pine bark at different inlet gas composition in a flow reactor (a) 100% O_2, (b) 50% O_2 + 50% N_2, (c) 21% O_2 + 79% N_2 (synthetic air) and (d) air until the smouldering ignition, and 100% N_2 afterward).
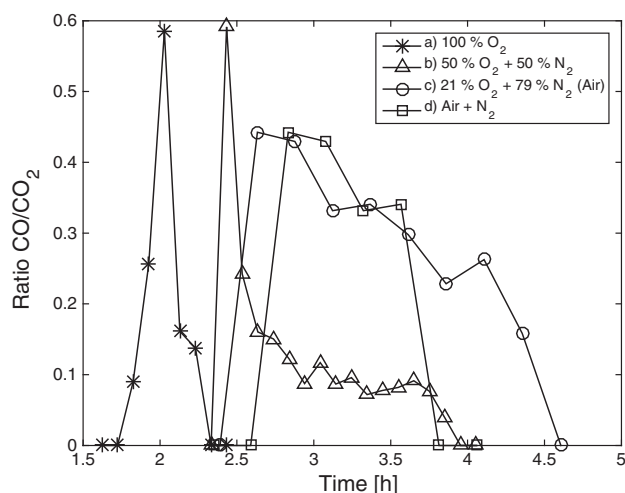

Fig. 16. Calculated ratio of CO/CO_2 in the products. Smouldering of pine bark at different inlet gas composition in a flow reactor.

oxidation and pyrolysis prevail. The CO/CO_2 ratio, Fig. 16, clearly highlights the earliness of ignition. The higher the O_2 concentration, the sooner the process starts and the shorter it lasts. A significant CO/CO_2 ratio, as high as 0.6 is not surprising for a biomass

burning in starvation of O_2, as discussed in detail for peat smouldering [37]. A more detailed characterization of the evolution of the CO/CO_2 ratio, combining a higher gas sampling rate combined with the tracking of the smouldering front is planned. It will provide evidences of the mechanism of an oxidation region downstream a pyrolysis region suggested in the Literature.

Interestingly, we measured some H_2 in the products, and surprisingly, its concentration (always quite small) is larger with larger O_2 concentration in the feed. Its presence confirms that partial oxidation and cracking (i.e. pyrolysis) reactions are taking place. The obtained concentration of H_2 with air, about 1%, was measured also by other Authors for similar fuels [35,36]. From the safety point of view, H_2 in the products of a smouldering process, with CO, may support local homogeneous combustion, that may end up in flaming or even explosions, depending on the confinement.

4. Conclusions

The present work provides information about the smouldering process of the pine bark and the related exothermic oxidation processes. Experimental observations confirm that pine bark has a reactive character, showing a self-heating behavior that triggers in the range between 190 and 240 °C. It clearly depends on the concentration of O_2 supplied, but the thermal balance between heat released by oxidation reactions and the heat lost because of

thermal dispersions still remains a crucial factor in controlling the development of self-heating of pine bark.

A set of experiment was carried out in an oven, where the ambient temperature was tuned to reproduce the heat dissipation expected in a bulk biomass storage. Investigation of several factors led to conclude that:

- smaller particle size determines a lower ignition temperature and more vigorous development of the smouldering process,
- larger samples allow smouldering to develop more abruptly and intensely,
- the initial moisture in the pine bark only affects its preheating, when moisture evaporation limits the biomass' temperature rise,
- a higher packing of the solids (smaller bulk density) limits the moisture release and the smouldering development,
- higher heating rate does not affect the smouldering evolution,
- the ambient temperature that triggers smouldering was as low as 190 °C,
- the larger the sample external surface to its volume (A/V) ratio, the faster the progress of smouldering and the earlier the onset of self-heating; the geometry is crucial for controlling the buoyancy effects and for balancing heat generated by the biomass oxidation and heat lost by thermal dispersions.

All together, they point out that the thermal inertia of the sample amount and its permeability are the key factors determining the development of the smouldering. The sample mass and permeability both affect the contact between the oxidant and the solids and, the thermal conductivity of the packed bed sample. Despite the evidence that the higher the sample amount, the higher should be the heat produced by the smouldering, we proved that a high permeability (i.e. low bulk density of biomass packed bed) supports a faster oxidation, but the self-sustaining feature reduces because of higher thermal dissipations.

Similar observations have been collected performing experiments in a flow tubular reactor, where inlet gas composition could be modified and the produced gas composition monitored. The analysis of gas emissions under different operating conditions confirmed that exothermic reactions prevails, needing O_2 to develop and that smouldering stops when the flux of oxygen is interrupted. The highest production of CO was obtained at the beginning of the smouldering, suggesting the importance of partial oxidation and pyrolytic processes. The O_2 concentration in the feed modifies the earliness of ignition and its temperature, that drops significantly (from 200 to 160 °C) at high O_2 concentration. The flow reactor configuration also allowed to independently investigate the competition between self-sustaining heat release and the rate of heat dissipation. The higher flow rates can limit the maximum temperature, still supporting the combustion, or prevent any smouldering to trigger.

Acknowledgements

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.2016.12.028.

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