

Devolatilization and Fragmentation of Solid Lignin-rich Residues from Bioethanol Production in Lab-scale Fluidized Bed Reactors

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The waste stream of second generation bioethanol production plant mainly consists of lignin - a polymer of several units of not fermentable phenylpropane - coming from lignocellulosic biomasses. This stream can be used only partly to energetically support the process of bioethanol production (about 40%), whereas the fate of the remaining 60% has to be found. Fluidized bed combustion technology can be considered as a viable option to recover thermal power from this waste stream. However, the understanding of the mechanisms of thermo-conversion and attrition of these lignin-rich particles in fluidized beds is scarce and it deserves further investigations. To this end, the combustion of lignin-rich residues were studied in lab-scale fluidized beds with the aid of different diagnostic and experimental protocols to analyze devolatilization, char burn-out and fragmentation of single fuel particles. Comparing devolatilization times with transversal mixing time of typical industrial-scale fluidized bed combustors, wet fuel particles larger than 10mm can be fed directly to the combustor chamber, whereas pre-dried fuel was extremely reactive with the risk of localized emissions of heat and micro- and macro-pollutants once fed to the fluidized bed reactors. Particles do not undergo primary fragmentation, whereas probably secondary and not percolative fragmentation occurs during the late stage of char burn-out.

1. Introduction

The deployment and the exploitation of alternative fuels became more and more relevant to reduce the emissions of greenhouse gases and to limit the dependence on countries supplying fossil fuels. In this perspective, the Community legislation regulated, with the 209/28 EC Directive, the minimum amount of biofuel at 10% for automotive fuels by 2020. OECD estimates predict that the production of second-generation bioethanol, i.e. ethanol produced from lignocellulosic biomass and scraps of agricultural crops will be of 155 billion litres by 2020. The composition of lignocellulosic biomass is typically: cellulose (35-45%), hemicellulose (25-30%) and lignin (25-30%). The cellulose and hemicellulose are made of fermentable sugars, while the lignin is a polymer consisting of several units of not fermentable phenylpropane. As a consequence, the residues of second generation bioethanol production, typically the solid residues after ethanol distillation and separation, are characterized by high lignin content. These residues can be used only in part to energetically support the process of bioethanol production (about 40%), whereas the fate of the remaining 60% has to be found. These lignin-rich residues can be exploited for the production of some chemicals (Ragauskas et al., 2014), as well as in thermochemical processes like combustion (Eriksson and Kjellström, 2010; Ren et al., 2015), co-combustion (Buratti et al., 2015), gasification (Barisano et al., 2013) or pyrolysis (De Wild et al., 2014). Fluidized bed combustion technology can be considered as a viable option to recover thermal power from this waste stream. However, the understanding of the mechanisms of conversion and attrition of lignin-rich particles coming from a second-generation bioethanol production plant in fluidized beds is scarce and it

deserves further investigations. To this end, the combustion of these lignin-rich residues were studied in lab-scale fluidized beds with the aid of different diagnostic and experimental protocols to analyze devolatilization, char burn-out and fragmentation of single fuel particles. Devolatilization experiments based on the analysis of the time-resolved CO₂ concentration were carried out to characterize the devolatilization process considering both wet and pre-dried fuel particles. Fragmentation and char burn-out experiments were performed using the basket technique retrieving fragmented and un-fragmented particles from the fluidized bed after devolatilization (primary fragmentation) and after char burn-out (secondary or percolative fragmentation).

2. Experimental

A stainless steel atmospheric bubbling fluidized bed combustor 41 mm ID and 1 m operated at 1123K was used for lab-scale devolatilization, fragmentation and combustion experiments (Figure 1). Two different configurations of the reactor were used for the experimental tests. In the first configuration (Figure 1A), used for particle fragmentation experiments, the top section of the fluidization column was left open to the atmosphere. A stainless steel circular basket could be inserted from the top in order to retrieve fragmented and un-fragmented particles from the bed. The second configuration (Figure 1B), used for single particle combustion/devolatilization experiments and char burn-out/fragmentation experiments, also consisted in leaving open the top section of the fluidization column. A stainless steel probe was inserted from the top of the column in order to convey a fraction of the exit gases directly to the gas analyzers. The analysis of the time-resolved CO₂ concentration was used to characterize both the devolatilization process considering wet and pre-dried fuel and char burn-out. The details of the experimental apparatus and procedures are reported in previous published works (Scala et al., 2000; Chirone et al., 2008; Solimene et al., 2010). The properties of the investigated fuel are reported in table 1 in terms of lower heating value, proximate and ultimate analysis, metal and components analysis.

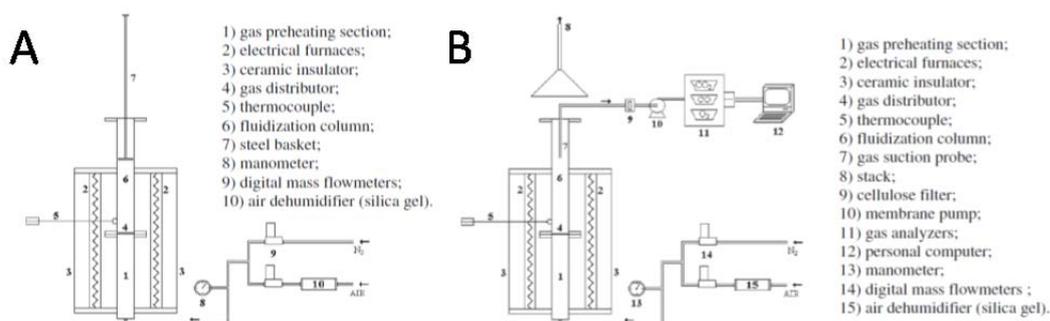


Figure 1: The experimental apparatus for devolatilization/fragmentation characterization: A) basket-equipped configuration; B) open-top configuration.

Table 1: Properties of lignin-rich residues

LHV (as received), kJ/kg	5645	Metal analysis (dry basis), % _w	
Proximate analysis (as received), % _w		Al	0.36
Moisture	60.7	Ca	0.30
Volatile matter	25.0	Fe	0.17
Fixed carbon	8.1	Mg	0.07
ash	6.1	P	0.07
Ultimate analysis (dry basis), % _w		Si	1.12
Carbon	47.0	Na	0.26
Hydrogen	5.4	Ti	0.02
Nitrogen	1.2	Components (dry basis), % _w	
Sulphur	0.1	extractives	18.1
Chlorine	0.0	lignin	57.9
ash	15.6		
Oxygen (by difference)	30.6		

The lignin content was obtained by Klason method. Silica sand was used as bed material in the size range 0.30-0.42mm. Some experiments with configuration-B experimental apparatus were carried out using a video

camera to visualize the bed surface during the combustion of both wet and pre-dried single fuel particles in order to characterize the phenomenology of the thermo-conversion of lignin-rich solid residues.

3. Results and discussion

3.1 Phenomenology

Figure 2 reports a sequence of snapshots of the surface of fluidized bed captured during the thermal conversion of both a wet (figures 2a, b, c and d; particle size 12mm) and a pre-dried (figures 2e, f, g and h; particle size 7.5mm before drying) fuel particle at a fluidization velocity of 0.4m/s using air as fluidizing gas. The analysis of the images allows to observe the thermo-conversion process since the fuel particle periodically appeared on the bed surface: it had a dark colour during drying and devolatilization stage (particle temperature smaller than that of the bed) while it was characterized by a bright colour during char combustion being its temperature larger than bed temperature. On the whole, it can be highlighted the following sequence of events during the combustion of a wet lignin particle: 1) once fed the particle inside the bed, it was not evident the presence of flames around it ($t=2.2s$); 2) small intermittent flames appeared nearby the particle without entirely enveloping the particle ($t=4.5s$ and $14.3s$); 3) once the devolatilization step was finished ($t=69s$), char combustion takes place: during this stage fragmentation phenomena were not evident. The phenomenology observed during the conversion of the dry lignin particle (see figures 2e, f, g and h) is similar to that highlighted for the wet fuel particle. However, the following differences have to be underlined: 1) devolatilization step began just once the particle was fed to the fluidized bed ($t=2s$); 2) volatiles flames were wide and intense completely inclosing the particle and generating a large amount of soot ($t=2s$ and $t=4s$). Char burn-out of the pre-dried fuel particle did not present qualitatively significant differences with respect to wet fuel case ($t=10.5s$, $t=55s$ and $t=98.7s$).

Ash particles of lignin-rich residues separated from bed material and collected at the end of the tests were analysed by SEM-EDX methodology and two images are reported in figure 3 referring to ash particles obtained after the combustion of wet and pre-dried fuel particles. It can be observed that: i) the shape of the ash particles was similar to that of the mother particle; ii) the structure presented a significant macroporosity with a more compact shell and a large void in the center of the particles; iii) the size of the pores in the outer shell was such to be penetrated by the bed material. On the whole, it seems that the ash particles are characterized by a very fragile structure much similar to that observed in the case of sewage sludge ash particles (Solimene et al., 2010; Urciuolo et al., 2012). EDX analysis shows a metal composition similar to that of the native fuel. Ash particles obtained during combustion tests carried out with wet and pre-dried fuel do not present significant differences in terms of both physical and chemical features.

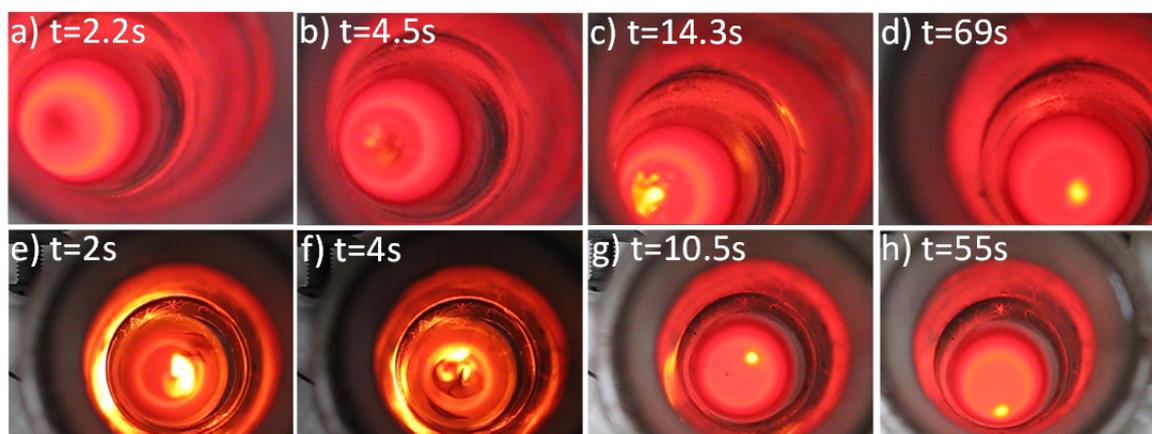


Figure 2: Bed surface images during the thermo-conversion of a single fuel particle at a fluidization velocity of 0.4m/s using air as fluidizing gas. a-d) 12mm wet fuel particle; e-h) pre-dried fuel particle of 7.5mm diameter before drying.

3.2 Primary fragmentation and devolatilization

Primary fragmentation experiments show that wet fuel particles do not undergo fragmentation during devolatilization, as matter of fact the multiplication factor (N_{out}/N_{in} , number of particles collected by basket divided the number of particles fed to the reactor) remains equal to 1 whereas a particle shrinkage of about 78% was observed. The level of particle shrinkage is comparable with that obtained when particles were dried in oven, indicating that it is likely that the particle shrinkage during particle devolatilization in the fluidized bed is related to the drying stage rather than to the pyrolysis process.

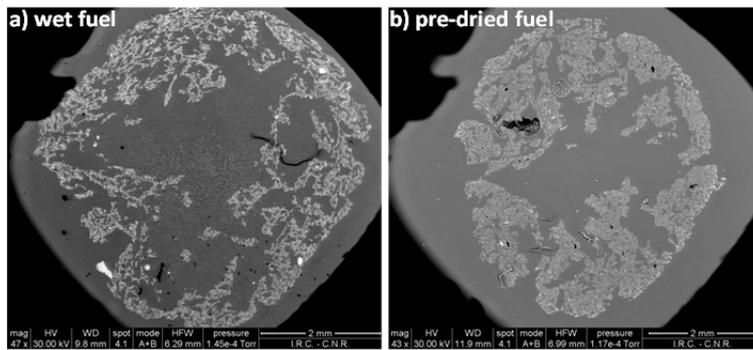


Figure 3: SEM images of cross sections of ash particles obtained after the combustion of wet and pre-dried fuel particles

Figure 4 shows the time-resolved CO_2 concentration profiles measured at the exhaust during the combustion of a both wet and pre-dried fuel particle. The sizes of the wet and of the pre-dried particle before drying stage were 10 and 9.5mm, respectively. These profiles can be analyzed to achieve in-situ the main characteristics of the devolatilization and char burn-out of fuel particles in fluidized bed reactors (Chirone et al., 2008). Two main steps can be distinguished: 1) an initial step just after particle injection characterized by a pronounced peak related to the progress of fuel devolatilization; 2) a final step corresponding to the combustion of the residual char. The CO_2 concentration time series can be deconvoluted into these two sequential steps in order to estimate the characteristic times of devolatilization and char burn-out. To this end, it was assumed the CO_2 release as the convolution of two Gaussian-like probability distribution functions. The time instant $t=0$ and that of the end of devolatilization $t=t_d$ were chosen as upper and lower limits of the time interval, centred around the maximum value, where the 95% of probability falls. From the analysis of figure 4, it is evident the peak associated to the combustion of volatile matter followed by a slow decay of CO_2 concentration due to the char combustion

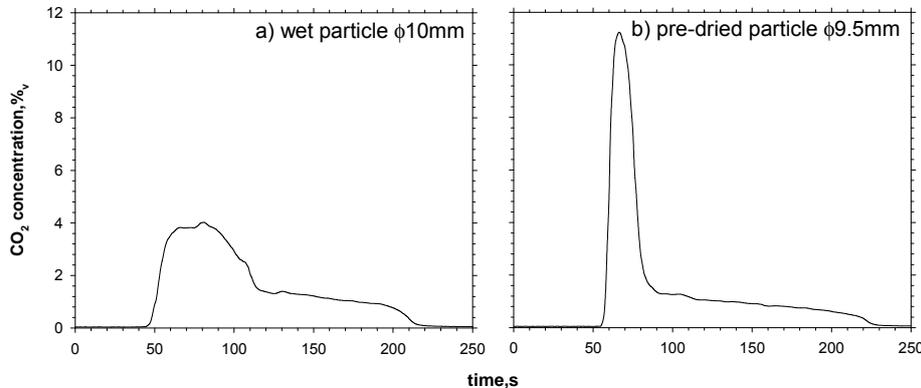


Figure 4: Time-resolved CO_2 concentration profile during the devolatilization and char combustion of a both wet and pre-dried fuel particle.

The comparison between the time-resolved CO_2 concentration profiles obtained with wet and pre-dried fuel particles highlights in quantitative way what it was observed qualitatively in the phenomenology section by visive observation of bed surface during fuel conversion. Specifically, it can be observed: 1) devolatilization of pre-dried fuel particle was quicker and, in turn, the CO_2 concentration reached larger values in a very short time interval; 2) the complete conversion time (combustion of volatiles + char combustion) remained constant. It is likely that the drying step of the wet fuel particle takes place in parallel with the fuel pyrolysis with the obvious consequence of reducing the temperature of both pyrolysis and combustion of volatile matter and of increasing the duration of drying/devolatilization step. On the other hand, the devolatilization step of the pre-dried fuel and the combustion of volatile matter are not mitigated by the vaporization of the moisture present in the fuel generating a char less porous and reactive than that achieved by the wet fuel. Overall, the overall complete combustion time for the pre-dried fuel is similar to that of the wet fuel, whereas t_d estimated by the analysis of data present in figure 4 are 70 and 20s for the wet and the pre-dried fuel particle, respectively.

Devolatilization time plays an important role for the localization and release pattern of volatile matter during fluidized bed combustion of solid fuels and, as a consequence, for the even heat release inside the reactor as well as the generation of macro- and micro-pollutants (Aprea et al., 2013; Solimene et al., 2010; Solimene et al., 2012). The comparison of devolatilization time with the transversal mixing time of typical industrial-scale fluidized bed combustors sheds light on the distribution of volatiles along the transversal section of the reactor. For instance, short devolatilization times determine a release of volatile matter localized nearby the feeding point of the solid fuel. The transversal mixing time (t_{mix}) can be estimated on the basis of the transversal sizes of the reactor (L_x, L_y):

$$t_{mix} \cong \frac{L_x L_y}{4D_r} \quad (1)$$

where D_r is the transversal dispersion coefficient evaluated by different diagnostic techniques for coarse particle like fuel particles in the order of $0.12 \text{ m}^2/\text{s}$. Taking into account the typical transversal size of industrial fluidized bed combustors, t_{mix} is in the order of 100s. As a consequence, the comparison of devolatilization times of lignin-rich fuel particles with transversal mixing time of typical industrial-scale fluidized bed combustors highlights that: 1) wet fuel particles larger than 10mm fed directly to the combustor chamber should generate a rather uniform distribution of volatile matter along the transversal size of the reactor; 2) the dry fuel is extremely reactive and once fed to the fluidized bed it could generate localized emissions of heat and micro- and macro-pollutants.

3.3 Char combustion

Char particles obtained by means of the procedure of primary fragmentation (fluidization velocity 0.8m/s, fluidizing gas nitrogen) and without undergoing fragmentation, were used for the tests of char burn-out and secondary or percolative fragmentation. The tests were carried out at a fluidization velocity of 0.8m/s using as fluidizing gas a mixture of nitrogen/air at a concentration of O_2 of 4.5%_v. The time-resolved CO_2 and CO concentration profiles at the exhaust during the conversion of a single fuel particle were measured and elaborated. The carbon conversion was obtained as a function of time by means of:

$$X_c(t) = \frac{M_c \int_0^t Q(C_{\text{CO}_2}(t') + C_{\text{CO}}(t')) dt'}{W_{c0}} \quad (2)$$

where, M_c , Q , C_{CO_2} , C_{CO} and W_{c0} are carbon molecular weight, the inlet fluidizing gas flow rate, CO_2 concentration, CO concentration and the initial carbon content of the char particle. This latter is calculated as the difference between the mass of the injected char particle and the ash mass of the parent particle. The ash particles after the complete conversion of the single char particle were retrieved by the basket technique in order to investigate char fragmentation phenomena.

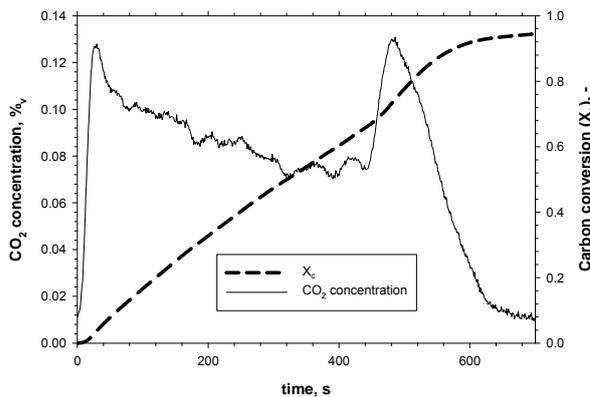


Figure 5: Time series of the CO_2 concentration measured at the exhaust and of the carbon conversion during a test of char burn-out of a single particle of about 9.3mm. Fluidization velocity: 0.8m/s; fluidizing gas: a mixture of nitrogen and air with O_2 concentration of 4.5%_v.

Figure 5 reports the time-resolved CO_2 concentration and carbon conversion profiles measured during a typical test carried out with a char particle of about 9.3mm. The time series in figure 5 shows that: 1) the carbon conversion initially increased almost linearly with time (CO_2 concentration slowly decreased with time);

2) a change of slope was observed at about 470-480s (a maximum of CO₂ concentration was correspondingly observed); 3) the carbon conversion stabilized at a value of about 0.94 (CO₂ concentration reached the baseline value). It is worth to note that 24 ash fragments were collected at the end of the run. On the whole, the analysis of these results highlights that: 1) char particle conversion is initially controlled by external diffusion; 2) it is likely that particle fragmentation occurs in the late stage of particle conversion at about 70%; 3) carbon elutriated with fine particles accounts for about 6% and it is probably related to the event of char fragmentation. It is worth to note that the observed char fragmentation depends on fluidization velocity because it was noted at fluidization velocity of 0.8m/s but it was not observed in previous experiments carried out at 0.4m/s. As a consequence, the char fragmentation can be considered secondary and not percolative, as a matter fact, this latter, differently from that observed, does not depend on fluidization velocity.

4. Conclusions

The fluidized bed combustion of lignin-rich residues coming from a second generation bioethanol production plant were investigated in lab-scale fluidized beds with the aid of different diagnostic and experimental protocols to analyze devolatilization, char burn-out and fragmentation of single fuel particles. The comparison of devolatilization times with transversal mixing time of typical industrial-scale fluidized bed combustor pointed out that wet fuel particles larger than 10mm can be fed directly to the combustor chamber, whereas pre-dried fuel was extremely reactive with the risk of localized emissions of heat and micro- and macro-pollutants once fed to the fluidized bed reactor. Fuel particles do not undergo primary fragmentation, whereas probably secondary and not percolative fragmentation occurs during the late stage of char burn-out.

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