TORREFACTION OF BIOMASS WASTES:
CHARACTERIZATION AS POTENTIAL REDUCING AGENTS FOR METALLURGICAL INDUSTRIES

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ABSTRACT: Torrefaction of low-cost poplar biomass was evaluated in this work for manufacturing bio-coal materials as reducing agents for metallurgical applications. Two different severity conditions were used in the multiple hearth furnace of the torrefaction pilot-plant CENTORRE (at an average flow rate of 45 kg h^{-1} in dry basis): i) 300 °C; ii) 350 °C, with a residence time of 45 min, respectively. The raw and torrefied biomasses have been characterized using thermal-gravimetric and elemental analyses (C, H, N, S, O). The kinetic profiles were evaluated using the pseudo-first order rate equation (PFORE). An increase of the carbon/oxygen ratio was obtained as a result of the torrefaction severities. The greater mass losses were evidently obtained at higher temperatures (52% at 300 °C, and 67% at 350°C). Additionally, the torrefaction process allows the storage of the feedstock for longer time; it reduces the energy consumption for grinding, and enhances the friability of the biomass for large-scale utilization in metallurgical furnaces. Abbreviations: CENTORRE: Multiple hearth furnace; PFORE: Pseudo-first order rate equation.

Keywords: biomass, poplar, residues, torrefaction, waste

1 INTRODUCTION

The depletion of fossil-fuels and the increased environmental pollution have boosted the exploration of the green-energy alternatives. The solutions are essentially associated to solar, wind, ocean, geothermal and biomass resources [1]. It was previously reported that biomass-based resources occupy 10 % of the primary energy demand [2].

The forestry residues are worldwide available and represent a feasible way for energy production. Several thermal processes such as torrefaction and pyrolysis can be used for the efficient upgrading of the feedstock into useful products (solid, liquid and gaseous fuels). Torrefaction is promising since the resulting materials have similar properties to coal, and these can be additionally densified into pellets or briquettes to increase the calorific content [3, 4]. Torrefaction is characterized by the low range of operating temperatures (usually between 200 °C and 350 °C) in an inert ambient.

The main advantage over pyrolysis is the low input of energy required into the system. It has been previously reported that torrefaction improves the physical characteristics of the bio-resources: it enhances the hydrophobicity and the brittleness [5, 6], and consequently, the energy input for grinding is also reduced [7].

Poplar biomass (*Populus, sp.)* was evaluated in this wok due to its highly abundance in different ecosystems, and to its low ash content. The characterization results of the materials (before and after torrefaction) are presented.

2 MATERIALS AND METHODS

2.1. Materials

The raw poplar biomass (*Populus sp.)* was provided in the configuration of standard French P-31 wood chips by RAGT-Energie (France). The initial moisture content of the samples was determined as 20.2 % w/w, and the density was estimated as 400 kg m^{-3}.

2.2 Torrefaction process

The preparation of the bio-coal materials was carried out through torrefaction process using a vertical furnace with multiple hearths (the so-called CENTORRE oven: i.d. Ø 1.82 m, hearth height: 0.74 m; including a rotatory shaft, i.d. Ø 0.42 m) provided by CMI Group technology (Seraing, Belgium). The column is equipped by six hearths or stages in which are present two burners by stage, achieving temperatures in the range of 200 °C to 350 °C. An internal rabbling system is provided for enhancing the transport and the displacement of the biomass into the hearths (Figure 1).

Before feeding the furnace with the raw biomass, it was firstly heated overnight at the temperature chosen for operating torrefaction. The flow rate of biomass (Q) was set at Q≥45 Kg h^{-1} (during 20 h of working time) for approaching to the real industrial production, and two torrefaction conditions were considered : i) 300 °C; ii) 350 °C with a residence time of 45 min, respectively. The torrefied biomass exiting the oven was cooled down into two successive screw conveyors and finally collected in airtight containers of 1 m^3 volume (in which it was additionally introduced nitrogen stream for maintaining low oxygen content, < 5%). The mass and energy yields of the tests were then calculated, and the torrefied biomass was characterized.

2.3. Characterization of the materials

The raw and torrefied biomasses were previously grinded by a cross beater mill SK 100 (Retsch, Haan, Germany) for characterization analyses; the particle size of the materials was reduced until: 0.1 mm<d50<0.5 mm. The average particle size (d50) was systematically verified through a dynamic image analyzer (CAMSIZER XT equipment) from RESTCH (Eragny, France).
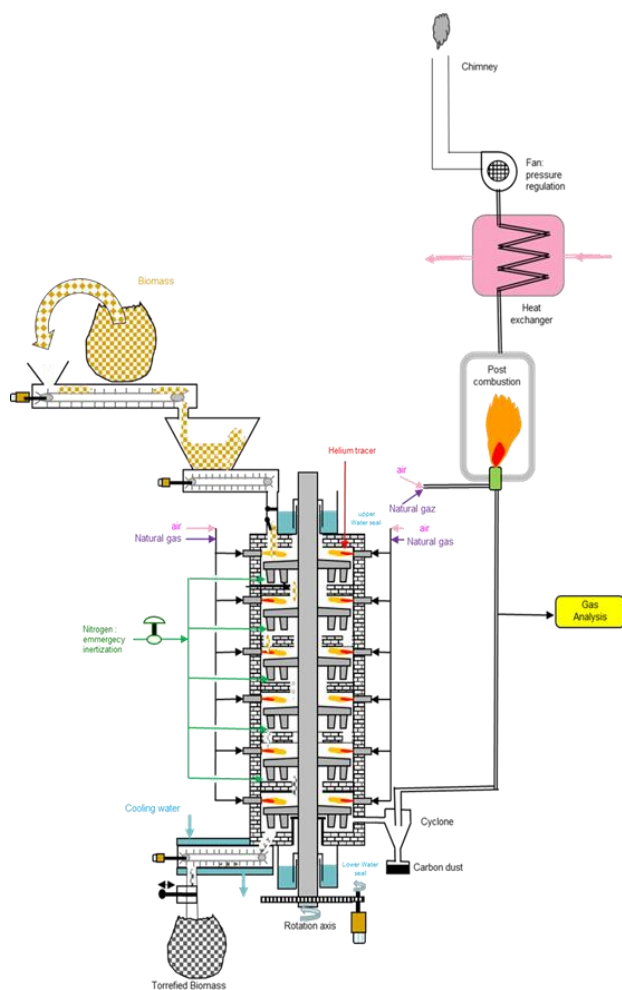
Figure 1. Scheme of the torrefaction pilot plant (CENTORRE)

2.3.1 Thermal gravimetric analyses (TGA)

Thermal-gravimetric analyses were performed under N2 atmosphere (with a flow rate of 50 mL min^{-1}) at a heating rate of 10 °C min^{-1} using a TGA-92 equipment (SETARAM instrumentation, Caluire-et-Cuire, France). The samples of 5 mg were degraded within a temperature range of 30-350 °C.

2.3.2 Elemental analyses

Elemental analyses were conducted with a Vario EL cube instrument (ELEMENTAR, Langenselbold, Germany). The weight content of the main elements (such as carbon, hydrogen, nitrogen and sulfur) was determined by the equipment in three replicated analyses to validate the repeatability of the results (the standard deviation was in the order of $\pm$ 5%). The following standard procedures were used for determining the elemental composition of the materials [1]: i) Carbon: XP CEN/TS 15104; ii) hydrogen: XP CEN/TS 15105; iii) nitrogen: XP CEN/TS 15107; iv) sulfur: XP CEN/TS 15289; v) ash content: XP 199 CEN/TS 14775. The oxygen content was calculated by difference after determination of C, H, N, S elements and ash content.

2.3.3 Calorimetric analyses

A 6200 isoperibol oxygen bomb calorimeter (Parr, Moline-Illinois, USA) was used for determining the higher heating values (HHV) of the raw and torrefied biomass. The ignition of 1 g of dried samples under oxygen atmosphere was performed at 30 bar pressure. Benzoic acid (Merck, Darmstadt, Germany) was used for calibrating the heat capacity of the calorimeter [5].

2.3.4 SEM analyses

The samples were analyzed using a Philips XL-30 microscope (Philips Electron Optics, BV, Eindhoven-The Netherlands); the specialized scanning electron microscope (SEM) with low-vacuum and high-vacuum modes, is capable of analyzing samples under low pressure (<5x10^{-4} Pa). The objective lenses of the XL series have optimum performance for both imaging and micro-analysis of specimens; this makes ideal for the monitoring of manufacturing processes, as well as for routine operations. A high magnification is easily obtained (which improves the study of several types of micro/nano-structures). The microscope is also equipped with an Energy Dispersive X-ray (EDX) spectrometer (INCA 250, Oxford instruments) for chemical analyses.

3 RESULTS AND DISCUSSION

3.1 Characterization of the materials

In Table I are reported the higher heating values (HHV), the ash content and the elemental analyses (C, H, N, S, O) of the raw and torrefied feedstock. As expected, at higher temperature the oxygen/carbon and hydrogen/carbon ratios decrease as a consequence of the by-products formation during the decomposition steps of hemicellulose and cellulose (into condensable and non-condensable gases). From the Van Krevelen plot (Figure 2) the O/C ratio is more affected than H/C ratio (the O/C uptake of the poplar biomass decreased from 0.72 to 0.19 at 350 °C). The temperature contributes to the densification of carbon concentration, which also favors the building of energetically dense materials. The HHV increases from 18.30 MJ kg^{-1} (raw biomass), to 24.8 MJ kg^{-1} (at 300 °C), and to 28.0 MJ kg^{-1} (at 350 °C). The greater fixed carbon (FC) values indicated that the torrefied poplar at 350 °C (with 64.6 % of FC) is the most interesting material for replacing mineral coal in the metallurgical industries (Table I).

The experimental higher heating values (HHV) obtained with the calorimeter bomb equipment were additionally compared with the predicted values obtained from the equation suggested by Friedl et al. [8]; Eq. (1) allows predicting well the energy content of the biomass by using its elemental composition:

$$HHV = 3.55C^2 - 232C - 2230H + 51.2CH + 131N + 20600 \quad (1)$$

where HHV is the higher heating value expressed in kJ kg^{-1}; C, H and N are the mass content (% w/w) of carbon, hydrogen and nitrogen, respectively.

Table I. Fixed carbon and ash content of poplar-based materials

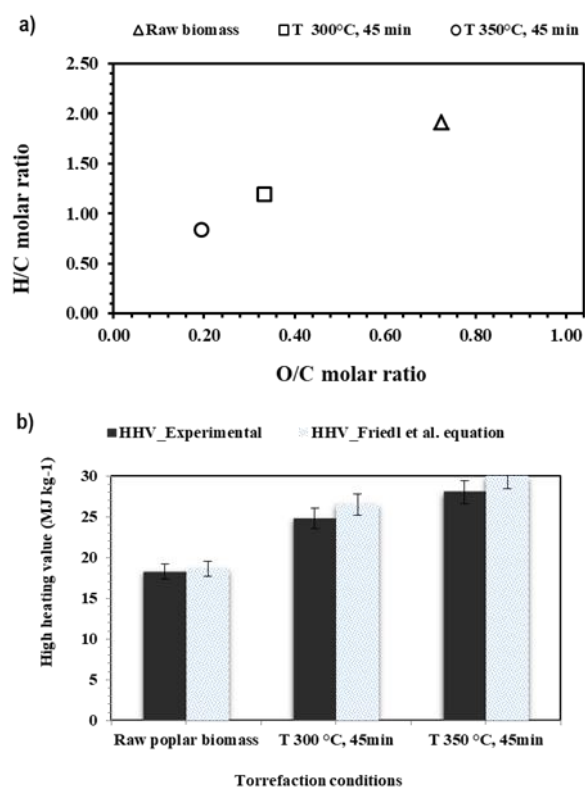| Material	Ash content at 815 °C (%)	Fixed carbon (%)
Raw poplar	1.20	16.30
Poplar_300°C	2.10	46.50
Poplar_350°C	3.10	64.60

Figure 2. Elemental composition and energy content of the materials: a) Van Krevelen plot; b) Higher heating values

3.2 SEM analyses

SEM micrographs were performed for examining the topography of the materials surface. Figure 3 shows the morphology of the poplar biomass (before and after torrefaction); the images are in agreement with those obtained by Demey et al. [9]. Some cavities are found around the entire surface, which correspond to the natural vessels of the sap channels of *Populus sp.* The torrefaction process impacts on the surface of the materials, generating an open structure as a result of the dilatation of the biomass cavities. This fact confirms that at harder torrefaction severities, wider "*craters*" are obtained on the torrefied biomass surface [9].

3.3 Thermal-gravimetric analyses (torrefaction tests at laboratory scale)

The mass yield of the biomass depends on the temperature and on the residence time of the samples into the torrefaction furnace. Thus, the kinetic profiles were plotted at laboratory scale (thermal-gravimetrical analyses, TGA) for monitoring the weight loss as a function of the time. The results in Figure 4 demonstrated that increasing the torrefaction time, the mass loss increases until a pseudo-plateau is achieved. The curves have the typical shape of the pseudo-first order reaction plots.

In our previous work [9], the so-called pseudo-first order rate equation (PFORE) (Lagergreen kinetic model [10]) has been adapted and tested for describing the thermal-conversion of the biomass at different temperatures.
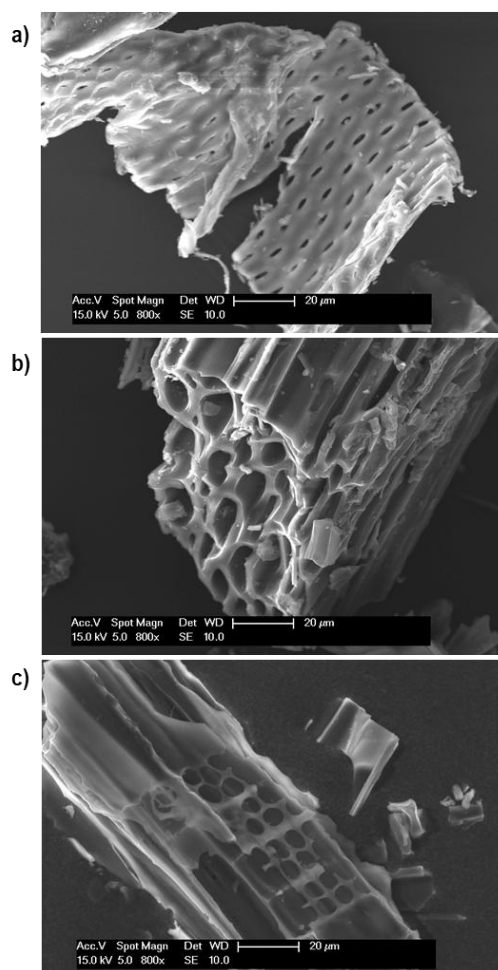

Figure 3. Scanning Electron Microscopy (SEM) images of poplar biomass: a) Raw biomass before torrefaction; b) Torrefied poplar at 300 °C; c) Torrefied poplar at 350 °C

In this work, the adapted PFORE equation [9] was used for describing the process in the range of temperatures of 300-350 °C. Although the original physical principles of the model were tested in systems different to torrefaction, the suggested empirical equation defines the kinetic profiles as a progressive rate in which an equilibrium time is reached. It is noteworthy that at 200–350 °C, the hemicellulose and cellulose decomposition plays an important role in the biomass upgrading, and the curves have a characteristic plateau in this interval, thus, the equation is well adapted for fitting the experimental data.

The relative mass loss (W_t) is defined as the ratio between the mass at the time t (m_t) and the initial mass of the sample (m_0) [9]:

$$W_t = 100 - \frac{m_t}{m_0} \qquad (2)$$

Similarly, the relative mass loss at the equilibrium time (W_p) is defined as the ratio (% w/w) between the mass at the plateau (m_p) and the initial mass of the sample (m_0) [9]:

$$W_p = 100 - \frac{m_p}{m_0} \qquad (3)$$

The variation of the relative mass loss as a function

of the time is defined as follows [9]:

$$\frac{dW_t}{d_t} = K_T(W_p - W_t) \qquad (4)$$

where K_T is the kinetic constant expressed in min^{-1}, t is the torrefaction time expressed in min, and the mass of the samples is expressed in mg. Eq. (4) states that the rate of thermal-conversion is directly proportional to the distance to the plateau (W_p-W_t), such distance is higher at time t=0, in which W_t=0, and decreases with the time until the equilibrium is reached, W_p-W_t=0. The integration of Eq. (4) gives:
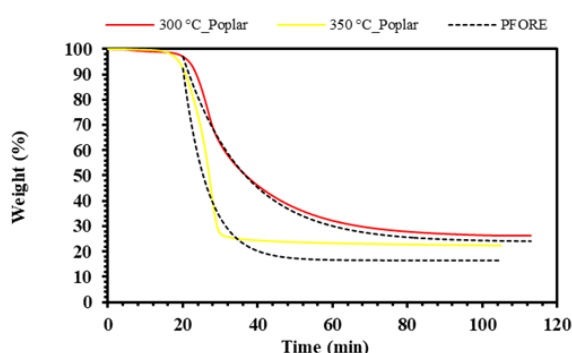
$$W_t = W_p(1 - e^{-kt}) \qquad (5)$$

Figure 4. Thermal decomposition kinetic of poplar-based biomass

The value of the kinetic constant (K_T) was found to be two times greater for the process at 350 °C (Table II), which is in agreement with the literature [9], since the increases of the temperature contribute to accelerate the thermal degradation of the feedstock. The AWL values reported in Table II for TGA curves correspond to the maximum mass losses, which are achieved at the equilibrium plateau. In the case of the condition at 300 °C, the torrefaction is slower and the plateau is reached at 70 min. However, it can be seen in Figure 4 that at 300 °C (45 min) the mass loss is around 50 %, and at 350 °C (45 min) it represents 71%. This is comparable with the results obtained at the CENTORRE pilot-plant (AWL: 52% and 67%, respectively).

Table II. Kinetic parameters of the thermal conversion of torrefied poplar biomass

Experimental (TGA)			Predicting model (PFORE)			Torrefaction pilot-plant (CENTORRE)		
Biomass	T (°C)	AWL exp (%)	K_T (min^{-1})	AWL TGA (%)	r^2	Inlet flow rate (kg h^{-1})	Outlet flow rate (kg h^{-1})	*AWL pilot-plant (%)
Poplar	300	72.91	6.2 x10^{-2}	73.24	0.992	44.0	21.0	52.27
	350	75.76	0.15	75.88	0.933	46.0	15.0	67.39

*AWL: average weight loss calculated in dry basis (d.b.)

4 CONCLUSIONS AND PERSPECTIVES

Torrefied poplar-based biomass at 350 °C is a promising material to be used as reducing agent for metallurgical applications. The torrefaction process contributes to increase the calorific content and the fixed carbon of the products. It was found that the higher heating values increased from 18.3 MJ kg^{-1} (raw poplar biomass) to 24.8 MJ kg^{-1} and 28.0 MJ kg^{-1}, for torrefied poplar at 300°C (45 min) and 350°C (45 min), respectively. The fixed carbon was increased from 16.3% (raw poplar) to 46.5% and 64.6%, for torrefied poplar at 300°C (45 min) and 350°C (45 min), respectively. The obtained values of fixed carbon content are interesting, since the manufactured materials could be used for partially replacing the mineral coal as a reducing agent in metallurgical applications, which will be the scope of the future work.

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