Torrefaction process for the improvement of solid lignocellulosic biofuel

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General aspects

Biomass for energy production has been extensively studied in the recent years. In order to overcome some constrains imposed by the chemico-physical properties of the biomass, several pre-treatments have been proposed. Torrefaction is one of the most interesting as torrefied biomass holds a wide range of advantages over raw biomass: the devolatilization of water and some oxygenated compounds determine the increase of the calorific value, both on mass and volumetric basis. The increase of the density approximately up to 750-850 kg/m^3, reduces the transportation costs. The reduction of the moisture content increases the resistance of the biomass to the biological degradation, thus facilitating its storage for long periods [1]. The process raises some concerns when waste biomass is used as feedstock as toxic pollutants such as heavy metals can contaminate it [2-4]. This is the case of plants used for soil restoration through phytoremediation technique.
The work aims at studying the torrefaction as eco-sustainable process for the combined production of a solid biofuel with improved characteristics with respect to the starting material and a vapor fraction, embedded in the gas carrier flow, to be directly burned in a MILD combustion burner (hence in highly diluted and pre-heated conditions) for energy recovery. The study wants to address the need of optimize the torrefaction stage with respect to energy sustainability and environmental impact. To this aim the energetic content of the torrefaction products as a function of the process temperature has been evaluated. At the same time the fate of the heavy metals in the raw biomass (Cd, Pb) at the different torrefaction temperature has been studied and their stability in the solid torrefied biomass has been investigated and compared to the stability in the in the raw biomass.

Experimental set-up and procedure

The tests were carried out under oxygen-limited conditions, at constant heating rate (10 °C/min), at three final temperatures, namely 523, 543 and 573 °C. For each temperature a different residence time was taken into account of the char in the reactor, namely 15 min for 523 K, 10 for 543 K and 5 min for 573K.
Populus nigra has been used for the torrefaction experiments in the SOLO furnace.
The cross section of the furnace is shown in figure 1. The cylindrical reactor is divided into two concentric and connected zones. In the internal cylindrical section the container with the biomass was positioned, whereas in the external section the recirculation of the exhausted gases from evolving during the torrefaction test occurs. The volatiles produced in the reaction unit entered the condensation device, which consists of two pyrex condensers where condensable volatiles cool and condense. At the condenser's outlet, a Pyrex flask was allocated for the collection of the liquid products. The non-condensing gases were fed to the analytical system for on-line characterization (Horiba Mexa 7170D).

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Temperature of the sample and of the reaction environment was monitored constantly through six K-type thermo-couples.

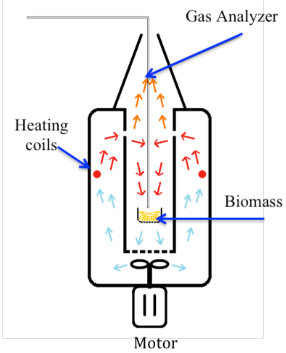

Figure 1: Cross section view of the furnace.

The experiments were performed with 100 g of Populus nigra branches, packed in aluminum paper and placed in steel container. The biomass was heated at the desired temperature and hold at the final temperature for the desired retention time. At the end of the test the temperature decreased gradually and the sample was quenched immersing the it in a metal vessel containing water at a temperature of 10 ° C. The quenched sample was heated in the furnace for 24 hours at 105 °C before measuring the final weight in order to remove the water and moisture of the quenching. The yields of the char and of the liquid were determined gravimetrically respect to the fed sample, whereas gas yield was evaluated as the amount needed to complete the mass balance. For the raw and torrefied materials the proximate and the elemental analysis were performed and HHV were measured. The CHONS content were measured using Analyseur Flash 2000 (Thermo Scientific) according to the ISO 16948:2015.
Proximate analysis has been conducted as follows. Char moisture was measured through the Sartorius Moisture Analyzer (Model MA35) according to the procedure ISO18134-3.
Carbolite AFF 1100 furnace was used for the determination of ash content with the procedure 815°C according to the ISO 1171/2015 and volatile fraction following the procedure ISO 18123:2015. The fixed carbon content was calculated as the amount needed to complete the mass balance. The char calorific value was determined using a bomb calorimeter (Oxygen Combustion Vessel 1108 - Parr Instrument Company) according to EN14918.
The content of the major inorganic elements and of the heavy metals was determined by dissolving the biomass samples via microwave-assisted acid digestion based on US-EPA Methods 3051 and 3052.
The energy yield, energy content, and energy density of the char were calculated on dry basis by Eqs. (1), (2) and (3).
In the equations "t" stands for torrefied material and "f " for feedstock.
(1) Energy content= Weight (f;t)* HHV (f; t)
(2) Energy yield= (Energy content (t))⁄(Energy content (f))*100
(3) Mass Energy density= (HHV (t))⁄(HHV (f))

Results and discussion

For the higher torrefaction temperatures and the higher residence times, the torrefaction treatment influenced, as expected, the final appearance of the treated samples, with the darker colors and more brittle texture being obtained. Figure 2 shows the products yield obtained at different final temperatures.

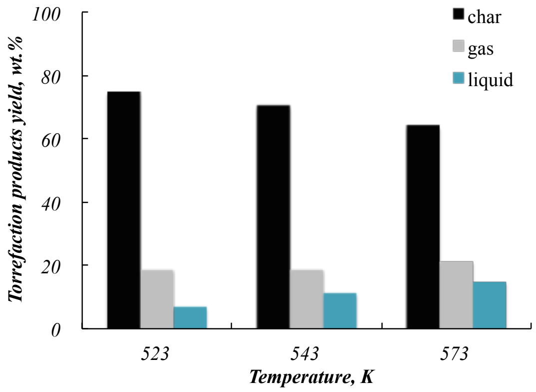

Fig. 2 Products yields at T = 523, 543, 573 K, respectively at residence time of 15, 10, 5 min.

A clearly trend was possible to observe for the char and liquid yield. The char yield decreased from 74.6% to 63.99% as the final temperature increases from 523 to 573 K. The decrease in the char yield is due to the significant loss of volatile matter at higher temperature. Liquid yield increased from 6.8% to 14.8%, whereas the gas yield is almost constant at around 20 %, ranging from 18.5% to 21.21% in the examined temperature range. At low temperature, the weight loss is due mainly to hemicellulose decomposition, whereas at 573 K the higher weight loss is due to the decomposition of cellulose and lignin. At 430 K CO_2 was released concurrently with a low releasing of CO and CH_4, both reaching the maximum at 545 K.
The effect of the different torrefaction conditions on char properties is presented in Table 1.

	moisture	*volatiles*	*fixed carbon*	*ash*	*O/C*	*C/H*
T, K	*wt % as recieved*				*wt % db*	
Populus nigra branches	8.4	77.0	18.3	4.8	0.7	1.5
523	1.2	69.1	25.7	5.2	0.6	1.3
543	1.5	67.9	28.8	4.9	0.5	1.2
573	1.6	62.5	31.7	5.8	0.5	1.1

Tab. 1 Elemental and proximate analysis of Populus nigra branches and of chars.

From Table 1 it can be seen that after the torrefaction treatment the most important advantage was the reduction of the moisture content, since this removal contribute to increase the calorific value of the starting material to prevent the biological degradation. The volatile matter gradually decreases with the temperature up to 573 K due to the decomposition of hemicellulose and in part of the cellulose. Fixed carbon and ash content increase during the process. As the temperature increases the chars contained less oxygen and hydrogen, and more carbon. The atomic ratios O/C and H/C of the chars decrease with the increase of the temperature. O/C ratio decreased from 0.73 to 0.55 and H/C ratio values from 1.49 to 1.13; this could be due to the loss of hydroxyl (OH) groups during torrefaction. The HHV, mass yield and the energy characterization of chars produced at 523, 543 and 573 K were reported in Table 2. The HHV of chars increased significantly with the increase of the torrefaction temperature, because of the increase of the relative concentration of C–C and C–H bonds after the removal of C–O bonds during the torrefaction. The highest value of HHV, 23.3 MJ/Kg, was obtained at 573 K. The energy content of the chars decreases with the increase of the temperature and the results were lower than the raw biomass, as well as the energy yield due to the reduction of the yield with the temperature. The energy density factor, directly correlated with the HHV value of the feedstock and the related chars, slightly increases with the temperature. Indeed the maximum mass energy density value was observed at 573 K, even if was close to 1.0.

	HHV	*Energy content*	*Energy yield*	*Energy density factor*
T, K	*MJ/Kg*	*KJ*	*%*	
Populus nigra branches	19.9	1604	100	
523	20.8	1253	78.14	1.05
543	21.5	1216	75.77	1.08
573	23.3	1201	74.96	1.17

Tab. 2 Calorific value, Energy content and Energy density of Populus nigra branches and chars.

In the Figure 3 (a) the concentration of Cd and Pb along the temperature was reported. Moreover, the amounts of Cd and Pb in the chars with respect to the corresponding amount in the raw material (Ion Recovery) have been calculated as a function of the temperature. The concentration of Pb and Cd in the chars increases with the temperature and the increase become remarkable above 573K. This is due to the organic and volatile fraction devolatilization. In the temperature range studied the Cd and Pb devolatilizaion was not observed as resulted from the value of the Ion Recovery that remains constantly equal to 1.

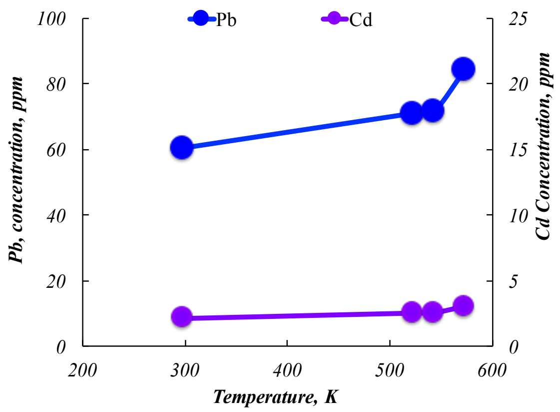

Fig. 3: Concentration of Pb and Cd in the chars produced different final temperatures.

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