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Working Group: WG1

STSM Title: Production of biofuels through torrefaction

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1. PURPOSE OF THE STSM

The scientific mission was focused on the study of the torrefaction as eco-sustainable process for the production of a solid residue and a vapour phase 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. Torrefied biomass holds a wide range of advantages over raw biomass as the moisture content in torrefied biomass is reduced to below 5 wt %; it increases energy density by removing some of the volatile matter in wood as water and CO₂, hence the calorific value increases. The density is increased to 750-850 kg/m³. This in turn reduces the transportation costs. Unlike raw biomass, which may rot when left unsheltered, torrefied biomass is not biologically degraded. Regarding the case of biomass from contaminated land, from forestry, and from demolition and construction activities, are difficult to manage both for the safe disposal in landfill that for a potential fuel to produce bioenergy. These biomass are characterized by high content high content of pollutants as PTEs (potentially toxic elements).

The torrefaction may be interesting as a pre-treatment for the safe use of contaminated

biomass. Essential is the distribution of the PTEs in the end-products mainly depend on the type and amount of metal and temperature. The objective for the valorisation of such biomass is to maximise the metal content in the solid and minimise it in the liquid and gaseous phases, thus preserving the high value of the newly generated products.

Therefore, the study of the effect of the metals during the torrefaction and on the end-products might be treated, in order to investigate the distribution in the solid or in liquid product.

The goal of the collaboration was the exploration of torrefaction as a possible pre-treatment of contaminated biomass with heavy metals. More specifically, the experimental activities was focused on the study of ligno-cellulosic biomass contaminated by Pb and Cd, under different torrefaction conditions.

An evaluation of the treatment was performed evaluating the yields of the products and the energetic characterization of the gas and solid product.

2. EXPERIMENTAL ACTIVITY AND MAJOR RESULTS

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. The period of the time considered was 15 min for 523 K, 10 for 543 K and 5 min for 573K.

2.1 MATERIALS AND METHODS

- Torrefaction tests

The torrefaction experiments on *Populus nigra* branches were conducted in the SOLO furnace.

The cross section of the furnace is shown in figure 1. The cylindrical cylinder reactor was divided into two zones concentric and connected. In the internal cylindrical section was positioned the container with the biomass, whereas in the external section was occurred the air recirculation zone.

The bottom and the upper area of the internal section were connected with the recirculating air zone by means a pierced grid. A motor forces air to circulate within the furnace. The gaseous stream exiting the container with the biomass, was flowed through the condensers where was condensed and collected. The volatiles produced in the reaction unit entered the

condensation device, which consists of two pyrex condensers (connected with cooler) 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 through the HORIBA motor exhaust gas analyser (Horiba Mexa 7170D). The furnace was connected to HVAC controller where the temperature and fan speed can be manually controlled. Temperature of biomass and concentration of different gases were monitored constantly online. The furnace was equipped with six K-type thermo-couples, which were connected to Keysight (Agilent/HP) 34970A Data Acquisition / Data Logger Switch Unit variable drive. Temperature of the feedstock inside the container (a small hole was pierced into the sample and a thermocouple tip was placed inside to measure the temperature of the sample), temperature up and below the container, temperature of the container, temperature of the flue gas and atmospheric temperature were measured.

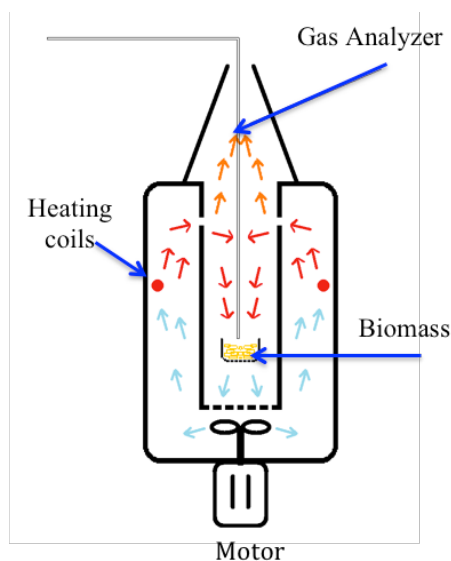


Figure 1: Cross Section View of the furnace

The experiments were performed with 100 g of *Populus nigra* branches, packed in aluminium paper and placed in steel container. The biomass sample was preheated in the furnace at least for a period of 2 hours. The temperature of the furnace was maintained at 105 C in order to remove the moisture. Then, the biomass is heated at the desired temperature and hold at the final temperature for the desired retention time. At the end of the test the temperature decreases gradually and was possible to remove the sample placed inside the furnace and to quench it. The quenching was taken place to immersing the char

sample in a metal vessel containing water at a temperature of 10 ° C. 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 the liquid were determined gravimetrically respect to the fed sample, whereas gas yield was evaluated as the amount needed to complete the mass balance.

- Analysis of the experimental results and characterization

For the raw and torrefied materials the proximate and the elemental analysis were performed and pH 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.

Char pH was measured with a digital pH meter (pH-mètre SevenGo (Duo) SG98, Mettler Toledo) in deionized water using a 1:20 wt/wt ratio following the EN15933827 standard procedure. The solution was hand shaken and allowed to stand for 5 min before measuring the pH.

The calorific value was determined using a bomb calorimeter (Oxygen Combustion Vessel 1108 - Parr Instrument Company) according to EN14918.

The mass yield, energy yield, energy content, and mass energy density of the char were calculated on dry basis by Eqs. (1), (2), (3) and (4).

In the equations “t” stands for torrefied material and “f” for feedstock.

$$(1) \text{Mass yield } (Y_{\text{mass}}) = \frac{\text{Weight } (t)}{\text{Initial weight } (f)} * 100\%$$

$$(2) \text{Energy content} = \text{Weight } (f; t) * \text{HHV } (f; t)$$

$$(3) \text{Energy yield} = \frac{\text{Energy content (t)}}{\text{Energy content (f)}} * 100$$

$$(4) \text{Mass Energy density} = \frac{HHV (t)}{HHV (f)}$$

2.2 RESULTS AND DISCUSSION

- Torrefaction products yields

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 colours and more brittle texture being obtained.

Figure 2 shows the products yield obtained at different final temperatures.

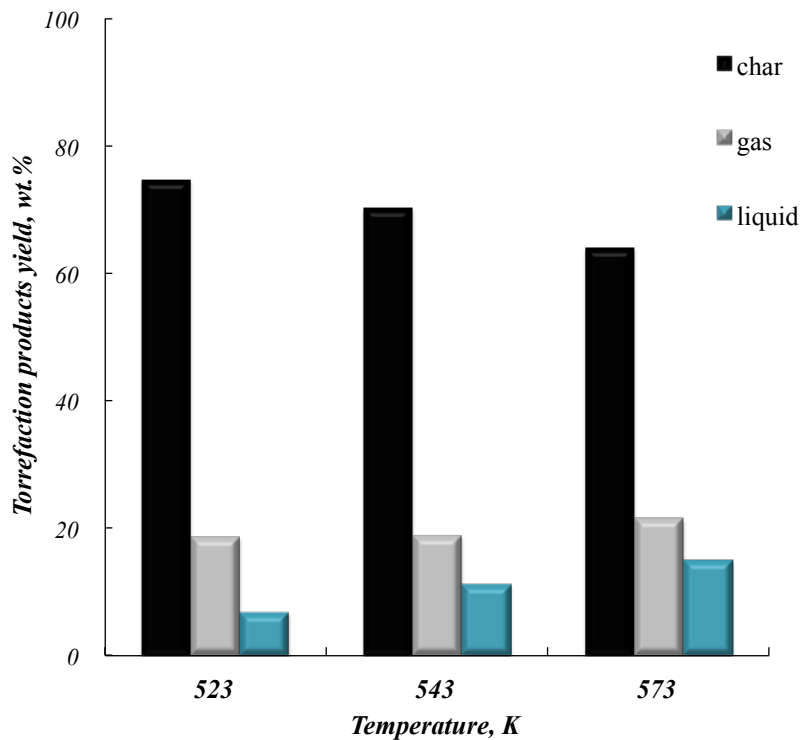


Figure 2: Products yields at $T = 523, 543, 573$ K, respectively at residence time of 15, 10, 5 min.

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. Substantially, a clearly trend was possible to observe for the char and liquid yield. 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. The gas was composed mainly of CO₂, CO and small amount of hydrocarbons and CH₄.

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. The overall weight loss variation observed in these experiments is within the range described in similar reports concerning torrefied biomass under inert atmospheres (El may et al., 2012). In the figure 3 are reported the species evolved during the torrefaction test at 573 K along the time.

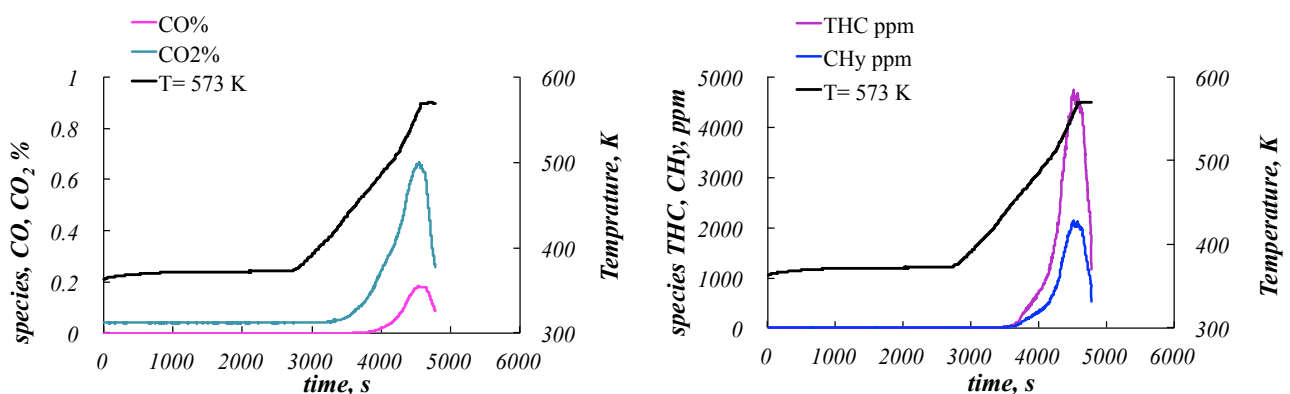


Figure 3: Weight loss of torrefied materials of Populous nigra branches at T = 523, 543, 573 K respectively at residence time of 15, 10, 5 min.

The species that evolve during the process were dependent on the stage of the degradation of the biomass that was to say dependent on the devolatilization of hemicellulose, cellulose or lignin. At 573 K a large amount of hemicellulose was already devolatilized and part of cellulose was decomposed. The CO, CO₂ emission up to 573 K vs time along with temperature vs time is shown in fig. 4. At 430 K the CO₂ was released concurrently with a low releasing of CO, reaching a maximum at 545 K.

- Char characterization and energy properties

The effect of the different torrefaction conditions on char properties is presented in Tables 1, 2 and 3.

<i>T, K</i> <i>Populus nigra</i> <i>branches</i>	<i>moisture</i>	<i>volatiles</i>	<i>fixed</i> <i>carbon</i>	<i>ash</i>	<i>pH</i>
	<i>wt % as recieved</i>				
	523	8.4	77.0	18.3	
543	1.2	69.1	25.7	5.2	6.2
573	1.5	67.9	28.8	4.9	6.3
	1.6	62.5	31.7	5.8	

Table 1: *pH and proximate analysis of Populus nigra branches and of char obtained at T = 523, 543, 573 K respectively at residence time of 15, 10, 5 min.*

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, in agreement with the results obtained in the previous literature (Lu et al., 2012; Park et al. 2012). However, the ash content was an important factor and constrains the valorization of chars as biofuel. The use of chars with high ash content enhances tendency to slagging and fouling in the reactors (Coulson et al., 2004).

									<i>PTEs</i>			
	<i>Na</i>	<i>Al</i>	<i>P</i>	<i>K</i>	<i>Mg</i>	<i>Ca</i>	<i>Fe</i>	<i>Si</i>	<i>Cd</i>	<i>Cu</i>	<i>Pb</i>	<i>Zn</i>
	<i>ppm (mg/Kg)</i>											
523	8327.5	87.5	742.9	3351.5	785.5	10540.0	43.9	106.5	3.4	7.9	161.2	37.2
543	15840.0	109.0	952.0	4878.0	1019.5	11560.0	58.5	115.5	4.1	8.7	190.0	43.3
573	16065.0	116.4	1744.8	7631.0	1766.5	23795.0	129.3	256.5	7.6	18.7	368.0	86.7

Table 2: *ICP/MS analysis of chars produced at T = 523, 543, 573 K, respectively at residence time of 15, 10, 5 min.*

The ash composition is reported in tab. 2. The concentration of the inorganic species increases with the temperature. In the Figure 4 (a) the concentration of Cd and Pb along the temperature was represented, whereas in the Figure 4 (b) the amounts of Cd and Pb in the chars with respect to the corresponding amount in the raw material (Ion Recovery) was reported. The concentration of the Pb and Cd in the chars produced between 543 and 573K was most remarkable than the result obtained at 423 K. With the increasing of the temperature the Cd and Pb content increase in the solid, due to the organic and volatile fraction devolatilization. In the temperature range studied was not observed the Cd and Pb devolatilizaion. The corresponding Ion recovery in the solid, represents in Figure 4 (b), was attested for all temperature range.

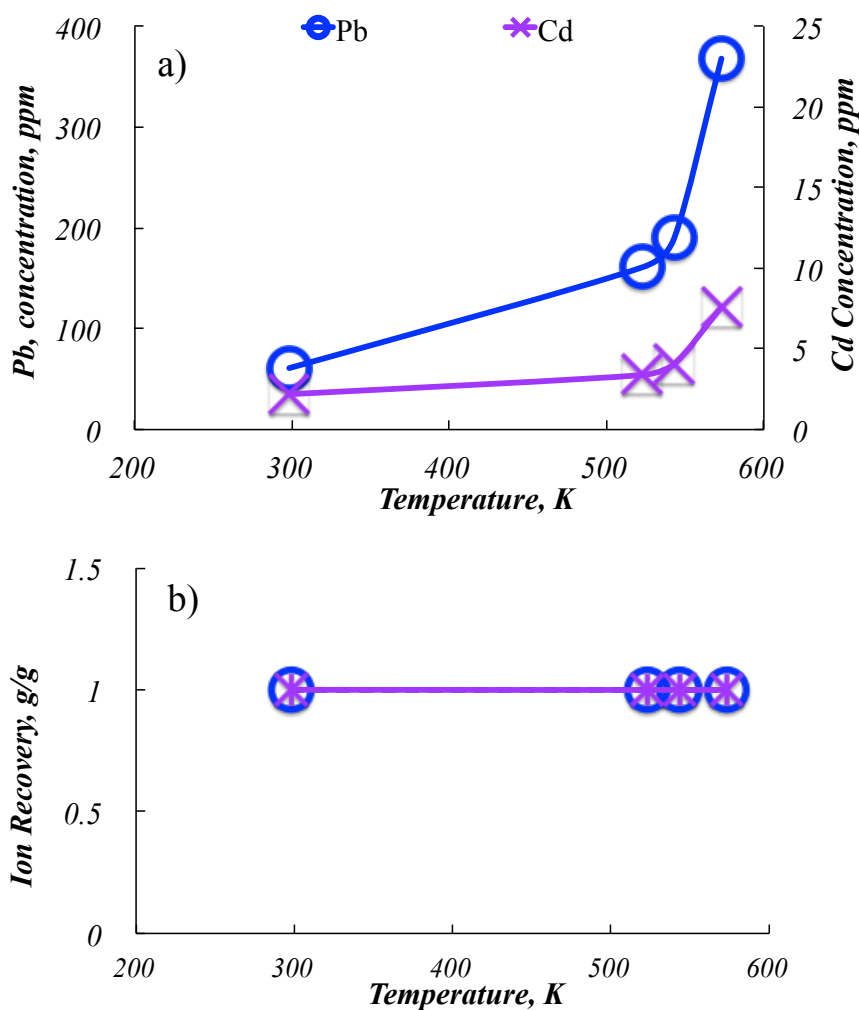


Figure 4: Concentration and Ion Recovery of PTEs in the chars produced different final temperatures.

The information regarding the high PTEs content in the chars assumed that the gas and liquid phase may were free of heavy metals content. However, in addition the investigation on the chlorine content in the feedstock and in related chars should be faced in order to have information of the catalytic effect of the chlorine on the devolatilizaion of Cd and Pb. Table 3 shows the elemental composition of the feedstock and related chars.

<i>T, K</i>	<i>C</i>	<i>H</i>	<i>N</i>	<i>S</i>	<i>O</i>
	<i>wt % db</i>				
<i>Populus nigra</i> <i>branches</i>	47.1	5.9	0.7	0.0	41.5
523	51.4	5.4	1.0	0.0	38.0
543	51.8	5.2	0.8	0.0	37.3
573	54.2	5.1	0.9	0.0	34.0

Table 3: Elemental analysis of populous nigra branches and of char obtained at T = 523, 543, 573 K.

As the temperature increases the chars contained less oxygen and hydrogen, and more carbon. In the Figure 6 it was possible to observe that 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 (Phanphanich and Mani, 2011). This result is a clearly indication of the improvement of the torrefaction treatment of the solid sample as for its fuel properties. The variations of the ratio H/C and O/C are depicted in the van Krevelen diagram, as shown in Figure 5.

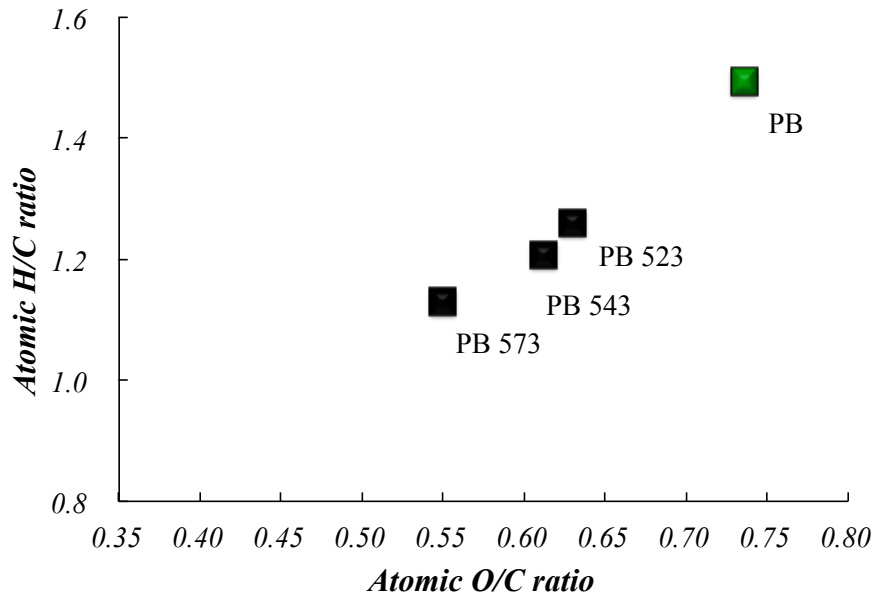


Figure 5: Van Krevelen diagram: H/C and O/C composition of populus branches and chars at 523, 543 and 573 K.

The HHV, mass yield and the energy characterization of chars produced at 523, 543 and 573 K were reported in table 4. 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, compared with the 19.9 MJ/Kg of feedstock.

<i>T, K</i>	<i>HHV</i>	<i>Energy content</i>	<i>Energy yield</i>	<i>Energy density factor</i>
	<i>MJ/Kg</i>	<i>KJ</i>	<i>%</i>	
<i>Populus nigra branches</i>	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

Table 4: Calorific value, Mass yield, Energy content and energy density of populus nigra branches and its derivate at $T = 523, 543, 573$ 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. The value decreases

from 1604 KJ for the raw biomass to 1201 KJ of the char produced at 573 K. The energy density factor, directly correlated with the HHV value of the feedstock and related chars, slightly increase. Indeed the maximum mass energy density value was observed at 573 K, even if was close to 1.0. Nonetheless, the corresponding value of the HHV was improved to 23 MJ/kg for 573 K.

3. HOW THE STSM HAS CONTRIBUTED TO THE ACTION'S AIM

In relation to the SMARTCATs COST Action (CM1404), this STSM is framed within the Working Group 1 activities (WG1: Smart Energy Carriers gas phase chemistry: from experiments to kinetic models). The content of the visit directly addresses the CM1404 action aims. The planned activity is very important for the definition of the optimal operating conditions of real integrated plant for the production and combustion of bio-based energy carriers. The data produced by the lab scale torrefaction reactor will contribute to define strategies for a clean and efficient valorization of contaminated biomass in energy applications trough the production of gas phase free of contaminants bio-fuel.

4. FUTURE COLLABORATION WITH THE HOST INSTITUTION

The collaboration between the IRC-CNR in Naples and the group of prof. Michel at HEIG-VD has been a good opportunity to obtain interesting advances and results concerning the characterization of contaminated biomass under torrefaction conditions. Interesting could be the study of the treatment of contaminated biomass from demolition wood. The possibility to valorise such biomass through the torrefaction treatment and pyrolysis, thanks to the background of the two groups.

5. Foreseen publications/articles resulting from the STSM (if applicable)

The main results from this research collaboration between the IRC-CNR in Naples and the group of prof. Michel at HEIG- VD will be presented at the “3rd General Meeting and Workshop on SECs in Industry” of the COST Action CM1404, that will take place in Prague next October, 2017.

6. Formal confirmation by the host institution of the successful execution of the STSM.

The STSM reported here was successfully executed in the Industrial Bioenergy Systems (IBS) laboratory of the School of Business and Engineering Vaud, Yverdon-les-Bains (CH) that is part of the University of Applied Sciences Western Switzerland.



Prof. Jean-Bernard MICHEL
IBS Group Head

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