

Effect of the presence of combustion exhaust gas on the characteristics of char produced by slow pyrolysis of biomasses

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Abstract

Among the low temperature biomass thermochemical processes slow pyrolysis produces a solid material, the char, and, at the same time, gaseous and liquid energy carriers. Interest in char production comes from its numerous applications: fuel in traditional and advanced power generation facilities, fertilizer and carbon sink, activated carbons precursor, filler in wood and polymer composites, contaminants adsorbent in wastewater and soil, catalyst or adsorbent in gas cleaning, catalyst for syngas conversion to liquid hydrocarbons and bio-diesel production [1]. Since pyrolysis is an endothermic process, feeding the gas stream produced from pyrolysis to a subsequent combustion stage provides for a heat recovery, and this could allow to operate in autothermal regime, thus to have a system able to produce continuously char from biomass. Pyrolysis gas consists of a homogeneous gaseous phase strongly diluted in CO₂ and water vapor. A MILD combustion process is particularly suitable because in this process fuel is supplied under high dilution (fuel concentration outside the flammability limits) and strong preheating (higher temperature than self-ignition one) conditions [2]. One solution for the integrated system provides for the recirculation of the combustion exhaust gas to the pyrolysis reactor, so that it acts as carrier gas and heats the biomass directly. At our knowledge data about the effect of the presence of combustion exhaust gas on the characteristics of char produced under slow pyrolysis conditions are scarce in literature. On the contrary, the effect of the presence of a reactive agent (CO₂, water vapor) during biomass one-step pyrolysis/activation treatment at 700-900 °C is well-known [3]. In the present work, slow pyrolysis of poplar branches in presence of N₂, CO₂, water vapor and a model mixture whose composition is representative of the output from the combustion unit was carried out to understand the effect of the carrier gas on the characteristics of char. Three final pyrolysis temperatures, 450, 480 and 550 °C were investigated because this is the desired temperature range for the pyrolysis unit in the integrated system.

Material and methods

Populus nigra branches were used for pyrolysis tests. The samples were completely dried in an electric oven at 105 °C for 2h to remove the moisture and milled in a blade shredder, and the sieved fraction in the 150–500 μm size range was collected for characterization and the tests. The ultimate and the proximate analyses of the samples were performed using a CHN 2000 LECO analyzer with EDTA as the standard and a TGA 701 LECO thermogravimetric analyzer, based on CEN/TS 15104 and ASTM E870 procedures, respectively.

The test reactor, described in detail in Ragucci et al. [4], consisted of a prismatic jacketed chamber (0.024m L×0.04mW×0.052m H) into which 6g of biomass was loaded. The sample holder comprises five sample trays allocated uniformly along the rectangular cross section of the inner reaction chamber, where biomass is loaded in thin layers

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(approximately 1mm thick). Carrier gas flows into the jacket and then its flow is reversed so that it enters the re-action environment through a ceramic flow straightener. The experimental apparatus includes a superheater, where the carrier gas is heated to the programmed temperature via a PID controller, a condensation device, which consists of a jacketed coil where condensable volatiles cool and condense, and a gas sampling and analysis system. The carrier gas mass flow rate was maintained constant at a value corresponding to an average residence time of 1.5–3s for the gas phase in the reactor, depending on the reactor temperature. Temperature and pressure were monitored using N-type thermocouples and pressure transducers along the carrier gas supply line and at the inlet and outlet of the test chamber.

Four sets of pyrolysis experiments were carried out at constant heating rate ($HR_{sp} = 10^{\circ}\text{C}/\text{min}$) and pressure ($P=1$ bar). N_2 , CO_2 , water vapor and a mixture of these three species (59%, 17% and 24%, respectively, on molar basis) were used as carrier gases. In each set, biomass was pyrolyzed up to the final temperatures of 450, 480 and 550°C , in presence of an established carrier gas.

Char yield was determined gravimetrically, with respect to the fed sample, using a MS105DU (Mettler Toledo) laboratory balance with 0.01 mg resolution.

Char was characterized in terms of elemental and proximate analysis according to the ASTM D5373 and ASTM D1762-84 procedures.

Characterization of the chars porosity was carried out by applying gas adsorption porosimetry. Sorption/desorption isotherms were obtained using argon at 87K as the adsorbate in an Autosorb-1 (Quantachrome) apparatus. Before analysis, the samples were degassed at 573K for 5h under vacuum conditions. The surface area was evaluated using the BET equation and the t-method of Halsey was used for the determination of micropore volume.

Char pH was measured with a digital pH meter (827 pH LAB, Metrohm) in deionized water using a 1:20wt/wt ratio following the ASTM D4972-13 standard procedure.

Infrared spectra of the samples were recorded on a Nicolet iS10 spectrophotometer using the transmission mode and KBr as blank. The spectra were acquired and processed using OMNIC 8 software.

Results

In general, temperature variations in the range $450\text{--}550^{\circ}\text{C}$ do not significantly affect char yields and composition in terms of elemental and proximate analysis, regardless of the carrier gas used during the tests. In fact, at 450°C a great part of devolatilization has already occurred. All the chars are characterized by H/C and O/C molar ratios which indicate the bio-char biochemical stability ($\text{H}/\text{C} < 0.7$ and $\text{O}/\text{C} < 0.3$).

Compared to N_2 and CO_2 , water vapor induces the lowest char yields. As reported in literature, this is related to the ability of the water vapor to penetrate the solid material and to help desorption, distillation and efficient removal of the volatile products. During pyrolysis in a flow of an inert carrier gas, some of the pores in the solid material may be blocked by deposition of carbonaceous material and this contributes also to higher yield of the solid residue.

The treatment in presence of water vapor result in chars with higher ash contents than in presence of N_2 and CO_2 , and this is related to the major devolatilization in presence of water vapor.

pH of chars slightly increases with the temperature and it is always alkaline. In particular, chars obtained in steam assisted tests are slightly more alkaline than the ones obtained in

N₂ and CO₂. Results from FTIR analysis suggests that one reason could be the lower presence of acidic aromatics on the surface of chars obtained in presence of steam. Concerning the porosimetry analysis, all the chars are characterized by type adsorption/desorption isotherms of type IV in IUPAC classification, typical of mesoporous materials. Temperature variations in the range 450-550°C strongly affect the surface area of the chars obtained in presence of all the carrier gases (Figure 1): BET surfaces increases with the temperature. The solid residue is still compact at temperature lower 480 °C, whereas the higher BET surfaces obtained for chars produced at 550 °C suggest the formation of a microporous region.

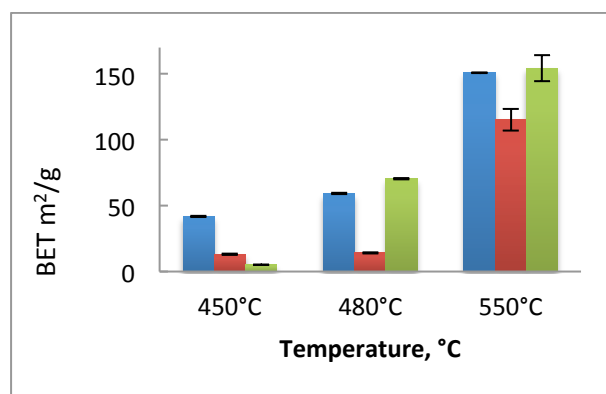


Figure 1: Surface area of chars produced by slow pyrolysis tests using N₂, CO₂ or water vapor as carrier.

At 480 and 550 °C water vapor induces lower char surface area than N₂ and CO₂. Potential causes could be the thinning of the walls and the coalescence of the pores due to the carbon skeleton oxidation (a phenomenon that should lead to the reduction of the microporous fraction in the presence of an oxidizing agent such as vapor) and a higher ash content which adversely affects BET development due to the formation of fused intermediates.

For chars obtained at 550°C, the micropore volume and surface was measured (Table 1). In presence of the two active agents (H₂O and CO₂) lower values of the micropore area and volume were obtained than in presence of N₂. The higher BET surface obtained in presence of CO₂ is mainly due to the meso/macroporous region, whereas in the case of N₂ both the micropore and the meso/macropore region are responsible of the higher value of BET.

Table 1: Micro, meso and macropore analysis for chars obtained at 550°C in presence of N₂, CO₂ and water vapor.

Carrier	BET, m ² /g	Micropore surface area, m ² /g	Total volume, cm ³ /g	Micropore volume, cm ³ /g	Meso/macropore volume, cm ³ /g
N ₂	150.8	91.4	0.077	0.033	0.044
H ₂ O	115.2	74.3	0.054	0.024	0.03
CO ₂	154.3	77.8	0.088	0.026	0.062

Results obtained from tests carried out in presence of a mixture of N₂, CO₂ and water vapor (59%, 17% and 24%, respectively, on molar basis) as carrier gas have been

compared with the results calculated as weighted average of the values obtained from tests carried out in presence of the single agents (calculated mixture).

At 480 and 550°C, char yields from mixture are lower than those obtained from the calculated mixture. Since water vapor is responsible for the lowest char yields, it may be the cause of a non-linear effect when included into the pyrolysis mixture. At the same temperatures, the ratios H/C and O/C are lower than those obtained for the calculated mixture: when the real mixture induces a greater devolatilization than the calculated one, a reduction of both H/C and O/C ratios is observed, pointing out a greater removal of oxygenated compounds.

For each treatment temperature, the surface area of the chars is lower than the one obtained from the calculated mixture (Figure 2).

Among the various carriers, the one that induces the lowest surface area seems to have greater influence on BET development.

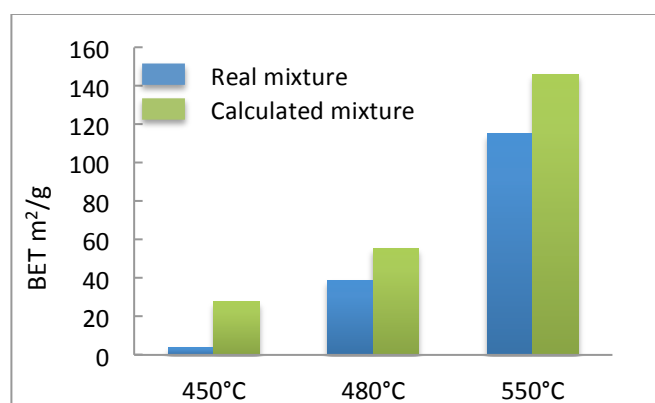


Figure 2: Surface area of chars produced using a mixture of N₂, CO₂ and water vapor as carrier (Real mixture) compared with the calculated mixture.

Conclusions

In the present study the effect of the gas carrier (N₂, CO₂ and steam) on the chemico-physical properties of chars produced under slow pyrolysis conditions in the temperature range 450-550 °C was studied. The results show that steam induces lower char yields and has a negative effect on the char porosity development, thus resulting in lower values of BET surface. This effect is evident also when a mixture of the three gases resembling the exhaust from a combustion unit is used as carrier gas. On the contrary, the influence of the nature of the carrier on the surface and bulk chemistry of the chars is negligible.

References

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