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Hydrothermal carbonization as an effective way of densifying the energy content of biomass

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ABSTRACT

Hydrothermal carbonization processes were studied under different conditions using two different biomass materials: walnut shell and sunflower stem. Coalification under mild conditions was promoted with the aim of increasing the calorific value of the solid hydrochar. Hydrocarbonization processes brought up an increase on the heating value of the materials up to 28.9 and 29.3 MJ kg^{-1}, for sunflower stem and walnut shell, respectively, which corresponds to an increase of 1.75 and 1.50 fold when compared with the natural biomass. Also, regarding the variables studied it was found that temperature and water/biomass ratio were more influent on the hydrocarbonization process than residence time. The hydrochars show negligible N_2 adsorption at 77 K and interesting surface morphology, characterized by the formation of microspheres which grow was temperature increases. Moreover, hydrochars are acid in nature and present several oxygen functionalities, as observed from FT-IR and pzc analysis.

1. Introduction

As a result of the several problems associated to fossil fuel exploitation, the current energy scheme, based on fossil fuel derived sources of energy, is moving towards a more sustainable model. In this line, the International Agency of Energy (IEA) has recently suggested on the "Clean Energy Progress Report" the realigning of fuel subsidies to support clean energy, by providing more incentives for private sector investment and market mechanisms [1]. In the transition to cleaner technologies, biomass stands out as one of the most important renewable energy sources. Apart from the advantage of involving zero net carbon dioxide emissions, it reduces the environmental impact of organic wastes and can be a key factor for the development of rural areas. However, the low energy density associated to biomass stands as a drawback since it involves high transportation costs and a low efficiency of gasifiers, which are often damaged due to the formation of tars during the pyrolysis processes.

Hydrothermal carbonization (HTC) has recently been suggested as a simple, cheap and effective way of increasing the carbon content of biomass, thus providing a higher calorific value [2–4]. HTC can be defined as a thermochemical conversion process in which a material (biomass in this case) is subjected to the action of moderate temperatures (180–230 °C) in a suspension with water under pressure (which can either be provided by the reactor or be due to the gases that are evolved during the decomposition process) for a period of time. Thus, HTC involves the use of mild conditions in comparison with the harsh conditions required by other methods used to produce carbonaceous materials, such as pyrolysis. During HTC processes, the biomass components are hydrolysed and the organic compounds are broken into smaller fragments that are very unstable and repolimerize into oily compounds [5], at the same time that a char (called hydrochar) is formed. Fig. 1 shows typical patterns followed by lignocellulosic biomass during hydrolysis processes [6].

The process dehydration and decarboxylation reactions at these experimental conditions are promoted by using water in the process [7–9], although the addition of different chemicals to provide a specific chemical functionalization on the hydrochar surface has also been studied [10].

Recent studies report that the physico-chemical characteristics of the two phases generated during HTC processes (solid and liquid) depend on the experimental conditions used. Also, the chemical and structural features have been studied on pure organic materials [11] and other complex biomass [12] trying to understand the pathway followed by the precursors during HTC process; how the breaking up of polymers take place, which factors can accelerate the process and how the surface morphology of the hydrochar particles is modified as the reaction occurs giving rise to singular formations such as microspheres. The results found in the bibliography show different behaviours depending on the feedstock used as well as different interpretations of the process. On the other hand, the studies on the influence of operating parameters on the energetic characteristics of the hydrochars are still very scarce.

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