HYDROTHERMAL CARBONISATION OF AGRICULTURAL WASTES

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Introduction

The increasing environmental concern and the need for pricewise market competitive products are becoming two major guidelines in modern material research. As a consequence the main effort in this field is primarily directed towards the production of new materials, which can be synthesised from cheap natural precursors and through environmentally friendly processes.

Among the most widespread ones, nano-structured carbonaceous materials have demonstrated to be very valuable and successful. The main reasons for this are that they have several potential applications, such as catalysis, energy storage, water purification, and they can be easily produced according to numerous different techniques.

In recent years hydrothermal carbonization (HTC) has been discovered to be a very effective and advantageous synthesis method for converting biomass into such useful materials [1]. The HTC process is in fact less energy intensive than other comparable processes. It is an easy process to carry out and it does not require any expensive technologies, which makes it a very suitable candidate for scaling up. It is environmentally friendly, since it uses water as reaction solvent and it does not generate any polluting side streams. In addition to all of this, its main advantage is that it allows the exploitation of cheap and renewable biomasses as raw materials. In fact HTC has been proved to be an effective means of conversion of simple monosaccharides and oligosaccharides into highly functionalized nanostractured carbonaceous materials [2].

Currently the feasibility of using more complex biomasses, such as agricultural wastes, as carbon precursors is under investigation [3],[4]. Since the main component of these raw materials is cellulose, which is essentially a polymer of the sugars that have already been successfully employed in HTC, there are clear expectations that this synthesis method will be an effective means of conversion of agricultural wastes into high value carbonaceous materials. However this further step is posing some challenges, which are mainly due to the limited knowledge about the HTC mechanism and to the higher degree of structural complexity of the newly employed biomasses

For the purpose of this investigation a relatively low lignin content agricultural waste was chosen (i.e. Rye Straw, Table 1). The effects of different HTC temperatures on the chemical composition and morphology of the carbonaceous product were analysed, in such a way as to achieve a better understanding of the overall HTC mechanism.

Cellulose	Hemicellullose	Lignin	Others
41.2	21.2	19.5	18.1

Table 1: Rye Straw wt% composition

Experimental

Hydrothermal Carbonisation:

Raw Rye Straw was grinded to a maximum size limit of 0.8 μm. for an easier processing.

A water solution, containing 10 wt% grinded rye straw, was prepared and placed into a 50 ml Teflon lined stainless steal autoclave, which, after having been sealed, was heated up into a programmable oven for 24hr. In the first set of experiments, the reaction temperature was changed from a starting value of 120^{o}C to a final one equal to 300^{o}C. The reaction liquid was then recovered by means of filtering and used to run a further reaction, having the same parameters as the former one. The solid residue, obtained from each experiment, was washed with plenty of water and then dried in a vacuum oven at 80 ^{o}C.

Characterisation:

Elemental chemical analysis was performed on a (C, N, O, S, H) Elementar Vario Micro Cube. SEM images were acquired on a LEO 1550/LEO GmbH Oberkochen provided with a Everhard Thornley secondary electron and In-lens detectors. FT-IR spectra were recorded using a Varian 600 FT-IR Spectrometer.

Results and Discussion

An analysis of the HTC yields (Fig.1) mainly underlines that increasing the reaction temperatures leads to a major loss in the final amount of solid residue. The main reason for this is that the gasification reaction of the fed biomass becomes more prominent at higher temperature values.

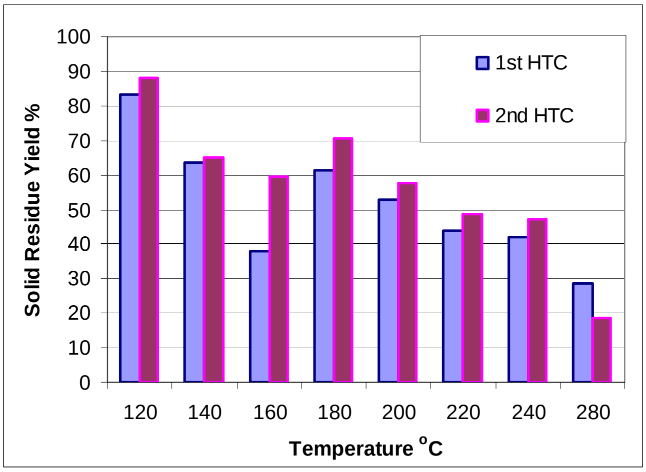


Figure 1: HTC yields of hydrothermally treated rye straw at different temperature values.

Furthermore Fig.1 also shows that the yield of the 2nd HTC is generally higher than the 1st one. The explanation for this outcome might be that the recovered liquid from the 1st HTC process contains some water soluble unreacted intermediate species, which then carbonises only during the 2nd HTC reaction.

Elemental analysis also shows that the C % content of the carbonaceous solid residue increases alongside with temperature. The increase is relatively steeper at lower temperature values (150°C – 220°C), whereas it becomes less significant for values, which are above 220°C.

The findings of the elemental analysis are in good agreement with the FTIR results. As it can be seen from Fig 2, the spectra of the carbonaceous materials, produced at temperatures lower than 200°C, still show a profile relatively similar to the original biomass, with the characteristic peaks at 3325 and 1029 cm^{-1} (respectively –OH and CO- vibrations). This evidence highlights that at these temperature values the extent of carbonisation might be relatively low. On the other hand the spectra of higher temperature products show a decreased absorbance of the two aforementioned peaks and an enhanced aromatic character, which is underlined by the stronger peaks in the range 1750-1500 cm^{-1}(grey shaded area, corresponding to C=C and C=O vibrations). This might be due to a higher extent of carbonisation.

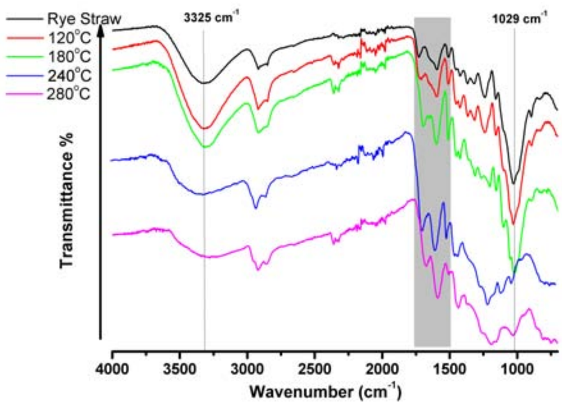
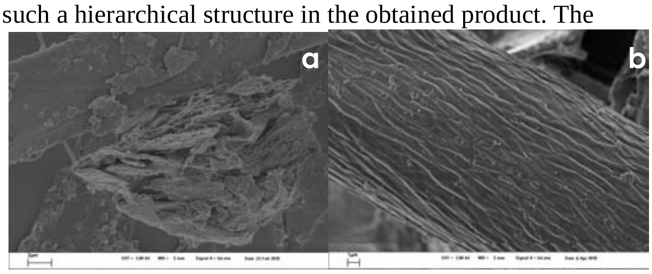


Figure 2: FTIR of carbonaceous material hydrothermally treated at different temperatures (graphs not in scale)

Fig 3. shows how the HTC temperature affects the final morphology of the carbonaceous solid residues. Low temperature products can be observed to partially retain the original fibre like structure even after HTC treatment. On the other hand higher temperature values seem to cause the loss of such a hierarchical structure in the obtained product. The



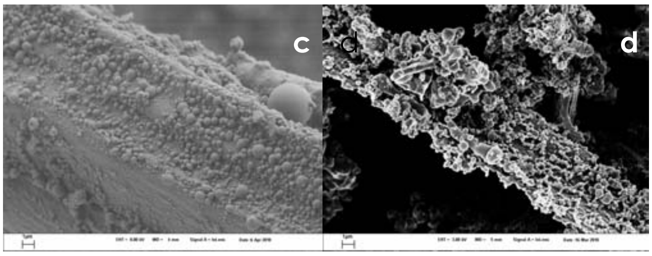


Figure 3: a) Raw rye Straw and hydrothermally treated rye straw at b)120°C c)200°C d) 280°C

explanation for this last finding might be that in the latter case the energy of the system is high enough to disrupt the stiff hydrogen bonding network, which holds together the cellulose fibers, leading to the formation of sphere-like carbonaceous particles.

Conclusions

In the course of this investigation temperature was found out to be a critical parameter of rye straw HTC affecting the key features of the produced carbonaceous material.

Firstly the yield of the reaction was observed to decrease upon increase of temperature.

Furthermore elemental analysis and FTIR revealed how the extent of carbonization depends upon the temperature value. As a matter of fact the condensed aromatic character of the HTC product was found out to increase alongside with temperature.

Finally the HTC temperature was seen to affect the morphology of the carbonaceous material as well. Higher temperature products were in fact composed of sphere-like particles instead of the original biomass fibre structure.

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