



Microwave-assisted hydrothermal carbonization of rapeseed husk: A strategy for improving its solid fuel properties



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ABSTRACT

Hydrothermal carbonization of a waste biomass material is a green and promising technique for improving its solid fuel properties, which does not require pretreatment procedure such as drying of the biomass. In this study, hydrothermal carbonization of rapeseed husk, a waste plant material was carried out under microwave heating and the effect of process parameters, such as reaction temperature and residence time on the mass yields and energy properties of the hydrochars was studied. The procedure involved the heating of the feedstock in de-ionized water in a microwave oven at temperatures of 150 to 200 °C for a specified period of time. The results indicated that the mass yields decreased, as the reaction temperature and residence time were increased, which led to improvement in the energy properties of the prepared hydrochars. The reaction was rapid within the first 20 min, and stabilized afterwards. The energy properties of the prepared hydrochars are consistent with previous studies, showing that the hydrochars have the potential of being used as solid fuel. The structural and morphological analysis carried out revealed that the feedstock was transformed during the process.

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1. Introduction

The use of waste product from industrial processing of biomass materials as solid fuel will be of importance because it will be readily available, cheap, and also helps in the management of these waste materials which would have otherwise being a nuisance if not properly managed. Presently, biomass materials are being promoted as an attractive feedstock for the production of solid fuel because it is commonly considered as a means of reducing carbon dioxide emissions, and can also be used as a direct alternative to replace fossil fuels that are presently in use [1,2]. However, there are challenges that are associated with the use of these waste biomass materials as solid fuels, which include their heterogeneous nature, high moisture content, low density, hydrophilic behaviour among others [3]. Thus, it will be necessary for a special pretreatment to be carried out in order to improve their physicochemical and combustion properties, which will consequently improve the energy conversion efficiency and their subsequent handling, storage and transport activities [2,4].

Hydrothermal carbonization is one of such pretreatment method before the biomass can be used as solid fuel. This method has been shown to be a green and efficient method for treating organic materials due to its comparatively low emission and production of non-toxic waste [5].

Hydrothermal carbonization is a process of decomposing an organic material in hot water at a temperature range of about 150–350 °C depending on the nature of the feedstock, under high pressure to produce solid carbon material (hydrochar) and water-soluble organics [6,7]. It can be carried out using either conventional or microwave heating, and has the advantage of using wet feedstock. Different authors have used microwave heating in the hydrothermal carbonization process of different materials [5,8,9]. This approach is an energy efficient process because it reduces the processing time greatly. Hydrothermal carbonization process has been applied as a pretreatment procedure for many biomasses, such as bamboo [8], dry leaves [10], orange pomace [11], lolly pine [12], and the energy properties of these materials have also been studied. However, no study has reported the energy properties of the hydrochars from the microwave-assisted hydrothermal carbonization of rapeseed husk to the best of our knowledge.

Rapeseed (*Brassica napus*) belongs to the family of Brassicaceae. It is a crop cultivated because of its nutritious oil-rich seed, and can be found in Northern part of England. The oil from rapeseed has been used as lubricant for steam engines as far back as in the 19th century, while the husk is the residue obtained when the rapeseed is crushed to remove the oil, and has been used to prepare cattle feeds over the years [13]. Converting the rapeseed husk into solid fuel could be an attractive alternative in the management of this readily available waste material.

In this study, microwave-assisted hydrothermal carbonization of rapeseed husk is presented, with emphasis on the effect of different process parameters, such as reaction temperatures and residence times on the mass yields and energy properties of the prepared hydrochars. The

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structural and morphological properties, as well as the thermal stability of the prepared hydrochar were also studied.

2. Materials and methods

2.1. Feedstock material

Ian Dobson of Department of Chemistry, University of Hull, UK provided the rapeseed husk used for the experiments. Prior to the experiments, the rapeseed husk was kept in plastic bags and stored at room temperature.

2.2. Microwave-assisted hydrothermal carbonization reactor

The feedstock was hydrothermally carbonized under microwave heating in a 2.45 GHz microwave oven (MARS, CEM, Milton Keynes, UK equipped with XP1500 digestion vessels). The pressure of the reaction system was monitored with a pressure sensor fitted into the reference vessel, while an infrared fibre optic sensor installed in a ceramic sleeve in the same reference vessel was used to monitor the temperature.

2.3. Experimental procedure

The experimental procedure was based on our previous study [14]. 2 g each of the feedstock were weighed into microwave reaction vessels made of Teflon. 30 ml of de-ionized water was added to each of the reaction vessels to cover the feedstock. The vessels were sealed and placed in the microwave oven. The feedstock was hydrothermally carbonized between 150 and 200 °C in the microwave oven set to ramp to a specified temperature in 5 min and was held at the temperature for 5–30 min. After the reaction, the vessels were allowed to cool down to room temperature and the hydrochars were filtered off using Whatman filter paper number 3, ashless 11 cm. The hydrochars were washed several times with de-ionized water to bring their acidic pH to neutral. The obtained hydrochars were dried in a conventional oven at 80 °C for 16 h, and were denoted as RSHX-Y, where X and Y represents the temperature (°C) and time (min) in the microwave oven respectively.

2.4. Analytical methods

Elemental analysis of the feedstock and hydrochars was carried out on a Fisons instruments EA 1108 CHN analyzer. Before the analysis, samples were ground into fine powder, weighed into tin capsules, before being placed on the autosampler for analysis. FTIR analysis was carried out on a Thermo Scientific Nicolet 380 FTIR (Thermo Scientific, Hemel Hempstead, UK), equipped with attenuated total reflectance (ATR). ZEISS EVO 60 SEM (Carl Zeiss, Cambridge, UK) was used for the SEM analysis; samples were pretreated by coating with gold and platinum alloy and were impregnated on a sticky disc before analysis. The surface area of the hydrochar was measured on a Micromeritics Tristar BET-N₂ surface area analyzer; before the analysis, samples were degassed under nitrogen (N₂) atmosphere at 120 °C for 3 h. Thermogravimetric analysis (TGA) was also carried out under nitrogen atmosphere at 30 °C min⁻¹ heating rate using a Mettler Toledo-TGA/DSC 1 instrument.

2.5. pH determination

The pH was determined by our previously described method [14]. Briefly, 1% (wt/wt) suspension of hydrochar sample in deionized water was prepared, and pH of the suspension was measured with a FisherBrand HydruS 500, Fisher Scientific, Loughborough, UK, pH meter which was calibrated with pH 4 and pH 7 buffer solutions.

Recalibration of the pH meter was carried out, if analysis of a pH 7 buffers after every five analyses varied by more than ±0.1 pH units.

2.6. Mass yield (%)

The dry mass of the hydrochar was measured in each case, and the mass yield was calculated as follows:

$$\text{Mass yield}(\%) = \frac{\text{Mass of hydrochar}(\text{g})}{\text{Mass of feedstock}(\text{g})} \times 100. \quad (1)$$

2.7. Energy properties of the hydrochars

The higher heating value (HHV) of each of the hydrochar was calculated based on Eq. (2) (Dulong's formula) as previously reported [15].

$$\text{HHV} = 0.3383\text{C} + 1.422(\text{H}-0/8). \quad (2)$$

The energy densification ratios of the hydrochars were calculated using Eq. (3)

$$\text{Energy densification ratio} = \frac{\text{HHV of hydrochar}}{\text{HHV of feedstock}}. \quad (3)$$

In each case, the energy yield of the hydrochar was calculated using Eq. (4)

$$\text{Energy yield}(\%) = \text{mass yield} \times \text{energy densification ratio}. \quad (4)$$

All experiments were carried out in triplicate, and the results are presented in Table 1.

3. Results and discussion

3.1. Elemental analysis and pH

The results of the elemental analysis and pH for the feedstock and the hydrochar are presented in Table 1. The hydrochars have higher carbon contents than the feedstock, while the hydrogen and oxygen contents were higher in the feedstock. The high carbon contents of the hydrochar samples show that the feedstock was transformed during the microwave-assisted hydrothermal carbonization process. The decrease in composition of hydrogen and oxygen in the hydrochar samples results from loss of hydrogen and oxygen during deoxygenating, dehydration and decarboxylation reactions that occurred during the hydrothermal carbonization process [16,17], and as a result, the fixed carbon content increased in the hydrochar samples. The high content of oxygen-containing functional groups on the hydrochar is responsible for the low pH values observed in the hydrochar samples [5].

The van Krevelen diagram (graph of atomic ratios of H/C against O/C of the feedstock and hydrochars) was plotted in Fig. 1, in order to investigate the differences in atomic composition of the feedstock and derived hydrochars. The microwave-assisted hydrothermal carbonization process led to a decrease in H/C and O/C atomic ratios in the hydrochars samples, as the reaction temperature and residence time were increased. This implies that transformation took place during the process resulting from dehydrogenation, decarboxylation, deoxygenation and dehydration reactions [11,14]. The H/C and O/C ratios of the feedstock fell into an area for biomasses, while that of the hydrochars fell into the peat area of a typical van Krevelen diagram [12]. The decrease in the H/C and O/C atomic ratios from the feedstock to the hydrochar samples basically followed a diagonal trend, which indicates that dehydration reactions were prevalent during the process [11]. Similar trend was observed in the hydrothermal carbonization of *Prosopis africana* shell [14].

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