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 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 the reaction temperature and the residence time on the mass yields and the energy properties of the hydrochars was studied. The procedure involved the heating of the feedstock in deionized 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 stabilizes 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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Keywords: Microwave-assisted, Hydrothermal carbonization, Hydrochar, Rapeseed husk, Mass yields, Energy properties

1. Introduction

The use of waste product from the 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 been 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 the fossil fuels that are presently in existence [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

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feedstock. Different authors have used the 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. The hydrothermal carbonization process has been applied as a pretreatment procedure for many biomasses, such as bamboo [8], dry leaves [10], orange pomance [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 the Brassicaceae. It is a crop cultivated because of its nutritious oil-rich seed, and can be found in the 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, the 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 the energy properties of the prepared hydrochars. The 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

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Ian Dobson of the 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 150-200 °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.

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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, the 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 Thermoscientific Nicolet 380 FTIR (Themo Scientific, Hemel Hempstead, UK), equipped with attenuated total reflectance (ATR). ZEISS EVO 60 SEM (Carl Zeiss, Cambridge, UK) was used for the SEM analysis; the samples were pretreated by coating with gold and platinum alloy and were impregnated on a sticky disc before the analysis. The surface area of the hydrochar was measured on a Micromeritics Tristar BET-N_2 surface area analyzer; before the analysis, the samples were degassed under nitrogen (N_2) atmosphere at 120 °C for 3 h. Thermogravimetic 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 the hydrochar sample in deionized was prepared, and the 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 (%)

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

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

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].

$$\mathrm{HHV} = 0.3383\mathrm{C} + 1.422\,(\mathrm{H} - O/8) \quad (2)$$

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

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

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

$$Energy\ yield\ (\%) = mass\ yield \times energy\ densification\ ratio \quad (4)$$

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

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The results of the elemental analysis, and the 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 the composition of hydrogen and oxygen in the hydrochar samples results from the loss of hydrogen and oxygen during the 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].

Table 1

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 increases. 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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Fig. 1

3.2 Mass yields of the hydrochar

Series of experiments were carried out in order to determine the effects of the reaction temperature and residence time on the mass yields of the hydrochars from the microwave-assisted hydrothermal carbonization of rapeseed husk. The first set of experiments were carried out based on our previous study [14], at a constant temperature of 200 °C, while the residence time was varied from 5 to 30 min to study the effect of reaction time on the mass yields of the hydrochars. Residence time has been described as a vital parameter affecting biomass conversion, as well as the composition of products during the hydrothermal carbonization process [18]. The hydrothermal carbonization process is generally a slow reaction process, with reported reaction time ranging from minutes to days, and in such a supercritical state, the rate of hydrolysis and biomass degradation are relatively high; therefore, a short residence time is necessary for an effective decomposition of the biomass [18,19]. From the results obtained from the first set of experiments, a second set of experiments was performed to study the effect of reaction temperature on the mass yields. Reaction temperatures of 150, 170, and 200 °C were used, while the residence time was kept constant at 20 min. The experimental results for the mass yields of the hydrochar samples are shown in Fig. 2.

The mass yields in this study decreased with increase in reaction time (Fig. 2a). The decrease was rapid between 5-20 min accounting for about 13.38% loss in the mass yield, and became almost stable subsequently. Sermyagina et al. [3] reported that increase in the residence time beyond certain limit during the hydrothermal carbonization of biomass appears not to have any effect on the mass yield, because

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complete hemicellulose and substantial cellulose decomposition would have occurred. Therefore, the effect of the increase in reaction temperature was studied between 150-200 °C for 20 min, and the result also indicated a decrease in the mass yields of the hydrochars by the average of 19.21% (Fig. 2b). Within the parameters considered, longer residence time and higher reaction temperatures led to more carbonization of the feedstock and as a consequence, lower hydrochar mass yields. The observed trend in this study is consistent with some previously published reports for biomass [3,20,21]. The decrease in the mass yield is usually attributed to oxygen and hydrogen loss that took place during the liquefaction and gasification reactions, which occurred as the reaction temperature and residence time were raised during the hydrothermal carbonization process of the biomass [22-24].

Fig. 2

3.3 Energy properties of the hydrochar

3.3.1 Higher heating value (HHV)

A fundamental feature of the biomass and the hydrochars is their higher heating values (HHVs), which shows the absolute quantity of energy that is present in a sample. Due to the increase in carbon contents and the decrease in oxygen contents, the HHVs calculated for the hydrochars (Fig. 3 a and b), increased with increase in reaction temperature and residence time, which is consistent with previous study [25]. The HHVs became stable after 20 min due to the removal of low HHV components namely, oils, fragrances, and the degradation of hemicellulose and cellulose [26], which shows the level of carbonization attained. The value of 21.57 MJ/kg obtained in this study after 20 min is similar to that of Converse School-Sub Coal (21.67

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MJ/kg), wood, paper, and palm kernel shell previous reported [8,18,27]. This suggests that the obtained hydrochar in this study can be employed as solid fuel.

Fig. 3

3.3.2 Energy densification

Hydrothermal carbonization of biomass is a process associated with dehydration, decarboxylation, and condensation reactions resulting in the carbonization of the feedstock. This leads to energy densification, which is used to assess the effectiveness of the hydrothermal carbonization processes [27,28]. Fig. 4 (a and b) shows the effect of process parameters variations on the energy densification ratios of the hydrochar samples. The energy densification ratio increased with increase in the reaction temperatures, and residence time up to 20 min and remained stable afterwards. This hydrochar (RSH200-20) has the highest energy densification ratio and showed an increase in energy densification ratio of about 33%. The energy densification ratios of the hydrochars in this study, ranged from 1.03–1.37, which falls within the range previously reported [2,3,10,25,29].

Fig. 4

3.3.3 Energy yields

The effect of the process parameters on the energy yields of the hydrochars is shown in Fig. 5 (a and b). The energy yields increased rapidly with increase in the residence time up to 20 min, and subsequently the increment became slow. On the

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other hand, the energy yields remained almost the same with increase in temperature. Reaction temperature of 150 °C appears to be the lower temperature limit at which the degradation of components of woody materials begin during the hydrothermal carbonization process [10]. As the reaction temperature increases beyond 150 °C, decomposition of the biomass components begins, resulting in mass loss and increase in the energy densification at the same time, which will almost balance each other; thus the energy yields will remain almost the same with increase in the reaction temperature [3].

Fig. 5

Some published results for the hydrothermal carbonization treatments of several biomass materials at different reaction temperatures (190–220 °C), and residence time (0.5–20 h) are presented in Table 2. The difference in their conversion rates is evident from their mass and energy yields. The mass yields of the hydrothermally carbonized biomass varied from 39.70-70.98% of the starting mass. Hydrochars from feedstock such as, dry leaves, grape pomace, and coniferous wood chips have very high mass yields, while those from the hydrothermal carbonization of residual biomass products such as walnut shell and sunflower stem have very low mass yields, which is consistent with the result obtained in this study. The energy yields for the hydrochars on the other hand varied from 81.64% for dry leaves to 57.50% from walnut shell during the hydrothermal carbonization process. Despite the similarity in the process parameters (reaction temperature of 200 **°C**, and residence time of 0.5 h) for some of the results presented, the mass and energy yields of the hydrochars still differ, which is an indication that the mass and energy yields are not only dependent on the process parameters, but also on the nature of the feedstock used in the preparation of the hydrochar, which is in agreement with Sermyagina et al. [3].

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Table 2

3.4 Structural and morphological characterization

The structural and morphological characterization for the hydrochars will be restricted to that of RSH200-20, which showed the highest values for the energy properties for brevity. The FTIR spectroscopy was used to study the functional groups present on the feedstock and the hydrochar (RSH200-20). In Fig. 6, the intensity of FTIR spectra shown for the hydrochar and the feedstock differs, which shows the changes that took place during the microwave-assisted hydrothermal carbonization process. The strong and broad peak observed in Section 1 (3600-3000 cm^{-1}) is due to the aliphatic OH stretching vibration of hydroxyl and carboxyl functional groups. Section 6 (1200-1000 cm^{-1}) represents the stretching vibration of C-O groups from esters, phenols and aliphatic alcohols. These peaks (Sections 1 and 6) were weak in the hydrochar, which indicated the dehydration and decarboxylation reactions that took place [28]. The peak in Section 3 (1800-1600 cm^{-1}) corresponds to the stretching vibration of C=O bonds in esters, carboxylic acids or aldehydes from cellulose [14]. The absence of the peak in the hydrochar shows the breakdown of cellulose during the hydrothermal carbonization process. The peak in Section 4 (1600-1500 cm^{-1}) corresponds to the C=C vibrations of the aromatic rings in lignin. After the hydrothermal carbonization process, this peak reduced indicating that the lignin only decomposed partially under the studied condition [21]. The peaks in Section 2 (3000-2800 cm^{-1}) are due to the C-H stretching vibration, while those in Section 5 (1450-1200 cm^{-1}) corresponds to the C-H bending vibration of aliphatic carbons, methylene, and methyl groups, which shows that aliphatic structures are present [23]. The peak in Section 7 (< 1000 cm^{-1}) present only in the hydrochar is results from the distortion of the C-H bonds in aromatic compounds [30].

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Fig. 6

The SEM images of the feedstock and the hydrochar are shown in Fig. 7. The SEM image of the hydrochar showed substantial change in morphology from that of the feedstock, which showed only a cellular structure. This is an indication that feedstock was transformed during the microwave-assisted hydrothermal carbonization process as expected. The aggregates of sphere-like microparticles (1-10 µm) observed on the hydrochar originated from cellulose decomposition [16], while the rough texture of these microparticles is due to the residual lignin in the hydrochar. Lignin has a greater thermal stability than cellulose, and was only partially degraded in the process [28]. The result of the SEM analysis showed that the lignocellulosic structure of the feedstock was destroyed during the process [14].

Fig. 7

The N_2 adsorption isotherm of the hydrochar (not shown) showed a Type II isotherm based on the IUPAC classification system. This is the type of isotherm usually observed for non-porous materials. Therefore, the hydrochar has a low surface area of 6.6±3.2 determined according to the BET method, which corresponds to the value of the external surface area due to lack of porosity in the hydrochar. The result obtained in this study is consistent with previous studies [14,16].

3.5 Thermal stability of the hydrochar

The thermal stability of the hydrochar was studied using thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) derived from the TGA profile, and the results are presented in Fig. 8. Three weight loss stages were observed in the TGA curve. The first stage (50-200 °C) represents the stage at which the

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existing moisture content in the hydrochar was removed. The second weight loss stage (220-410 °C) represents the decomposition of cellulose and hemicellulose, which results from the breaking of chemical bonds, leading to the formation of volatiles [31]. The third stage (410-680 °C) corresponds to the decomposition of lignin, which is the most difficult among the components (cellulose, hemicellulose and lignin) of the feedstock to be decomposed, and usually takes place slowly through out the entire temperature ranged applied [14,32]. The DTG profile of the hydrochar showed three peaks. The first is a small peak in the drying region (50-100 °C), which is due to the residual water content from of the hydrothermal treatment [33]. The Second is a high and sharp peak between 300-350 °C, which results from the degradation of cellulose and hemicellulose [33]. The nature of this peak suggests that the loss in weight could be predominantly linked to the cellulose and high reactive hemicellulose contents of the hydrochar after the removal of the moisture [31]. The third peak (450-700 °C) is broad and corresponds to the thermal decomposition of lignin and other molecules with higher molecular mass [33,34].

Fig. 8

4. Conclusion

The microwave-assisted hydrothermal carbonization process of rapeseed husk is reported in this study. As a result of the decomposition of the feedstock during the process, higher reaction temperature and longer residence time led to mass loss of about 19% between 150-200 °C, and 16% between 5-30 min, which led to an increase in the heating value of the hydrochars. Thus, the heating value of hydrochar increased by about 32% and 25% at the highest reaction temperature and residence time respectively. The decrease in the mass yields also led to an increase in the energy

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yields. The structural and morphological characterization revealed the transformation that took place during the process. The result obtained in this study is consistent with previous reports and showed that the hydrochar produced from rapeseed husk has the potential to be used as solid fuel.

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Tables

Materials	**C (%)**	**H (%)**	**N (%)**	**O^a (%)**	**pH**	**H/C***	**O/C***
Feedstock	42.56±0.08	6.62±0.02	6.41±0.01	44.41±0.11	6.18±0.02	1.86	0.79
RSH200-30	54.03±0.90	6.61±0.01	5.84±0.49	33.52±1.38	5.12±0.00	1.46	0.46
RSH200-20	54.62±1.02	6.45±0.13	6.74±0.22	34.19±1.37	5.26±0.01	1.40	0.47
RSH200-15	50.86±0.80	6.40±0.25	6.53±0.14	37.21±0.41	5.38±0.01	1.50	0.55
RSH200-10	48.01±1.00	6.37±0.38	6.45±0.09	39.17±1.47	5.45±0.00	1.57	0.62
RSH200-5	46.35±0.52	6.32±0.21	6.39±0.02	40.94±0.29	5.60±0.02	1.63	0.67
RSH170-20	46.21±1.12	6.35±0.32	6.61±0.11	40.83±1.55	5.78±0.00	1.67	0.67
RSH150-20	44.13±0.75	6.38±0.22	6.40±0.01	43.09±0.54	5.92±0.01	1.71	0.75

^{a}The oxygen content was determined by difference [100% - (C%+H%+N%)] [9,10,14]

*** Atomic ratio**

Table 1: Elemental analysis, pH, H/C and O/C atomic ratios of the hydrochars.

Feedstock	**Temperature (°C)**	**Time (h)**	**Mass yield (%)**	**Energy yield (%)**	**Reference**

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Rapeseed husk	200	0.5	47.14	64.32	This study
Dry leaves	200	0.5	70.98	81.64	[10]
Grape pomace	200	0.5	60.00	74.90	[25]
Walnut shell	190	20	48.60	57.50	[1]
Sunflower stem	190	20	39.70	58.90	[1]
Coniferous wood chips	220	3	63.00	78.00	[3]

Table 2: Mass and energy yields for the hydrothermal carbonization treatments of different biomasses.

Figures

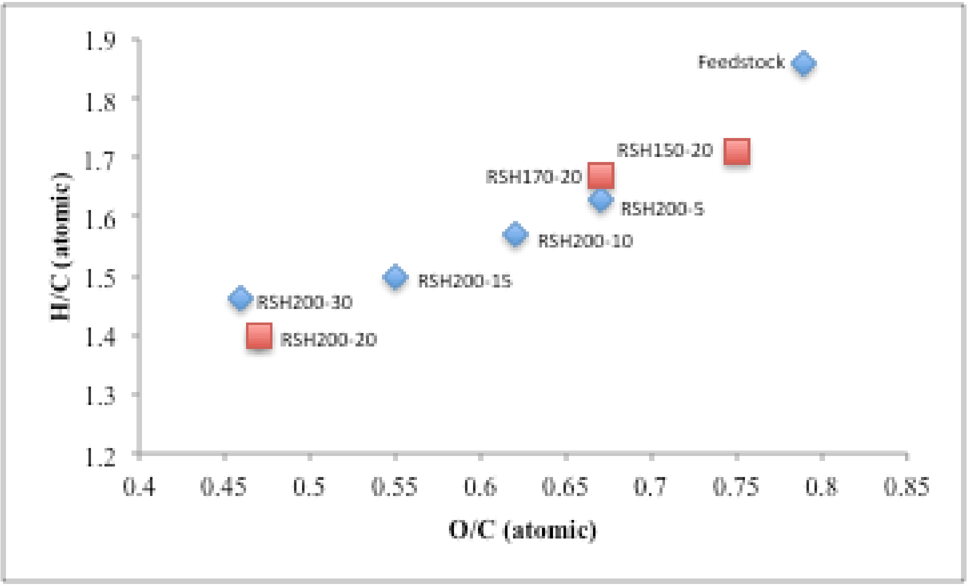

Fig. 1 van Krevelen diagram for the feedstock (rapeseed husk) and the hydrochar samples

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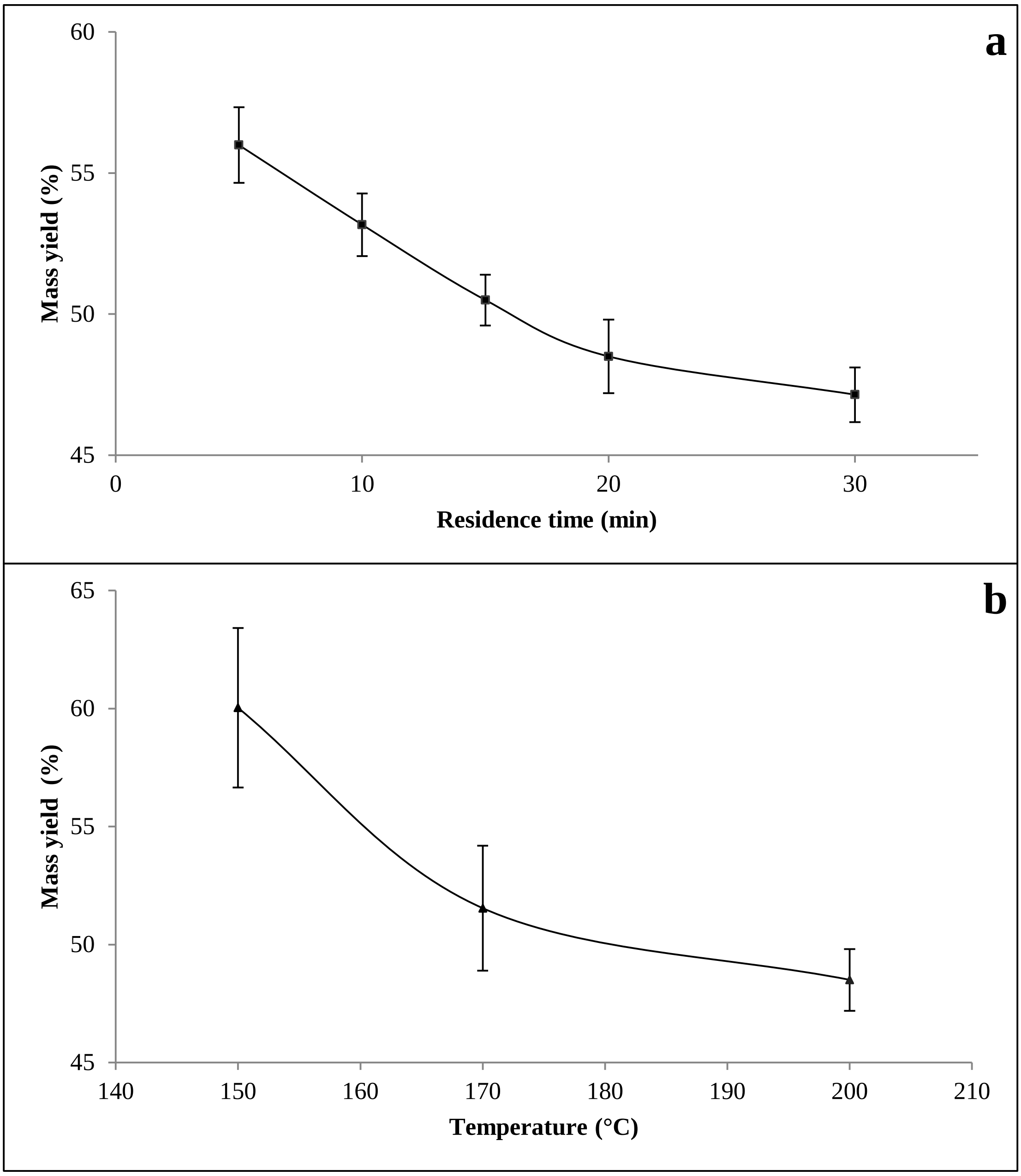

Fig. 2 Effect of (a) residence time, (b) reaction temperature on the mass yield of the hydrochars

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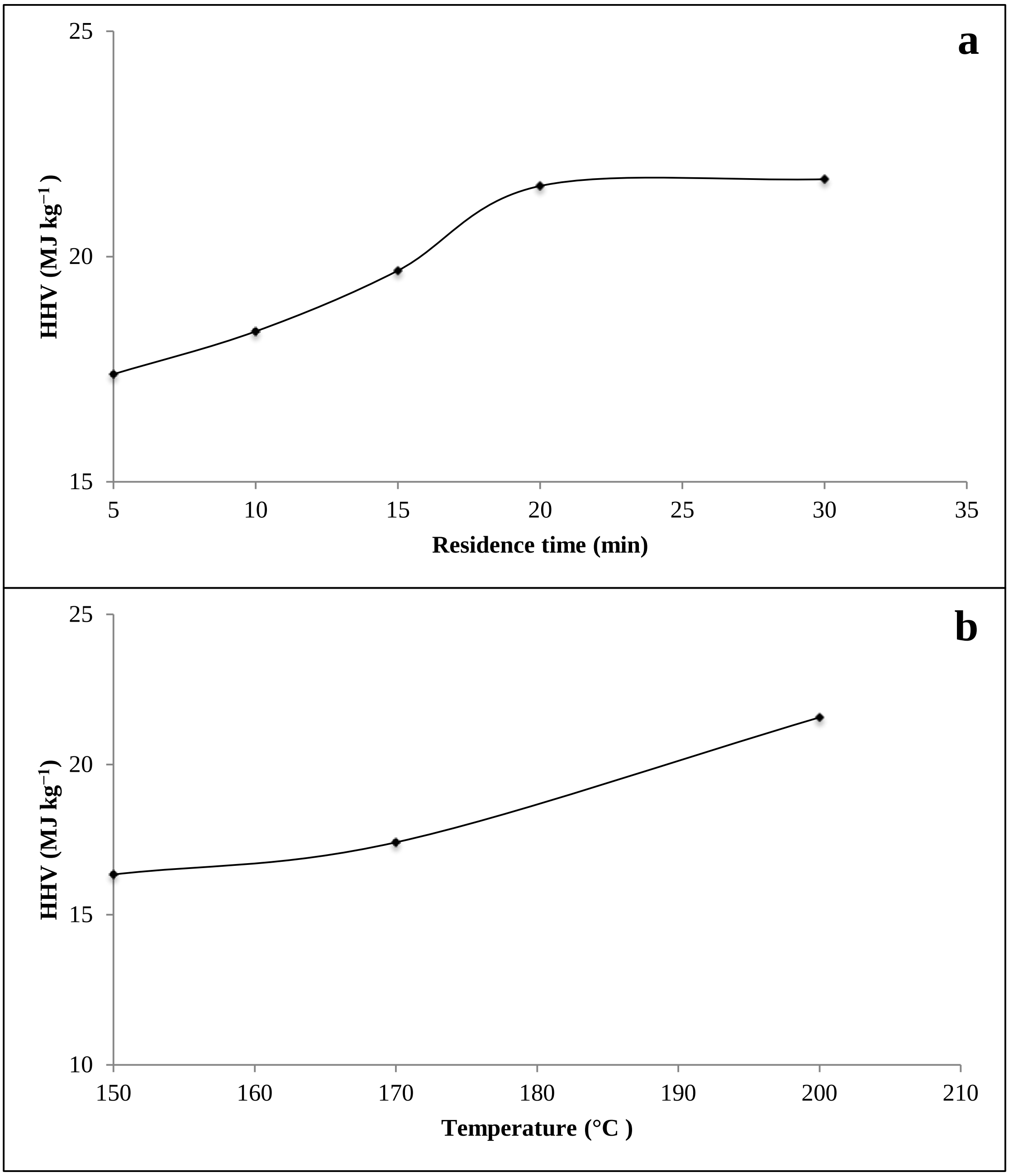

Fig. 3 Effect of (a) residence time, (b) reaction temperature on the higher heating value (HHV) of the hydrochars

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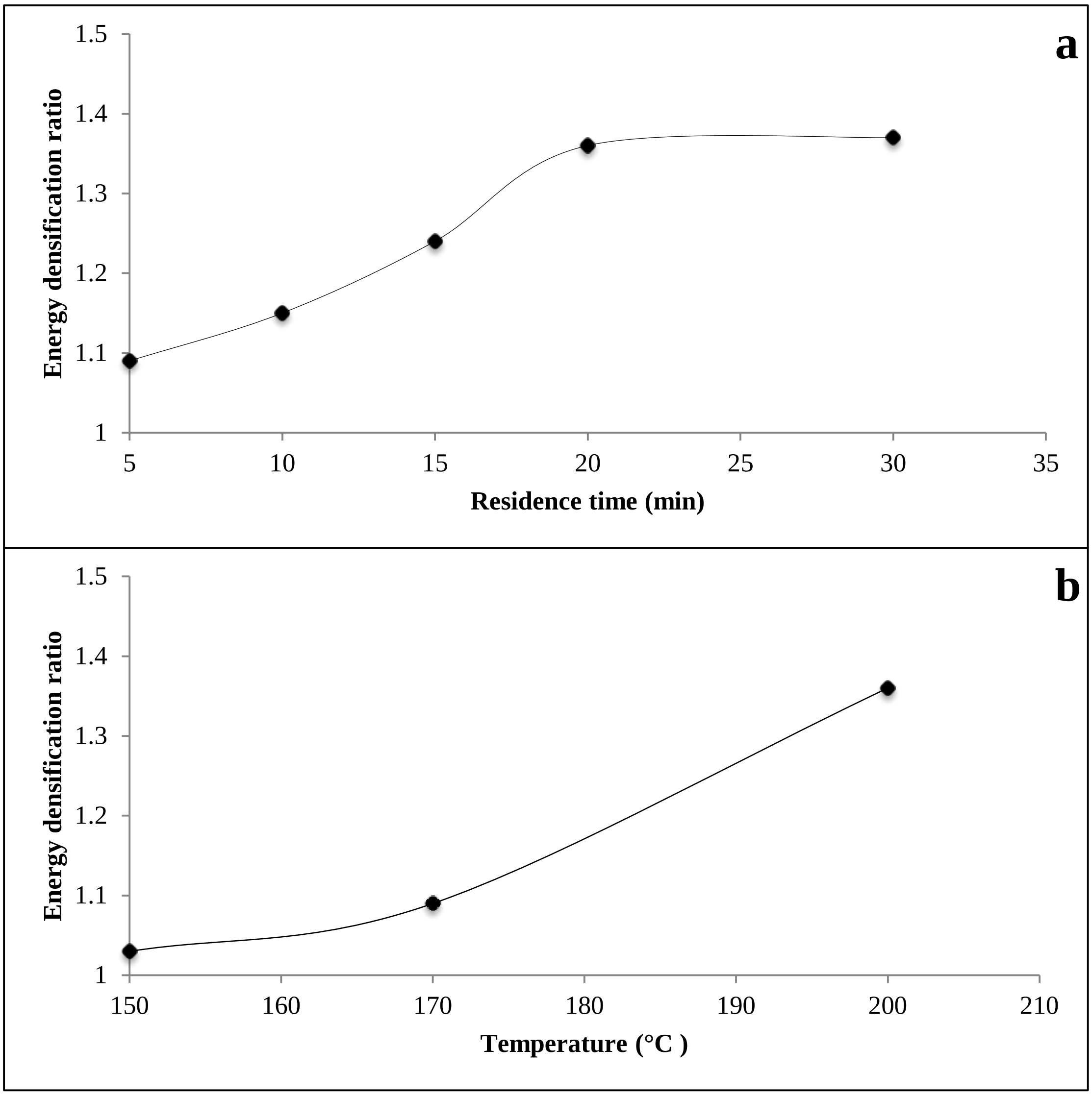

Fig. 4 Effect of (a) residence time, (b) reaction temperature on the energy densification ratio of the hydrochars

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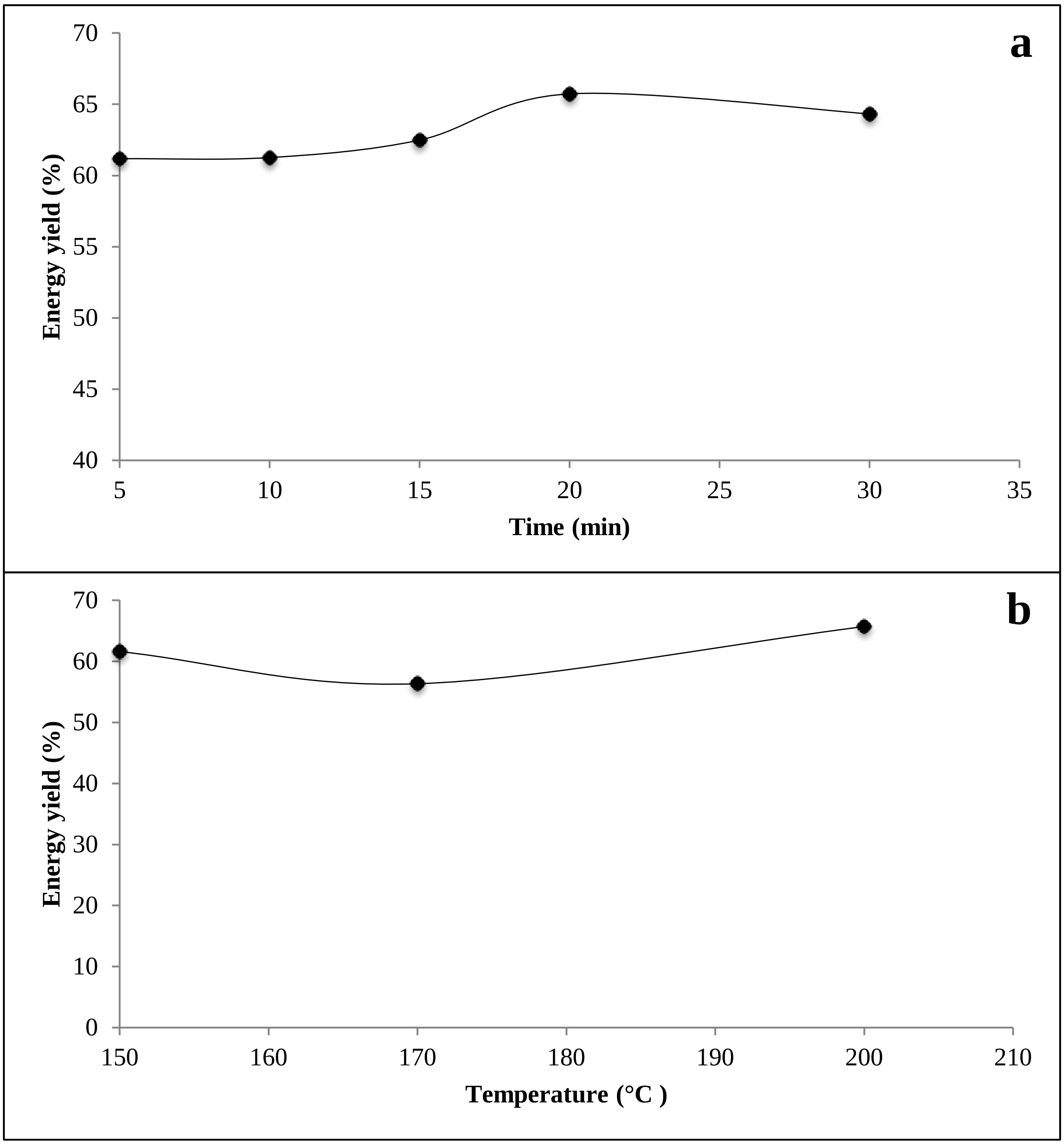

Fig. 5 Effect of (a) residence time, (b) reaction temperature on the energy yield of the hydrochars

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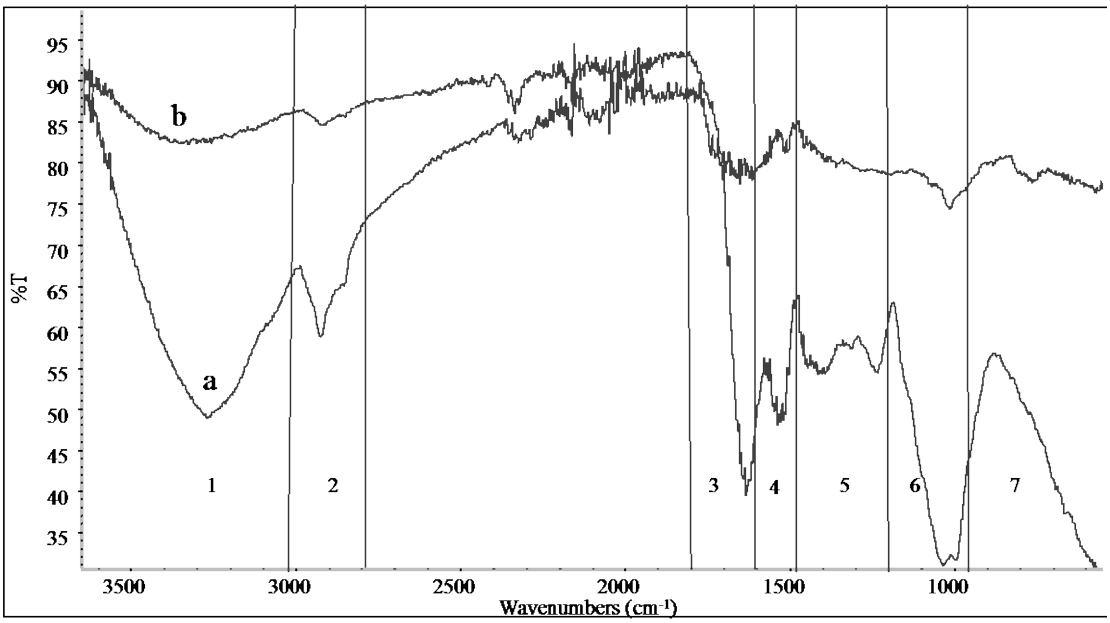

Fig. 6 FTIR spectra of (a) feedstock, (b) hydrochar (RSH200-20)

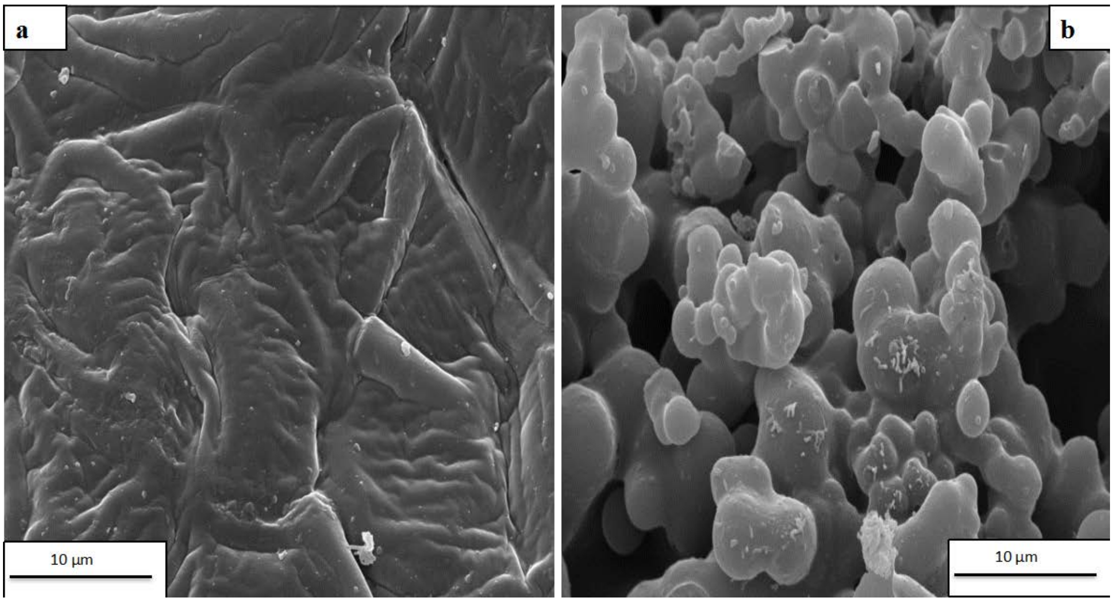

Fig. 7 SEM images of (a) feedstock, (b) hydrochar (RSH200-20)

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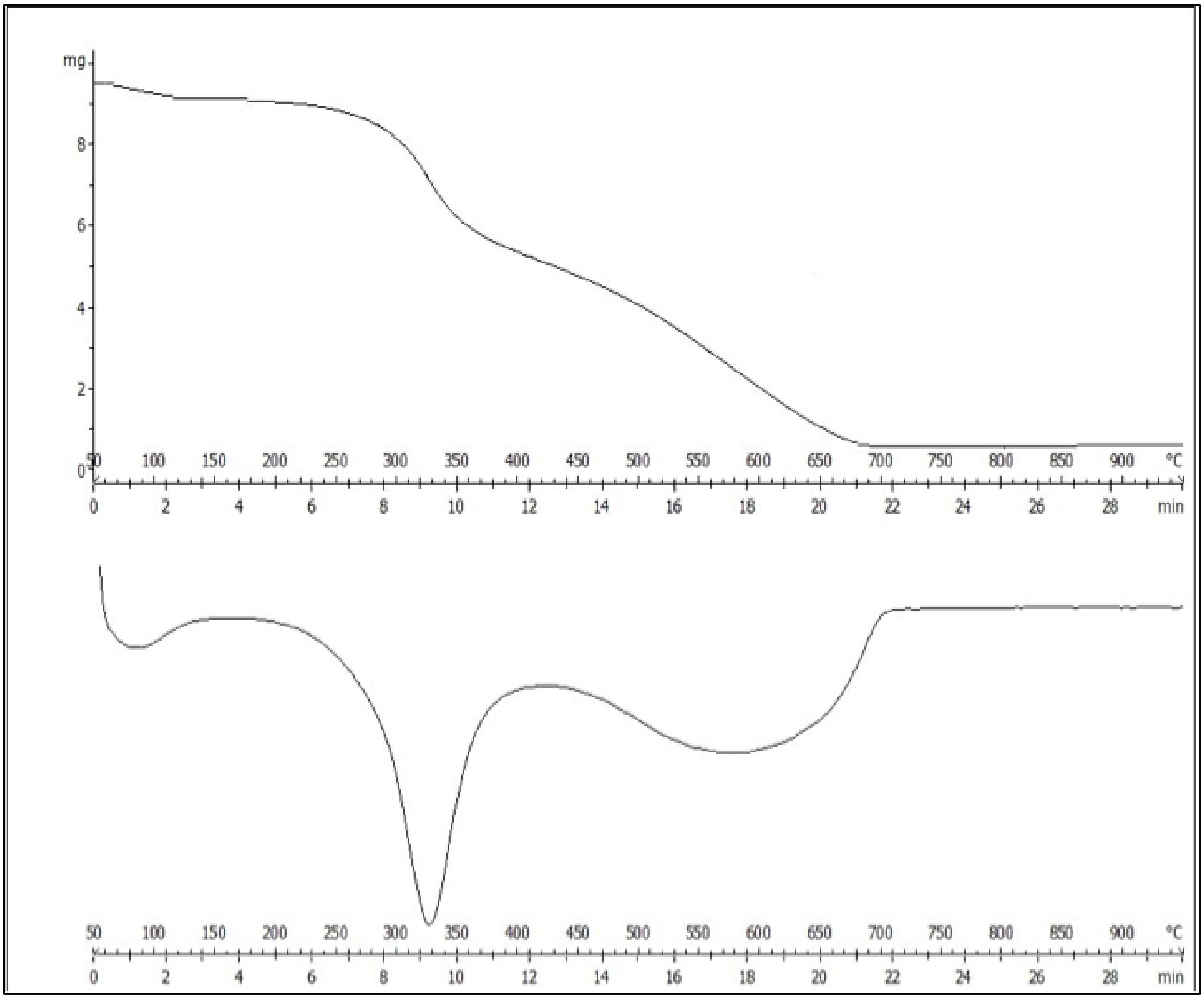

Fig. 8 TGA and DTG profiles of the hydrochar (RSH200-20)

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