RESEARCH ARTICLE

Energy Densification of Groundnut Shell through Microwave-Assisted Hydrothermal Carbonization

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ABSTRACT

Modern technology of microwave synthesis was utilized for hydrochar production from groundnut shell biomass. Hydrochar was produced at three different temperatures (180, 200, and 220°C) with 20 minutes of holding time and analyzed for the physicochemical characteristics. The yield of hydrochar and hydrocrude were in the range of 45 to 61 % and 51 to 56 % respectively. The maximum value of the higher heating value of 19.11 MJ/kg was obtained for hydrochar produced at 220°C, which is similar to the higher heating value of lignite (19 MJ/kg). The energy densification ratio of respective hydrochar was 1.13 with 51.77 % energy yield. The result implied that microwave-assisted hydrothermal carbonization was an energy-efficient method to produce hydrochar. Hydrochar produced from groundnut shells was an eco-friendly, energy enriched product that can be used as a solid fuel.

Keywords: *Groundnut shell; Microwave-assisted; Hydrochar; Energy quality*

INTRODUCTION

The world's energy supply mainly relies on fossil fuels like coal, crude oil, and natural gas. Energy production through eco-friendly natural resources is a great challenge. Agricultural residues are carbon-neutral, low-cost, lignocellulosic materials and feasible for greener energy generation to mitigate greenhouse gas emissions (Basso *et al.*, 2013). Abundant availability with intriguing physicochemical properties makes it a suitable material for energy generation. Higher moisture content, lower density, and lower energy content are the major drawbacks of raw agricultural waste materials. Converting the raw biomass through various pathways (thermal/ chemical/biological) significantly improves the characteristics. The selection of the conversion method depends on the feedstock characteristics and intended application (Ahmad *et al.*, 2019; Frombo *et al.*, 2009).

Hydrothermal carbonization (HTC) is a thermochemical conversion process in which wet biomass is converted into char like product known as hydrochar under mild temperature and autogenerated pressure. Other thermochemical conversion methods require drying of feedstock before the treatment whereas in HTC, wet waste material is directly utilized for energy generation and energy-intensive drying is avoided (Basso *et al.*, 2013). In HTC, biomass and water mixture is heated in a closed vessel at 180-250°C temperature and at a residence time of minutes to several hours. As an alternative to conventional heating, microwave heating is increasingly applied in different fields like synthesis and digestion due to selective and homogenous heating. Microwave-assisted hydrothermal carbonization (MWAHTC) is an energy-efficient process that offers fast and uniform heating. It aids in the reduction of processing time and process energy requirements (Guiotoku *et al.*, 2009). Elaigwu and Greenway (2016a) produced hydrochar using both conventional and microwave modes of heating. It was reported that hydrochar produced from Prosopis Africana shell at 200°C, 20 minutes in MWAHTC, and 240 minutes in conventional HTC shows similar conversion levels. Numerous study has been carried out in MWAHTC for different waste materials like rice straw, pig feces, human biowaste, dairy manure, corn stalk, and sawdust (Afolabi *et al.*, 2015; Bundhoo, 2018; Gao *et al.*, 2018; Kang *et al.*, 2019; Li *et al.*, 2019; Wang *et al.*, 2020). No study has been conducted on MWAHTC for groundnut shell. This study aims to produce groundnut shell hydrochar at different temperatures using MWAHTC and to study the effect of temperature on hydrochar yield, characteristics, and higher heating value.

MATERIAL AND METHODS

Groundnut shell

Groundnut shells were collected from the Department of Oilseeds, TNAU. The collected shells were washed with distilled water to remove the impurities and dried in a solar tunnel drier. The dried shells were ground and sieved using a 0.2 mm sieve.

Microwave-assisted hydrothermal carbonization (MWAHTC)

Experiments were carried out in a 100 mL Teflon vessel using a modified microwave oven (2.45 GHz, 1.5 kW magnetron). 1 g of groundnut shell was mixed with 20 ml distilled water and fed into the reaction vessel. The vessel was placed inside the microwave oven and heated at temperatures of 180, 200, and 220°C at a 10°C/ min heating rate. A thermocouple inserted in a reference vessel and PID controller controlled the temperature inside the oven. The treated biomass water mixture was held at 180,200 and 220°C respectively for 20 minutes. After the completion of the process, the reactor was cooled to room temperature. The produced hydrochar were washed and filtered using Whatman filter paper number 2 (ashless) and dried at 105°C for 12 hours. The yield of hydrochar and hydrocrude (liquid product) were measured gravimetrically.

Product yield

The yield of hydrochar (Eqn. 1) and hydrocrude (Eqn. 2) were measured and expressed in percent-

$$Hydrochar\ yield\ (\%) = \frac{Dry\ weight\ of\ hydrochar\ (g)}{Initial\ weight\ of\ feedstock\ (g)} \times 100 \quad (1)$$

$$Hydrocrude\ yield\ (\%) = \frac{Final\ weight\ of\ liquid\ after\ filtering\ (ml)}{Initial\ weight\ of\ water\ taken\ (ml)} \times 100 \quad (2)$$

Hydrochar characterization

The proximate properties of groundnut shell and groundnut shell hydrochar were measured as per American Standard Testing Method (ASTM) procedures using ASTM D3173, D3175, and D3174 to quantify moisture content, volatile matter, and ash content. Fixed carbon was determined by subtracting the sum of volatile matter and ash content expressed in percentage from 100. The elemental composition of raw material and produced hydrochar were quantified using an elemental analyzer and expressed in percentages (Flash 2000, Thermo Scientific, USA). The higher heating value of hydrochar (HHV) was determined using a digital bomb calorimeter and expressed in MJ/kg (C200, IKA, USA). Van-Krevelen diagram was plotted to determine the degree of carbonization.

Energy qualities of hydrochar

The percentage increase in HHV and carbon content were calculated using the Eqn. 3 and Eqn. 4 respectively. Eqn. 5 and Eqn. 6 were used to calculate the Energy densiication ratio and Energy yield.

$$\%\ increase\ in\ HHV = \frac{HHV_{hydrochar} - HHV_{feedstock}}{HHV_{feedstock}} \times 100 \quad (3)$$

$$\%\ increase\ in\ carbon\ content = \frac{C_{hydrochar} - C_{feedstock}}{C_{feedstock}} \times 100 \quad (4)$$

$$Energy\ densification\ ratio\ (EDR) = \frac{HHV_{hydrochar}}{HHV_{groundnut\ shell}} \quad (5)$$

$$Energy\ yield\ (EY) = EDF \times Hydrochar\ yield\ (\%) \quad (6)$$

RESULTS AND DISCUSSION

The physicochemical characteristics of groundnut shell biomass and hydrochar are given in Table 1. The raw biomass contains higher volatile matter content and lower fixed carbon.

Solid and liquid yield

When increasing the process temperature, the yield of hydrochar and hydrocrude decreased from 61.84 to 45.76% and 56.67 to 51.25% respectively. Other studies also reported the same trend of decrease in yield with the increase in HTC temperature for different biomass materials like corncob (Zhang *et al.*, 2015), rice husk (Nizamuddin *et al.*, 2019), green waste (Shao et al., 2019), switchgrass (Reza *et al.,* 2013). At 180°C, hemicellulose starts to degrade whereas cellulose and lignin remain stable. Cellulose starts to degrade at 200°C and lignin imparts partial degradation at 220°C. This may be the reason for the decrease in yield when increasing the temperature. With the given residence time and biomass to water ratio (1:20), partial degradation of hemicellulose occurred at 180°C and the yield was 61.84%. The increase in temperature from 180 to 220°C ameliorated the complete degradation of hemicellulose, partial degradation of cellulose and lignin and the yield decreased from 61.84 to 45.76%.

Physicochemical characteristics

With the increase in temperature, a reduction in the volatile matter and ash content was observed resulting in the increased fixed carbon content. The primary reactions of HTC are hydrolysis, dehydration and decarboxylation, which caused the reduction in the volatile matter. The hot compressed water environment improves the solubility of biomass and the developed porous structure allowed some inorganic minerals to leach out into the liquid. Due to this, ash content was decreased. The reduction in the volatile matter and ash content was also seen in

Miscanthus (Reza *et al*., 2013), rice husk (Zhang et al., 2016) and bamboo sawdust (Dai *et al*., 2017).

Carbon content increased from 50.88 to 54.35 %. Hydrogen and oxygen content of hydrochar decreased with the increase in hydrothermal process temperature from 180 to 220 °C, which results in a reduction in atomic ratios of O/C and H/C. The severity of dehydration, deoxygenation, and decarboxylation reactions intensified with the increase in HTC process temperature from 180 to 220°C, which triggered the reduction of hydrochar hydrogen and oxygen content. The reduction in hydrogen and oxygen content which results in increased carbon content was in agreement with different studies carried out for rapeseed husk (Elaigwu and Greenway, 2016b), sugarcane bagasse (Chen *et al*., 2012), and bamboo sawdust (Dai et al., 2017).

Energy qualities of hydrochar

Energy values of hydrochar and different energy parameters are presented in Table 2. The HHV of hydrochar was in the range of 16.89 to 19.11 % and was maximum for the hydrochar produced at 220°C. This increasing trend of HHV with the increase in temperature was also observed for sugarcane bagasse (Chen *et al*., 2012), coconut shell (Elaigwu and Greenway, 2019), and green waste (Shao *et al*., 2019). Due to dehydration, decarboxylation, aromatization, and polymerization reactions, lower energy bonds were broken. With the increase in temperature, higher energy bonds were developed in the hydrochar product, which may be the reason for the increase in HHV of hydrochar. Compared to the raw groundnut shell, HHV of hydrochar was increased by 14.2 % at 180°C and 29.21 % at 220°C. Similarly, carbon content was also increased by 8, 12.4 and 15.37 % for process temperatures of 180, 200 and 220°C respectively.

The energy densification ratio of hydrochar was in the range of 1.05 to 1.13 and was maximum (1.13) for hydrochar produced at 220°C. Hydrochar energy yield was in the range of 51.71 to 64.71 %. This is in accordance with a previous study reported by Elaigwu and Greenway (2019).

Van – Krevelen diagram

Figure 1 shows the plot of the atomic ratios of O/C against atomic H/C. During the hydrothermal carbonization, the evolution of the chemical structure of groundnut shell biomass was assessed using Van-Krevelen diagram. Due to the dehydration, deoxygenation, and decarboxylation reactions, the hydrogen, and oxygen content of hydrochar were decreased with the increase in the process temperature from 180 to 220°C and results in reduced O/C and H/C atomic ratios. This trend was also observed in the work carried out by Elaigwu and Greenway (2016a). The linear trend between the hydrochar and raw biomass indicates that the predominant reaction was dehydration (Erdogan *et al.,* 2015).

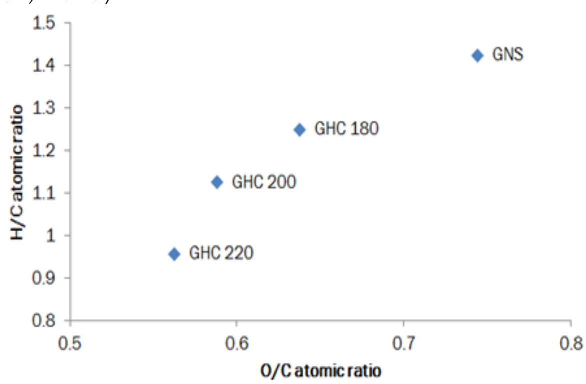

Figure 1. Van – Krevelen diagram

Table 1. The yield and physicochemical properties of HTC products

Product	Hydrochar yield (%)	Hydrocrude yield (%)	VM (%)	FC (%)	Ash (%)	C (%)	H (%)	O (%)	N (%)
GNS	-	-	73.1	23.8	3.1	47.11	5.6	46.69	0.6
GHC180	61.84	56.67	68.93	29.75	1.32	50.88	5.31	43.18	0.63
GHC200	54.33	53.33	62.02	37.16	0.82	52.95	4.98	41.47	0.6
GHC220	45.76	51.25	55.34	44.43	0.23	54.35	4.35	40.69	0.61

Table 2. Energy values and quality of hydrochar

Product	HHV (MJ/kg)	% HHV increase	% Carbon increase	EDR	EY (%)
GHC180	16.89	14.20	8.00	1.05	64.72
GHC200	18.35	24.07	12.40	1.08	58.63
GHC220	19.11	29.21	15.37	1.13	51.71

CONCLUSION

Biomass is a feasible option for renewable energy generation. Among the various conversion pathways available, Microwave-assisted hydrothermal carbonization (HTC) is an efficient process to handle wet waste and produces energy-intensive hydrochar with improved carbon and energy value in a shorter duration under mild temperature and self-generated pressure. Energy-consuming drying is not necessary for the MWAHTC process. Groundnut shell hydrochar produced in this study was a hydrophobic, carbon-rich material that possesses improved energy properties compared to raw biomass. With the increase in process temperature from 180 to 220°C, the HHV of hydrochar was improved compared to the raw biomass (14.79 MJ/kg). The HHV of hydrochar was maximum (19.11 MJ/kg) for the hydrochar produced at 220°C with 20 minutes holding time and a 1:20 biomass to water ratio. The developed hydrochar can be used as an alternative solid fuel with enhanced properties.

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Ethics statement

No specific permits were required for the described field studies because no human or animal subjects were involved in this research.

Consent for publication

All the authors agreed to publish the content.

Competing interests

There were no conflict of interest in the publication of this content

Data availability

All the data of this manuscript are included in the MS. No separate external data source is required. If anything is required from the MS, certainly, this will be extended by communicating with the corresponding author through corresponding official mail; komalabharathi2012@gmail.com

Author contributions

Research grant - ICAR, Idea conceptualization - PK, Experiments - PK, Guidance - PS, Writing original draft - PK, Writing - reviewing and editing -PK, PS

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