



Synthesis of engineering carbon from agricultural waste biomass by hydrothermal carbonization process

S. Rasam, H. Sedaghatzadegan Esfahani, M. Bagi, M. Keshavarz Moraveji*

*Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), 424 Hafez Avenue, Tehran 15875-4413, Iran
moraveji@aut.ac.ir*

Abstract

Hydrothermal carbonization (HTC) among other pretreatment process to convert feedstock into coal-like material is known as a suitable process for synthesis of novel carbon-based material from agricultural waste biomass that received increased attention recently. The black solid product known as main product of HTC is called hydrochar and has shown promising applications in many fields such as carbon fixation, water purification, fuel cell catalysis, energy storage, CO₂ sequestration, bioimaging, drug delivery, and gas sensors. Depending on the desired quantities, properties and application of products selection of the proper treatment method is important and limited. In this investigation HTC is applied to *Saffron* flower waste as an agricultural waste and to understanding the complex process and finding correlation between process parameters and product properties the effect of reaction temperature and residence time were investigated at the range of 180-260°C and 1-4 h respectively. Analysis applied for the raw feedstock and its hydrochar were including hydrochar yield, BET surface area, elemental composition (C, H, N, S and O) and thermogravimetric analysis (TGA). The results of this characterization showed that hydrothermal carbonization in high temperature media resulted in decreasing in hydrochar yield, increasing in surface area (BET) and carbon content. Residence time has the effects like temperature.

Keywords: Hydrothermal carbonization, Optimization, Hydrochar, Saffron flower waste

Introduction

Conversion of biomass to valuable products is of significant importance from both economical and environmental aspects. Using this organic waste as a renewable, cheap, available and environmentally friendly material can have widespread applications as an effective absorbent and a replacement of fossil-based fuels being convertible to any form of energy like gas, liquid and solid [1]. There are diverse thermochemical processes for conversion of biomass to high-quality products. Choice of these processes is based on the properties and applications of the final products. Pyrolysis, gasification, hydrothermal carbonization, combustion and torrefaction are different techniques in biomass conversion to high-value products [2-7]. Each method has its own benefits and drawbacks. Meantime, hydrothermal carbonization (HTC) has been inspected more than other methods and is considered as the best strategy for carbonization of wet materials [7-9]. Mild operating temperature, reduced produced toxic gases, no need for drying the wet biomass, higher yield



compared to pyrolysis process, higher HHV (higher heating value) than torrefaction, utilizing the cheap, available and non-toxic water as solvent and catalyst are the advantages of HTC process relative to other methods [5, 10-13]. In HTC procedure, a determined amount of biomass is submerged in water and placed into a closed system. Depending on the initial structure of the biomass, the temperature rises to about 180 and 350 °C and after reaching to this temperature, it is kept in this condition under autogenous pressure for a certain period of time (from 30 minutes to 12 hours [8]). Products of HTC process are classified into solid, liquid and gas products. The major product of HTC process is a black brownish solid rich in carbon content named hydrochar. The liquid fraction consists of water and oil while the gas phase is composed of mainly CO₂, CO and H₂O [5, 8]. The produced hydrochar or in other words, the solid product with high carbon content has the capability to be used both as a solid fuel or absorbent. Owing to low energy density, presence of ash, moisture and toxic emissions, the raw biomass in its nature is not a good option for fuel while hydrochar in light of its higher heat value is a suitable choice as a solid fuel [11]. Literally, dehydration and decarboxylation reactions can lead to a decrease in solid mass and consequently, an increase in energy density of hydrochars [9]. Generally, physical and chemical properties of the produced hydrochar rely on the reaction condition and initial structure of the biomass [14]. Effective parameters on HTC process are temperature, residence time, ratio of biomass to water, pressure, feed water pH, particle size of biomass, recyclability of process water and in the case of catalyst usage, the type and mass ratio of the catalyst to the biomass [8, 15]. However different studies have investigated the effect of these parameters on the hydrochar properties [16-20], but there are less details about the correlations between the process parameters and the product properties.

The main objective of this study is to investigate the effect of the reaction parameters on final properties of the product in HTC process from *Saffron* flower waste as raw biomass

Experimental

In the HTC experiments, a full factorial experimental design was used to investigate the effects of parameters governing on this process. Temperature and residence time were tested. For each experiment, a pre-weighted sample of biomass was dispersed in 40 ml distilled water and stirred manually. The mixed solution was transferred into a teflon sealed vessel and then inserted into the 100-mL 316 L stainless steel autoclave reactor. Then the reactor was placed in oven with air circulation and heated up to the target temperature (180-220°C) at 5 °C min⁻¹ heating rate. The reactor with autogenous pressure was held at pre-set temperature for five residence times of 1, 2 and 4 h. After that it was cooled naturally to ambient temperature. The gas produced in the headspace of the reactor was released and the solid residual (named hydrochar), as the main product of HTC, were collected and separated from aqueous phase by vacuum filtration.

firstly, hydrochars were washed with 10 wt% HCl solution to remove any impurity and residual organic and mineral matters from the surface of samples, then they washed with hot deionized water several times until becoming neutral. Wet hydrochars were dried in an oven at 105 °C overnight. The dried hydrochars were weighted to calculating the yield of hydrochars and subsequently stored in a desiccator for further analysis.

Results and discussion

According to Nitrogen adsorption-desorption isotherms at 77 K, surface area of the samples were obtained via a Quantachrom Autosorb-1-MP surface area analyzer. As shown in Table 1,



the BET surface area was generally low for hydrochars produced at all conditions, ranging from 12.02 to 28.81 m² g⁻¹. Limited porosity and low surface area is, however, one limitation for hydrochars, and potential use of hydrochars for its surface activity, such as adsorbents and catalysts. For catalytic or energetic applications, it is necessary to improve the hydrochar's porosity and surface area by combination of thermal and chemical activation.

Table 1. Surface area of hydrochar driven from SFW.

sample	H-180-4	H-200-4	H-220-1	H-220-2	H-220-4	H-240-4	H-260-4
surface area(m ² g ⁻¹)	12.02	17.61	18.47	19.14	24.52	28.81	26.34

As explained by Xu, Qian, et al. [21] and by Liu et al[22] higher reaction temperature lead to cracking the porous structure and it might be partially blocked as a result of the softening and melting of the biomass constituents, which could lead to a low surface area. Chemical elemental analysis (C, H, N, and S) of the samples was conducted with a PE 2400 Series II CHNS/O elemental analyzer. The O content was determined by sub-traction of the CHNS results and the ash content from 100. After the HTC process, the carbon content increased from 45.12% in the raw material to 48.05–73.16% in the hydrochar samples. The carbon content in hydrochar is strongly dependent on hydrothermal processing conditions and the carbon content in its feedstock[21]. While due to dehydration and decarboxylation process, H and O content during HTC decrease from 5.77 to 4.92 and from 37.69 to 16.89 respectively. The theoretical higher heating value (HHV) was calculated using an empirical correlation developed by Channiwala and Parikh[23]:

$$\text{HHV}_{\text{predicted}} = 0.3491\text{C} + 1.1783\text{H} + 1.005\text{S} - 0.1034\text{O} - 0.0015\text{N} - 0.0211\text{A} \quad 1$$

Table 2 gives the amount of C, H, N, S, O and ash content in different process condition.

Table 2 Chemical elemental analysis

Sample	Elemental analysis (wt%)						
	C	H	N	S	O	Ash	HHV
Raw SFW	45.12	5.77	0.41	0.8	37.69	10.21	19.24099
HC-180-4	48.05	5.34	0.36	0.7	45.55	3.4	19.35928
HC-200-4	50.10	5.26	0.39	0.7	43.55	3.56	20.18060
HC-220-1	55.62	5.27	0.37	0.65	38.09	3.42	22.62223
HC-220-2	61.21	5.22	0.38	0.65	32.54	3.37	25.08453
HC-220-4	62.64	5.21	0.41	0.63	31.11	3.24	25.6889
HC-240-4	65.27	4.92	0.35	0.62	28.84	3.8	26.68898
HC-260-4	73.16	4.95	0.30	0.6	20.99	4.1	30.142355

HHV indicates the total amount of energy that is available in a sample. The raw SFW had a HHV of 19.24099 MJ kg⁻¹, while the HHVs of its derived hydrochars were in the range of 19.35928–30.142355 MJ kg⁻¹. The HHVs of hydrochars are strongly depended on their initial feedstock composition. The HHVs increased with increasing reaction time and temperature. Higher HHVs of hydrochars could be caused by more complete carbonization due to rearrangement and change in conformation of molecules with time. The hydrochar yield



was determined as the percentage of weight ratio of the dry produced hydrochar to the initial dry weight of SFW loaded. Hydrochar yield as a function of carbonization temperature and residence time is shown in Fig. 1.

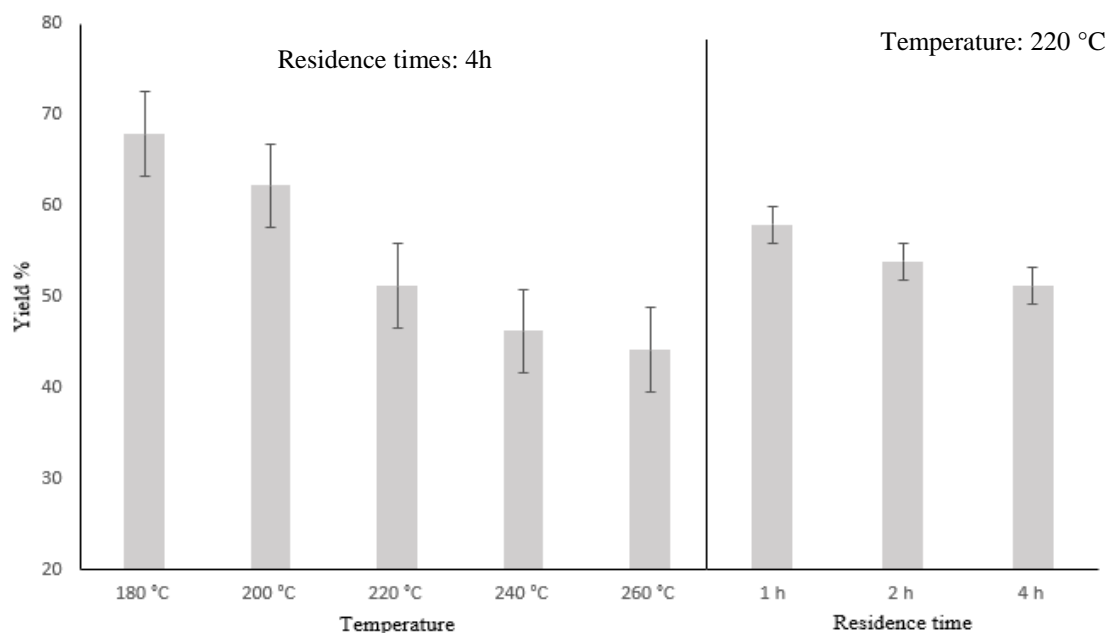


Fig. 1. Yield percent of hydrochars at different condition

In general, the mass yields of the solids recovered decrease by 34.95% and 14.42% with an increase in temperature from 180 °C to 260 °C (for 4h) and a reaction time from 1 h to 4 h (at 220 °C). Thus, the reduction of the hydrochar yields in the HTC can be explained by the degradation of the macromolecules in the biomass and the formation of liquid or oil. Thermal stability analysis of hydrochar was investigated with a METTLER Thermogravimetric Analyzer TGA1 instrument. The TG (weight loss) and DTG (rate of weight loss) of samples were obtained continuously as a function of temperature. Fig. 2 shows the TG-DTG profiles of thermal behavior between 30 °C and 900 °C for raw SFW and hydrochar that obtain in 220 °C and 4h. Three major stages in the thermal decomposition of raw SFW were found in Fig. 2(a). The first stage occurred at a temperature ranging from 30 °C to 130 °C, with one peak centered at 67 °C, due to the weight loss of moisture content. In the temperature range 195e410 °C, one sharp peak at 340 °C with a slight left “shoulder” at 295 °C was detected, mainly ascribing to the decomposition of hemicellulosic components.

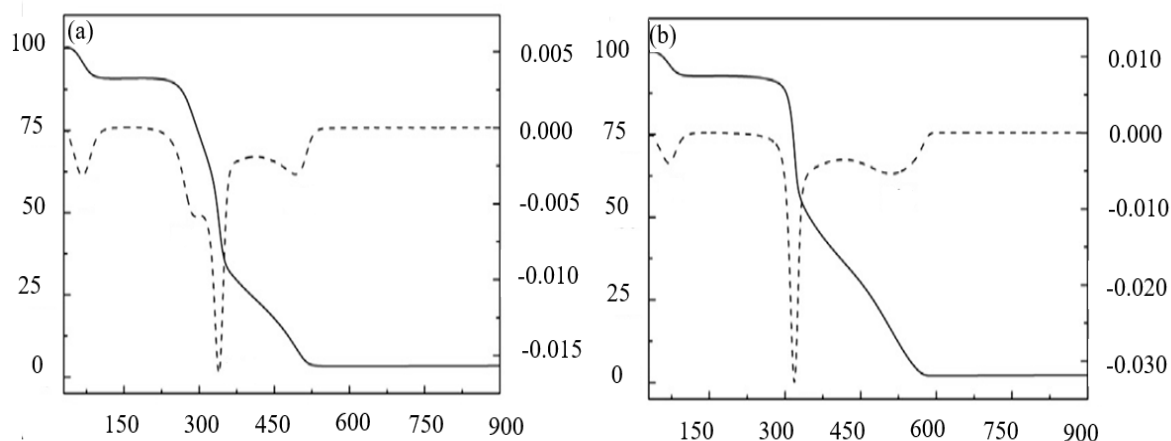


Fig. 2. TG-DTG curve of (a) raw SFW, (b) Hydrochar at 220 °C and 4 h,



A total weight loss of 66% and 56% was obtained for raw SFW and hydrochar obtained in 220°C and 4h, respectively. In the temperature range 410-490 °C, the weight loss for raw SFW was about 21% owing to further decomposition of lignin.

Conclusions

The hydrothermal carbonization process was applied to SFW to produce hydrochars at mild conditions of 180–260 °C for 1– 4 h. The carbonization process increased the carbon content by up to 73.16%. The highest HHV achieved after HTC process was 30.142355 MJ kg⁻¹, with very low ash content and relatively high yield. Therefore, there is potential for hydrochars from SFW to be used as a solid fuel. Among the temperature and residence time that tested, it was found that reaction temperature had the most important parameters for controlling the HTC process. While in higher temperature BET due to cracking decrease. HHV increase with increasing both parameters.

References

- [1] Özbay, N., et al., " Biocrude from biomass: pyrolysis of cottonseed cake" *Renewable Energy.*, 24, 3-4, 615-625 (2001).
- [2] Alvarez, J., et al., " Improving bio-oil properties through the fast co-pyrolysis of lignocellulosic biomass and waste tyres", *Waste management.*, 85, 385-395 (2019).
- [3] Zhang, C., et al., " Oxidative torrefaction of biomass nutshells: Evaluations of energy efficiency as well as biochar transportation and storage", *Applied Energy.*, 235, 428-441 (2019).
- [4] Dhahak, A., et al., " Development of a detailed kinetic model for the combustion of biomass", *Fuel.*, 242, 756-774 (2019).
- [5] Wilk, M., et al., " Hydrothermal carbonization characteristics of sewage sludge and lignocellulosic biomass", A comparative study. *Biomass and bioenergy.*, 120, 166-175 (2019).
- [6] Gil, M., et al., " Assessing the influence of biomass properties on the gasification process using multivariate data analysis", *Energy Conversion and Management.*, 184, 649-660 (2019).
- [7] Heikkinen, J., et al., " Possibilities to improve soil aggregate stability using biochars derived from various biomasses through slow pyrolysis, hydrothermal carbonization, or torrefaction", *Geoderma.*, 344, 40-49 (2019).
- [8] Wang, T., et al., " A review of the hydrothermal carbonization of biomass waste for hydrochar formation: process conditions, fundamentals, and physicochemical properties", *Renewable and Sustainable Energy Reviews.*, 90, 223-247 (2018).
- [9] Danso Boateng, E., et al., " Kinetics of faecal biomass hydrothermal carbonisation for hydrochar production. *Applied energy.*, 111, 351-357 (2013).



- [10] Susanti, R. F., et al., " Activated carbon from citric acid catalyzed hydrothermal carbonization and chemical activation of salacca peel as potential electrode for lithium ion capacitor's cathode, *Ionics.*, 1-11 (2019).
- [11] Fang, J., et al., " Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass", *Journal of industrial and engineering chemistry.*, 57,15-21 (2018).
- [12] Kambo, H. S. and A. Dutta., " A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications", *Renewable and Sustainable Energy Reviews.*, 45, 359-378 (2015).
- [13] Libra, J. A., et al., " Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis", *Biofuels.*, 2, 1, 71-106 (2011).
- [14] Gupta, D., S. Mahajani. and A. Garg," Effect of hydrothermal carbonization as pretreatment on energy recovery from food and paper wastes", *Bioresource technology.*, 285, 121329 (2019).
- [15] Nizamuddin, S., et al., " An overview of effect of process parameters on hydrothermal carbonization of biomass", *Renewable and Sustainable Energy Reviews.*, 73, 1289-1299 (2017).
- [16] Wüst, D., et al., " Hydrothermal carbonization of dry toilet residues as an added-value strategy–Investigation of process parameters", *Journal of environmental management.*, 234, 537-545 (2019).
- [17] Basso, D., et al., " In Deep Analysis on the Behavior of Grape Marc Constituents during Hydrothermal Carbonization", *Energies.*, 11, 6, 1379 (2018).
- [18] Park, K. Y., K. Lee. and D. Kim., " Characterized hydrochar of algal biomass for producing solid fuel through hydrothermal carbonization", *Bioresource technology.*, 258, 119-124 (2018).
- [19] Nizamuddin, S., et al., " Upgradation of chemical, fuel, thermal, and structural properties of rice husk through microwave-assisted hydrothermal carbonization", *Environmental Science and Pollution Research.*, 25, 18, 17529-17539 (2018).
- [20] Yao, Z., X. Ma. and Y. Lin., " Effects of hydrothermal treatment temperature and residence time on characteristics and combustion behaviors of green waste", *Applied Thermal Engineering.*, 104, 678-686 (2016.).
- [21] Xu, Q., et al., " Hydrothermal carbonization of macroalgae and the effects of experimental parameters on the properties of hydrochars", *ACS Sustainable Chemistry & Engineering.*, 1, 9, 1092-1101 (2013).



[22] Liu, Z., F. S. Zhang and J. Wu., " Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment" *Fuel.*, 89, 2, 510-514 (2010).

[23] Channiwala, S. and P. Parikh," A unified correlation for estimating HHV of solid, liquid and gaseous fuels", *Fuel.*, 81, 8, 1051-1063 (2002).