Journal of Science and Technology ***54*** *(4B) (2016) 138-145*

OPTIMIZING THE PROCESS OF TRANSFORMING COFFEE HUSKS INTO BIOCHAR BY MEANS OF HYDROTHERMAL CARBONIZATION

Tran Thi Hien[1, *], Nguyen The Vu[2], Phan Thi Que Phuong[3, 4], Pham Huu Thien[3, 4], Nguyen Dinh Thanh[4], Phan Dinh Tuan[5]

[1]*Industrial University of Ho Chi Minh City, Go Vap District, Ho Chi Minh City.*

[2]*Ho Chi Minh Vocational College of Technology, District 9, Ho Chi Minh City.*

[3]*Dong Nai University of Technology, Bien Hoa City, Dong Nai province.*

[4]*Institute of Applied Materials Science, Vietnamese Academy of Science and Technology, District 1, Ho Chi Minh City.*

[5]*University of Natural Resources and Environment, Tan Binh District, Ho Chi Minh City.*

[*]Email: *tranhien86@gmai.com*

Received: 15 August 2016; Accepted for publication: 10 November 2016

ABSTRACT

The conditions of the hydrothermal carbonization process to produce biochar from coffee husk will be optimized for maximum yield. Besides, response surface methodology (RSM) and central composite face-centered (CCF) method will be used in designing experiments. Also, the optimal value of factors such as temperature, time and biomass: water ratio which can provide a maximum yield of biochar will be worked out using Modde 5.0. As a result, the optimal conditions for maximum yield of biochar was obtained as temperature of 180 ^{o}C, 3.5 h and biomass: water ratio of 15 %. It can also be concluded that temperature has greater impact on the transformation of biochar than time and biomass: water ratio.

Keyword: optimization, coffee husks, agricultural waste, hydrothermal carbonization, biochar.

1. INTRODUCTION

Hydrothermal carbonization method (HTC) is a promising method for transforming agricultural waste products with high yield [1]. It has the capability of decomposing biomass feedstock sources with high humidity (up to 80 %) at low temperature of about 160 – 270 °C, solid component (biochar) and the liquid (mixture containing organic compounds). HTC process takes place through a major chain reactions including hydrolysis, dehydration, carboxyl reduction reaction, polymerization and aromatase [1]. The product of these reactions is carbon-containing biochar which has some practical application like pollutant absorption in water,soil amendment [2], electrode materials for litium battery, supercapacitor [3]. Thereby optimizing the conditions of hydrothermal carbonization process to obtain the desired product is essential.

The objective of this study is to provide more data about optimizing hydrothermal carbonization process to obtain the best biochar efficient in Modde 5.0 software. The results will lay the foundation for the study of high value materials from coffee husks discarded by means of hydrothermal carbonization.

2. MATERIALS AND METHODS

2.1. Coffee husk

Coffee husks collected at a mill in Buon Ma Thuot City, Vietnam is of Robusta coffee, Canephora species. Coffee husk is ground into powder, dried at 105 °C for 12 h to constant mass and sieved through a sieve. The particle size of the coffee husks powder was 250 µm.

2.2. Experimental procedure

Hydrothermal carbonization of coffee husk is done in batches. The surveyed parameters are as follow: temperature from 180 – 220 ^oC, reaction time from 1 – 6 h and biomass: water ratio from 10 – 20 % by weight. The experiments were carried out in Teflon jars of 400 ml. After cooling to room temperature, biochar is collected by vacuum filtration and is then repeatedly washed with deionized water and dried at 105 °C for 12 h to constant mass.

2.3. Characterization techniques

The X-ray diffraction (XRD) analysis was performed using Siemens D-5000, sweep angle of 10 - 70 degree, scan step 0.03 degree, scan speed 0.7 degree/second. Surface and the structural features were analyzed by scanning electron microscopy (SEM) images. SEM was processed by SEM – Hitachi S 4800 device. Specific surface areas of biochar highest performance and lowest performance were measured using nitrogen adsorbed method, while their pore volumes were calculated by the amount of nitrogen adsorption–desorption isotherm perfuming at temperature (-196 ^oC) through Quantachrome NOVA 1000e.

2.4. Optimization of biochar yield using Modde 5.0 software

Designing the experiment in a way that meets response surface methodology (RSM) - plans (CCF) to find the optimal values of the following elements: temperature, reaction time and the biomass: water ratio in order to get the maximum efficieny of biochar through hydrothermal carbonization method. Optimization can help survey the interaction between parameters affecting the yield as well as define the key elements in order to optimize the reaction [4]. These factors and the extent of the experiments are listed in Table 1.

Table 1. The influencing factors and extents of the experiments.

Parameters	Encode	Level		
Temperature (^oC)	x_1	180	200	220
Reaction time (h)	x_2	1	3.5	6
Biomass to water ratio (%)	x_3	10	15	20
Encode	-	-1	0	1

Experimental conditions of hydrothermal carbonization methods are run according to Modde 5.0 software to identify optimal conditions. Complete design matrix for experiments and biochar yield (%) are presented in Table 2.

Table 2. Complete design matrix for experiments and biochar yield (%).

STT	Temperature (^oC)	Reaction time (h)	Biomass: water ratio (%)	Yield (%)
1	-1	-1	-1	71.77
2	1	-1	-1	49.29
3	-1	1	-1	57.26
4	1	1	-1	42.95
5	-1	-1	1	71.43
6	1	-1	1	45.61
7	-1	1	1	57.30
8	1	1	1	39.65
9	-1	0	0	59.71
10	1	0	0	49.76
11	0	-1	0	57.71
12	0	1	0	52.65
13	0	0	-1	54.05
14	0	0	1	53.60
15	0	0	0	54.85
16	0	0	0	54.82
17	0	0	0	54.83
18	0	0	0	54.82
19	0	0	0	54.81
20	0	0	0	54.86

2.5. Biochar yield

The yield of biochar is determined according to the percentage of the dry biochar mass and dry coffee husk:

$$\text{Biochar yield } \% = (W_{db} / W_{dch}) \times 100$$

where W_{db} is dry weight of biochar and W_{dch} is the dry weight of the coffee husk.

3. RESULTS AND DISCUSSION

3.1. Effect of process parameters on the synthesis of biochar

The influence of temperature in hydrothermal chemical process on biochar yield is shown in Figure 1.a. More than 59.5 % of biochar yield can be obtained at about 180 °C. However, when the temperature rose to 220 °C, biochar yield dropped to about 50.2 %. This can be explained by the occurrence of hydrolysis reactions, dehydration, carboxyl reduction reaction, and aromatase and polymerization at higher temperatures which resulted in reduction of biochar [5]. Temperature has a decisive effect on the hydrolysis of compounds present in biomass such as hemicellulose which is completely hydrolyzed at about 180 °C, the majority of lignin in the range of 200 °C [6]. Similar result was also found in the studies conducted previously [7].

Hydrothermal carbonization is a slow response process and reaction time of the process is from a few hours to several days. The longer residence time generally increases reaction severity [6]. The reaction time is selected based on previous studies [8]. Effect of response time on biochar yield is shown in Figure 1.b. Biochar yield gradually decreases to 57.7 %, 54.7 % and 52.5 % over time at 1 h, 3.5 h, 6 h respectively. Biochar yield at 180 °C is the highest at 1h although biochar has not been completely transformed through experimental observation. Therefore, the best time for the course is over 3.5 h. The decrease in biochar yield when there is a longer reaction time is due to the fact that during carbonization there is a formation of CO_2 and lighter organic compounds. If biochar yield reduces, the porosity of the carbon increases [9]. Also, a longer reaction time will facilitate the bio-oil production with larger biomass ratio [10].

The biomass: water ratio has little effect on the yield of biochar, as illustrated in Figure 1.c Biochar yield percentage obtained at a biomass: water ratio of 10, 15 and 20 % was 54.7 %, 54.7 % and 54 % respectively. Higher quantity of biochar is obtained when conducting the process in the biomass: water ratio of 15 %. Biochar quantity decreased slightly when the biomass: water ratio increases to 20 %. Therefore, the biomass: water ratio has less effect on biochar yield and this result are consistent with published studies. Furthermore, it has been reported that the biomass concentration and particle size have little effect on the mass yield [11]. On the other hand, a slight change in the mass yield percentage was observed by doubling the biomass: water ratio [12].

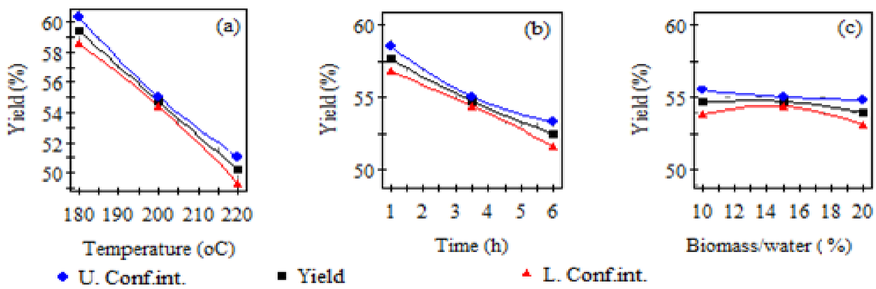

Figure 1. Effect elements of on yield percentage of biochar: (a) temperature, (b) reaction time, (c) biomass: water ratio.

3.2. Statistical analysis of biochar production

A series of experiments related to the optimization study was carried out based on the design of experiment (Modde 5.0) software. The experimental results were analyzed by analysis of variance (ANOVA) via Modde 5.0, as shown in Table 3. The regression model can be assessed on the basis of Fischer (F) test values and probability (p value). A higher F value and lower p value show the higher reliability of the regression model [13]. A higher F value of

617.53 and lower p value less than 0.0001 were observed in this study, which confirms the significance of the model. The developed model equation is:

$$\text{Yield} = 54.7306 - 3.3692x_1 - 1.8716x_2 - 0.2472x_3 + 0.0469x_1^2 + 0.1736x_2^2 - 0.2138x_3^2 + 0.8993x_1x_2 - 0.3829x_1x_3 - 0.0162x_2x_3 - 1.1096x_1^2x_2 - 0.1644x_1^2x_3 - 1.9286x_1x_2^2$$

Table 3. Analysis of variance (ANOVA) of biochar yield.

Yield	DF- Degrees of freedom	SS - Total squared	MS - Mean Square	F - Statistical values	p - The probability	SD - Standard deviation
Constant	1	59921.7	59921.7			
Total Corrected	19	1083.35	57.0183			7.55105
Regression	12	1082.33	90.1938	617.53	0.000	9.49704
Residual	7	1.02239	0.14605			0.38217
Lack of Fit	2	1.02051	0.51025	1354.71	0.000	0.71432
Pure Error	5	0.00188	0.00037			0.01940

The models predicting the theoretical versus experimental values of biochar yield are given in Figure 2. The theoretical value of biochar yield is close to the experimental values. The model of development showes a good effect in the correlation between factors affecting the hydrothermal carbonization process with biochar yield.

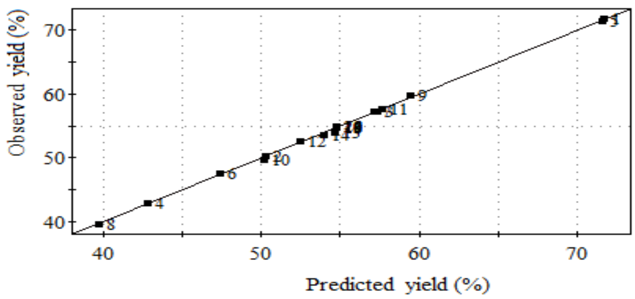

Figure 2. Graph of theoretical prediction versus actual yield of biochar.

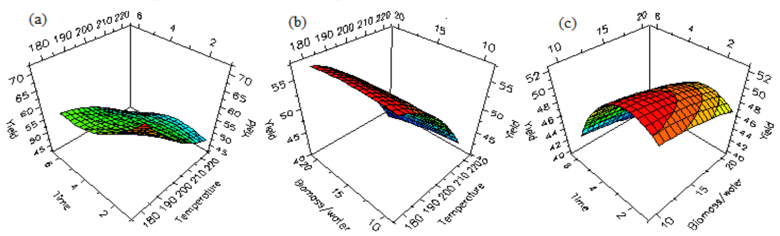

Figure 3. Three-dimensional response surface (a) the temperature and time, (b) temperature and the biomass: water ratio and (c) time and the biomass: water ratio on the yield percentage of biochar.

The simulated three-dimensional response surfaces showin the effects of the factors affecting the hydrothermal carbonization process and the interactions of these factors on the yield of biochar are shown in Figure 3. Figure 3.a shows the interaction of lower temperature and lower time will generate a higher yield percentage of biochar. Figure 3.b indicates the biochar yield is higher at low temperature and high biomass to water ratio. Figure 3.c emphasizes the effect of the interaction of time and biomass to water ratio on the yield of biochar. The higher biochar yieldis obtained at shorter time and higher biomass to water ratio. Therefore, the temperature is a decisive factor which means that the lower the temperature is, the higher the yield. The longer the response time is, the biochar yield of the process tends to decrease. The biomass to water ratio has little impact on the yield of biochar in hydrothermal carbonization process.

3.3. Characteristics structural and morphology of coffee husks and biochar

The chemical composition of coffee husk is shown in Table 4.

Table 4. The chemical composition of coffee husks.

Parameters	Cellulose content	Hemicellulose content	Acid insoluble Lignin content	Acid solube Lignin content	Ash content	Humidity at 105 °C	Other
Value (%)	14.52	16.29	16.35	5.21	3.48	8.7	35.45

In Figure 4 shown the results of XRD the characteristic peaks of lignocellulose became more obvious in biochar, showing that singles hydrothermal process only removed impurities but without destroying the ‘‘core’’ structure of coffee husks. After the hydrothermal carbonization, signals of lignocellulose were completely depleted, the X-ray diffraction pattern for biochar, a broad diffraction peak (2θ = 15 - 30 °) can be caused by aromatic carbon became dominant [12].

This shows that by hydrothermal carbonization bring a polycyclic aromatic carbon structure at low temperatures.

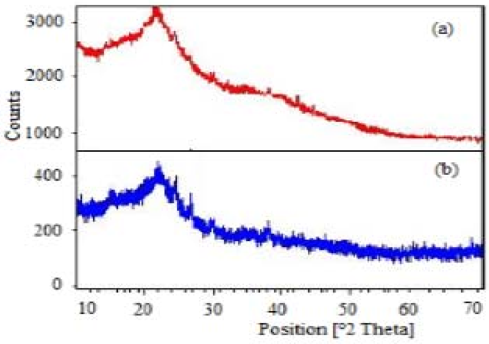

Figure 4. XRD of (a) coffee husk, (b) biochar.

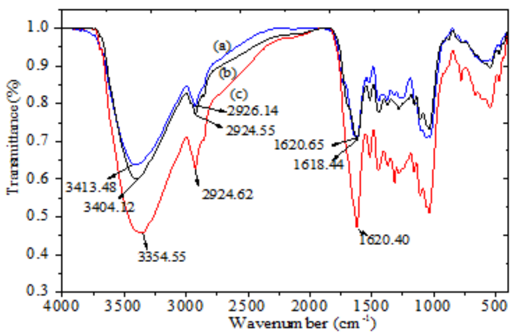

Figure 5. FTIR spectra of (a) coffee husk, (b) higher yield biochar, (c) lowest yield biochar.

Based on the results of fourier transform infrared spectroscopy (FTIR) spectrum analysis shown in Figure 5, we can see the appearance of 3413 cm^{-1} peak of coffee husks which is typical of -OH functional group. This is likely to be found in alcohol compounds, carboxylic, phenol.

Also, at the peak of 2926 cm^{-1} which is typical of valence oscillations of the link C-H likely found in $-CH_2$, $-CH_3$ and $-CH_n$ group, the presence fat and aromatic compounds is expected. The peak at 1620 cm^{-1} of coffee husks showed the presence of link C=C, possibly from the aromatic ring of lignin. The absorption peak observed in biochar is similar to coffee husks. More noteworthy, at 3413 cm^{-1} peak coffee husks has shifted after hydrothermal carbonization process. This confirms the removal of water by dehydration reaction taking place at high temperatures. The groups in 1620 cm^{-1} shows coffee husks reduction which means that there is inorganic carbonate removal in hydrothermal carbonization process. The decrease in the intensity at 1620 cm^{-1} shows lignin amount is removed from the shell beans [14].

SEM images in Figure 6 shown, the structure of coffee husks was changed after hydrothermal carbonization. Notably, the original coffee husksare less porous and rough in surface. After the hydrothermal carbonization process, the number of pores has increased on the surface of biochar. The surface structure is influenced by the reaction time. Hemicellulose and cellulose were significantly decomposed at different reaction temperatures.

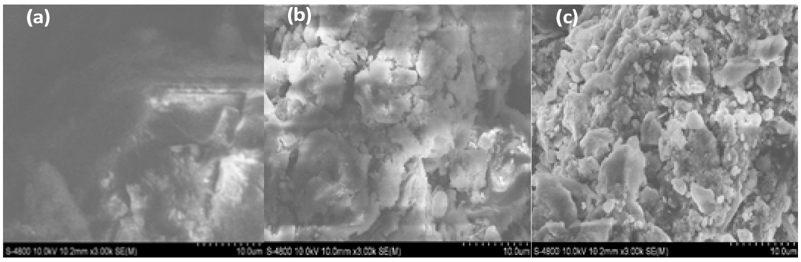

Figure 6. SEM images of (a) coffee husks (b) higher yield biochar, and (c) lowest yield biochar.

Moreover, time is an element that induced the increase in the pores on the surface of biochar. The SEM results were also verified by the results of the sample BET biochar highest performance and lowest performance at 15.14 m^2/g and 48.84 m^2/g respectively. The result shows that temperature has a decisive effect on the hydrolysis of these compounds in the biomass [1].

4. CONCLUSIONS

Study optimal factors in the converting process of coffee husk into biochar with high performance by means of hydrothermal carbonization using software Modde 5.0. The results showed that biochar performance depends on the reaction temperature and time more than the biomass to water ratio. The results coming from SEM, BET analysis show that when the effieciency of biochar reduces, the surface area increases. This result is consistent with published studies. Temperature is a decisive factor and long reaction time can induce a decrease in biochar yield.

Acknowledgements. Thanks Institute of Applied Materials Science, Industrial University of Ho Chi Minh has created an opportunity for us to make this study.

REFERENCES

1. Oliveira I., Blöhse D., and Ramke H. G. - Hydrothermal carbonization of agricultural residues, Bioresource Technology **142** (2013) 138-146.

2. Cao X., Ro K. S., Chappell M., Li Y. - Chemical structures of swinemanure chars produced under different cacbonization conditions investigated by advanced soild-state C nuclear magnetic resonance (NMR) spectroscopy, Energy Fules **25** (2011) 388-397.
3. Kruse A., Funke A., and Titirici M.-M. - Hydrothermal conversion of biomass to fuels and energetic materials, Current Opinion in Chemical Biology **17** (3) (2013) 515-521.
4. Tan I. A. W., Ahmad A. L., and Hameed B. H. - Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology, Chemical Engineering Journal **137** (3) (2008) 462-470.
5. Uzun B. B., Apaydin-Varol E., Ateş F., Özbay N. - Synthetic fuel production from tea waste: Characterisation of bio-oil and bio-char, Fuel **89** (1) (2010) 176-184.
6. Funke A. and Ziegler F. - Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering, Biofuels, Bioproducts and Biorefining **4** (2) (2010) 160-177.
7. Hoekman S. K., Broch A., and Robbins C. - Hydrothermal Carbonization (HTC) of Lignocellulosic Biomass, Energy & Fuels **25** (4) (2011) 1802-1810.
8. Ma H., Li J. B., Liu W. W. - Novel synthesis of a versatile magnetic adsorbent derived from corncob for dye removal, Bioresource Technology **190** (2015) 13-20.
9. Arami Niya A., Abnisa F., Sahfeeyan M. S., Daud W. W., and Sahu J. N. - Optimization of synthesis and characterization of palm shell based bio char as a by product of biooil production process, BioResources **7** (1) (2011) 0246-0264.
10. Boocock D. and Sherman K. - Further aspects of powdered poplar wood liquefaction by aqueous pyrolysis, The Canadian Journal of Chemical Engineering **63** (4) (1985) 627-633.
11. Reza M. T. - Hydrothermal carbonization of lignocellulosic biomass. 2011, University of Nevada, Reno.
12. Nizamuddin S., Mubarak N. M., Tiripathi M. - Chemical, dielectric and structural characterization of optimized hydrochar produced from hydrothermal carbonization of palm shell, Fuel **163** (2016) 88-97.
13. Mubarak N., Yusof F., and Alkhatib M. - The production of carbon nanotubes using two-stage chemical vapor deposition and their potential use in protein purification, Chemical engineering journal **168** (1) (2011) 461-469.
14. Pang J., Zheng M., Wang A. - Catalytic conversion of concentrated miscanthus in water for ethylene glycol production, AIChE Journal **60** (6) (2014) 2254-2262.