Journal of Scientific & Industrial Research
Vol. 80, January 2021, pp. 87-90

A Study on the Torrefaction of Rice Husk as an Attempt to Enhance Its Energy Content

Dejene Mandefro and S Anuradha Jabasingh*
Process Engineering Division, School of Chemical and Bio Engineering, Addis Ababa Institute of Technology, Addis Ababa University, Addis Ababa, Ethiopia

Received 31 January 2019; revised 03 November 2020; accepted 12 November 2020

Torrefaction refers to the thermal and chemical treatment of organic substances (at atmospheric pressure, between 200–300°C, under inert conditions). The objective of this study is to torrefy the rice husk of Ethiopian origin, after a pretreatment with dilute sulfuric acid in order to enhance its energy density. The torrefaction temperature, holding time, and acid concentration investigated in this study were (200, 250, and 300°C), (20, 40, and 60 min) and (0.75, 1.50, and 2.25 g/L), respectively. Box-Behnken experimental Design (BBD) was applied for optimization using Design-Expert ® Version 7 software (Stat-Ease Inc., Minnesota, United States).

Keywords: Chemical treatment, Experimental design, Optimization, Pyrolysis, Rice husk, Statistical analysis

Introduction

Organic substances are a prominent source of renewable energy due to its wide availability and carbon neutral characteristics.[1,2] It is anticipated as a more affordable energy producer.[3,4] Bioenergy is the energy produced from food crops, agricultural residues, organic wastes, and forestry products.[5] Accommodating the low quality biomass fuel for their inclusion in any of the sustainable energy utilization infrastructure could be highly capital intensive. Hence, arises the need to upgrade the biomass. Torrefaction is one such treatment process, which reduces the oxygen content and moisture absorption, thereby increasing the energy content.[6] Biomass charring and volatile cracking increases the amount of fixed carbon, due to the conversion of hemicelluloses into more thermally stable compounds.[7] Torrefaction is a complex process and the torrefied biomass could be applied during the briquetting, pelletization, gasification, or co-firing, applications.[8] In this study, the rice husk from the farms of Ethiopia is used as the organic substance that was subjected to torrefaction. The effect of rice husk torrefaction after the dilute acid pretreatment is examined and the physico-chemical properties were investigated.

Materials and Methods

Rice Husk Torrefaction

Rice husk was dried until 10–15 (% wet basis) moisture, was retained. It was transferred to a vibrating screen separator to remove the larger (> 4mm) and smaller particles (< 2mm) and then used in the torrefaction experiments. Torrefaction was performed in tubular furnace with heater (AM-5250A) with a N_2 (99.99% purity) cylinder, and other adjuncts. The rice husk was then subjected to torrefaction. Torrefaction experiments were conducted at different temperatures (A), at three treatment times (B) using dilute sulfuric acid concentration (C) as a pretreatment agent. All the experiments were designed using the three-level-three-factor BBD design using the Design-Expert 7.0.0 software and the response variable was measured.

Feedstock Characterization

Proximate analysis were performed according to ASTM standards (ASTM E871, ASTM E872, and ASTM D1102 for moisture content, volatile matter, and ash content, respectively).[9] The higher heating value (HHV) was calculated according to a unified correlation.[10] Ash content was determined by ASTM test protocol E-1755-01 (biomass). Ultimate analysis was determined by an EA 1112 Flash CHNS-O-analyzer with helium at a flow rate: 120 mL/min and energy density was calculated using the mass yield and energy yield.[11] Equilibrium moisture content (EMC) was measured at 79% relative humidity at 25°C.[12] Thermogravimetric analysis (TGA) was carried out using *BJ HENVEN*, *Model:* ATAT 2012 TGA analyzer. The functional groups were determined by using FT-IR (*PerkinElmer Spectrum 65 FT-IR Spectrometer*).[13]

*Author for Correspondence
E-mail: anu3480@gmail.com

Results and Discussion

RSM Design

The regression coefficients are presented in Table 1. The regression model was found to be highly significant with coefficients of determination of R^2, adjusted R^2 and predicted R^2 values of 0.987, 0.969 and 0.897, respectively. The Model F-value 13.00 implies the model is significant. Values of "Prob > F" less than 0.05 indicate that, the model terms A, B, A^2, B^2, AB are significant.[3] The model equation that correlates the response to torrefaction process variables after excluding the insignificant terms is provided in terms of the coded factors,

$$Torrefaction\ yield\ (\%) = 120.28 + 1.6A - 6.51B + 24.95C + 0.055AB + 0.174AC + 1.94BC - 0.124A^2 - 1.427B^2 - 34.46C^2$$

where, A, B and C represents the temperature, time and dilute sulfuric acid concentration in °C, min, and %, respectively.

Rice Husk Assessment After Torrefaction

With the increasing temperature, the surface morphology showed a change in color and volume. Carbonization of the biomass was found to increase with the intensity of the torrefaction. The color change was due to the oxidation of phenolic, hydroxyl, carboxylic and other ester, ether groups in the polycyclic aromatic skeleton of the torrefied rice husk compounds during the torrefaction process.[8] The H_2SO_4 treatment modified the fibre structure, leading to a better carbonization.[7] There was a great reduction in the solid yield, which could be attributed to the release of moisture and volatile matter. The parameters had a significant effect on mass yield. When the torrefaction temperature was 200°C and 20 min, the solid yield was 82.15% for the H_2SO_4 treated torrefaction process.[10] When torrefaction temperature was higher than 250°C, most of hemicellulose and the cellulose started to decompose, and this resulted in a quick decrease in the solid yield. At 300°C and 60 min, the solid yield was 68.41% for the H_2SO_4 treated torrefaction. Increasing the torrefaction temperature from 200 to 300°C, caused a decrease in the mass yield with respect to the time.[11]

Table 1 — Box-Behnken experimental design showing the torrefaction yield

Response	A: Temperature (ºC)	B: Time (min)	C: Acid conc. (g/L)	Mass yield of torrefied rice husk (%)	
Run				Actual	Predicted
1	200	20	1.5	81.25	81.81
2	300	20	1.5	78.33	78.83
3	200	60	1.5	85.23	84.73
4	300	60	1.5	69.33	68.77
5	200	40	0.75	87.15	86.11
6	300	40	0.75	75.76	74.78
7	200	40	2.25	83.44	84.42
8	300	40	2.25	75.76	76.80
9	250	20	0.75	82.57	83.92
10	250	60	0.75	80.99	82.46
11	250	20	2.25	80.99	81.03
12	250	60	2.25	80.99	80.53
13	250	40	1.5	83.44	82.46
14	250	40	1.5	83.44	82.46
15	250	40	1.5	83.44	82.46

Proximate and Ultimate Analysis

The starting value of the moisture content of the raw rice husk was 8.45% (wet basis). After the torrefaction, the moisture content significantly decreased. The low moisture content observed was 2.93% at 300°C and 60 min.[6] Volatile content of the torrefaction product showed a noticeable reduction at high torrefaction temperature and time.[8] During the torrefaction treatment, increasing the torrefaction temperature to 250 and 300°C at 60 min, showed a 45.51% and 53.73% reduction in the volatile content, respectively.[14] The highest ash content of 31.11% was observed for the torrefied samples at 300ºC and 60 min. The initial fixed carbon of the raw biomass was 18.06 %. Increasing the temperature to 200, 250, 300°C and at 60 min, increased the fixed carbon content to 30.85%, 35.42%, and 38.72%, respectively. At 300°C and 60 min, the fixed carbon content was 40.13%. The energy density of biomass is increased, thereby enhancing the carbon/oxygen (C/O) and carbon/hydrogen (C/H) ratios.[12] The initial elemental carbon in the rice husk sample was about 30.12 %. And during the torrefaction, heating the biomass at 200, 250 and 300°C for 60 min, increased the elemental carbon content to 22.75%, 44.10% and 40.98%, respectively.[13] The release of CO_2 and CO occurs in the process. The reduction is increased at higher torrefaction temperatures due to the release of CO, CO_2, and H_2O. The decrease in oxygen and hydrogen content resulted in an increase in the carbon content, which lowers the O/C atomic ratio from 1.098 to 0.558 after the torrefaction. Temperatures higher than 300°C may not be needed, because it may cause a significant loss in the higher energy content of the volatile matter and also increase the relative ash content of the biomass. The initial nitrogen and sulfur content observed for the raw biomass samples were

0.25% and 0.03% respectively.[9] Increasing the torrefaction temperature to 250 and 300°C at 60 min, increased the nitrogen content by 0.1% and the sulfur content remained unchanged. The HHV of the untreated raw Rice husk was found to be 15.96 MJ/kg. This was a mean value calculated from three proximate analysis runs. This has been used to calculate the energy yields after the torrefaction. The bulk density was found to decrease due to the decrease in mass (moisture and volatile matter). The increments of energy content for torrefied rice husk (300°C and 60 min) was 29.53%. The energy density was determined from the ratio of HHV of torrefied product to raw biomass. Torrefaction at 300°C for 40 min, resulted in an enhancement of HHV from 13.04 MJ/kg to 16.61 MJ/kg. Henceforth, the highest energy density obtained at this treatment condition was found to be 1.274. The energy density increased with torrefaction temperature, due to the increase in the C/O and C/H ratios with increasing temperatures. The maximum higher heating value and fixed carbon content of the torrefied rice husk was 21.25 MJ/kg and 43.73%, respectively.[10]

FT-IR and TGA Analysis

FT-IR spectrum is shown in Fig. 1(a). The FTIR spectra for the untreated rice husk shows the band at 1750 cm^{-1} corresponding to the C=O stretching vibration peak and peaks between, 3430 cm^{-1} and 2364 cm^{-1} corresponding to the O-H stretching vibration. In addition to the phenolic C-OH, C=C, C=O, O-H stretching vibrations, the carboxylic C-OH bending vibration bands appear at 1191 cm^{-1}, 1608 cm^{-1}, 1750 cm^{-1} to 1788 cm^{-1}, 2928 cm^{-1}, and 1425 cm^{-1}, demonstrating the presence of COOH and phenolic OH groups. The band at 3445 cm^{-1} is attributed to the saturated C-H stretching vibration and indicates the completion of carbonization. Thus, the presence of the above said peaks in the spectra shows the abundance of phenolic, hydroxyl, ester, ether, carboxylic groups in the skeleton of the torrefied rice husk.[8] TGA analysis of the torrefied rice husk (300°C, 40 min) was performed and presented in Fig. 1(b). Thermal decomposition of rice husk occurred within a temperature range of 250 to 300°C as indicated by the torrefaction peaks. On increasing the temperature above 500°C, ash was produced. Hemicellulose, cellulose and lignin peaks

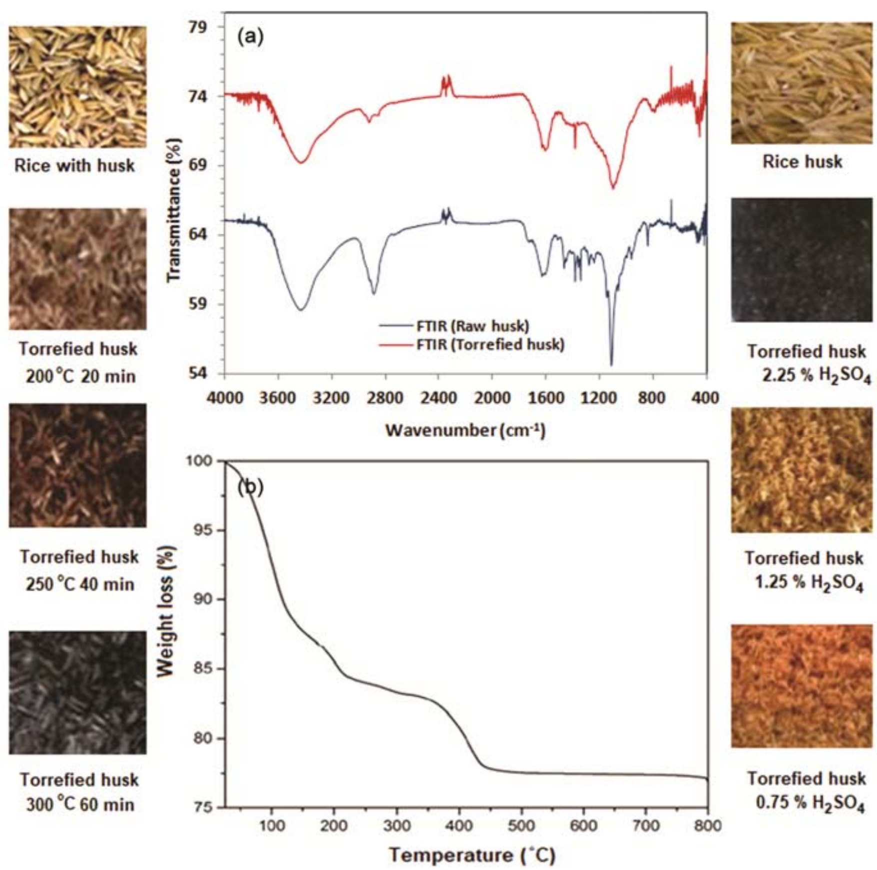

Fig.1 — (a) FTIR analysis of the untreated and torrefied rice husk, (b) TGA curve of torrefied rice husk

were observed at temperatures of 200–250°C, above 360°C, and 500–900°C, respectively. The first stage (< 200°C) corresponds to the drying period where the light volatiles, mainly water was liberated. In the second stage (200–550°C), devolatilization of condensable products was observed through a remarkable slope caused by the liberation of volatile hydrocarbon from the rapid thermal decomposition. In stage three, there was a dawdling change in the weight. Torrefaction peak of the rice husk was observed between 200 and 300°C.[13]

Conclusions

In this study, torrefaction of rice husk was found to enhance its energy content. Torrefaction temperature and holding time had a significant effect on the process. The optimal torrefaction treatment conditions were observed at 300°C and 40 min for the rice husk torrefaction. TGA analysis shows the torrefaction peaks between 200°C and 300°C. The energy density value proves the efficiency of the torrefaction treatment adopted in this study.

Acknowledgment

The authors are thankful to the Ethiopian Geological Survey Organization and Leather Industry Development Institute, Addis Ababa, Ethiopia for all the inputs.

References

1 Berhanu M, Jabasingh S A & Kifile Z, Expanding sustenance in Ethiopia based on renewable energy resources - A comprehensive review, *Renew Sust Ener Rev*, **75** (2017) 1035–1045.

2 Tesfamichael B, Gessesse N & Jabasingh S A, Application of rice husk and maize straw biochar for carbon sequestration and nitrous oxide emission impedement, *J Sci Ind Res*, **77** (2018) 587–591.

3 Fissha A & Jabasingh S A, Production of bioethanol from barley spent grains (BSG) by two stage dilute acid hydrolysis, *Schol Reps*, **3** (2018) 78–86.

4 Jabasingh S A, Lalith D, Prabhu M A, Yimam A & Zewdu T, Catalytic conversion of sugarcane bagasse to cellulosic ethanol: TiO_2 coupled nanocellulose as an effective hydrolysis enhancers, *Carbo Polym*, **136** (2016) 700–709.

5 Mamo T Z, Dutta A & Jabasingh S A, Start-up of a pilot scale anaerobic reactor for the biogas production from the pineapple processing industries of Belgium, *Renew Ener*, **134** (2019) 241–246.

6 Du S W, Chen W H & Lucas J A, Pretreatment of biomass by torrefaction and carbonization for coal blend used in pulverized coal injection, *Bioresour Technol*, **161** (2014) 333–339.

7 Pelaez-Samaniegoa M R, Yadamac V, Garcia-Perez M, Lowell E & McDonald A G, Effect of temperature during wood torrefaction on the formation of lignin liquid intermediates, *J Anal Appl Pyrolysis*, **109** (2014) 222–233.

8 Bridgeman T G, Jones J M, Shield I & Williams P T, Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties, *Fuel*, **87** (2008) 844–856.

9 Chen W H & Kuo P C, Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass, *Energy*, **36** (2011) 803–811.

10 Nhuchhen D R & Afzal M T, HHV predicting correlations for torrefied biomass using proximate and ultimate analyses, *Bioengineering*, **4** (2017)1–15.

11 Chen W H, Lu K M, Lee W J & Lin T C, Non-oxidative and oxidative torrefaction characterization and SEM observations of fibrous and ligneous biomass, *Appl Energy*, **114** (2014),104–113.

12 *Arias* B, Pevida C, Fermoso J, Plaza M G, Rubiera F & Pis J J, Influence of torrefaction on the grindability and reactivity of woody biomass, *Fuel Process Technol*, **89** (2008)169–175.

13 Harun N Y & Afzal M T, Torrefaction of agriculture and forestry biomass using TGA-FTIR-MS, in *Progress in Exergy, Energy, and the Environment*, **1st edn**, edited by I Dincer, A Midilli & H Kucuk (Springer International Publishing, Switzerland) 2014, 805–813.

14 Singh T, Singh A P, Hussain I & Hall P, Chemical characterisation and durability assessment of torrefied radiata pine (*Pinus radiata*) wood chips, *Int Biodeterior Biodegrad*, **85** (2013) 347–353.

15 Umair A, Naveed R, Zaheer A, Tanveer I, Shahzad S, Syed W U H & Abdullah M, Enhancement of fuel characteristics of rice husk via torrefaction process, *Waste Manage Res*, **37** (2019) 737–745.

16 Chang S H, Rice husk and its pretreatments for bio-oil production via fast pyrolysis: a Review, *Bioenerg Res*, **13** (2020) 23–42.