Environmental Research & Technology, Vol. 1(4), pp. 47-51, 2018

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

CONFERENCE PAPER

Pyrolysis of walnut shell biomass in fluidized bed reactor: Determination of optimum conditions for bio-char production

Zeynep Yildiz[1,*] Selim Ceylan[1]

[1] 19 Mayıs University, Chemical Engineering Department, 55210 Kurupelit, Samsun, TURKIYE

ABSTRACT

The pyrolysis of the walnut shell was carried out in a lab-scale continuous fluidized bed reactor at a temperature range of 400 to 600 °C. Thermogravimetric analysis technique was used to determine the thermal properties of the walnut shell. The bio-char product obtained from pyrolysis was analyzed to evaluate the effect of the pyrolysis temperature. Increasing the pyrolysis temperature to 600 °C improved the High Heating Value (HHV) and % C value of the bio-char product. These results showed that the optimum temperature value for bio-char production from walnut shell was 600 °C.

Keywords: Biomass, bio-char, fluidized bed reactor, walnut shell, pyrolysis

1. INTRODUCTION

Unlike fossil fuels such as coal, oil and natural gas, biomass samples are clean, abundant, cost-effective, CO_2-free, low-sulfur and environmentally friendly substances used for fuel production. Biomass is a sustainable resource with a faster life cycle than fossil fuels. Biomass energy is one of the fourth largest potential energy sources in the world and is considered as the energy carrier of the biomass future. At the same time, biomass accounts for more than 10% of the world's global energy demand [1, 2].

The walnut shell is an agricultural biomass waste and is that forms the shell of the walnut tree fruit. According to the TURSTAT reports, walnut production in Turkey in 2017 is approximately 210.000 tons. Walnut is an industrial agricultural product has many different application areas from confectionery to the food industry. The ratio of the inner walnut to the total walnut knee is approximately 50% (by weight). Accordingly, the approximate amount of shell is about 105 thousand tons. Although the walnut shell is a valuable waste, it is not yet widely used and is directly burned inefficiently. Therefore, it is an important issue to convert the walnut shell into products with valuable commercial potential [13, 14].

Biomass sources are evaluated in energy technology by applying various conversion processes (combustion, gasification, pyrolysis etc.) and increasing the quality of the fuel to obtain alternative biofuels (easily transportable, storable and usable fuels) [2]. One of the transformation processes applied to biomass species is pyrolysis and pyrolysis is decomposition of substances in an inert environment. Especially with biomass pyrolysis technology (bio-oil) solid (bio-char or bio-adsorbent) gas (bio-gas) liquid products are obtained [3]. The characteristics of the gas, liquid and solid products obtained from pyrolysis depend on the pyrolysis method and working conditions. Characteristics of bio-char products in pyrolysis process the duration of the reactor and temperature. One of the most important factors affecting pyrolysis is temperature. Increasing the pyrolysis temperature changes the solid product properties as it causes the thermal decomposition of hydrocarbon materials in the biomass structure. For example; long-time and low-temperature pyrolysis can achieve maximum bio-char product yield. Although there are many literature studies on the effect of pyrolysis temperature on bio-char yield, it is not easy to find suitable temperature for bio-char production. Because the optimized temperature for high bio-char production varies

Corresponding Author: zeynepyildiz.omu@gmail.com (Zeynep Yildiz)
Received 30 June 2018; Received in revised form 3 November 2018; Accepted 5 November 2018
Available Online 07 November 2018
Doi: ISSN: 2636-8498

This paper has been presented at EurAsia Waste Management Symposium 2018, Istanbul, Turkey

depending on the biomass composition and the product [3,4]. In fluid bed reactors, the effect of temperature on the bio-char product can be examined and optimum pyrolysis conditions can be improved. Such reactors are widely used in laboratory studies to describe the effect of temperature on pyrolysis behavior [5].

The aim of this study is to transform waste walnut waste in abundant quantities into solid product with fuel potential in the fluidized bed reactor by pyrolysis method which is one of the thermochemical conversion methods. The effect of temperature on the properties of the solid product obtained from the fluidized bed reactor through pyrolysis was investigated and the optimum temperature for the pyrolysis process was determined in this study. Thermal decomposition behaviors of raw walnut shell wastes were investigated using thermogravimetric analysis technique. Characterization of the bio-char product to be obtained after raw walnut shell and pyrolysis was carried by proximate analysis (Moisture, Volatile matter, Ash analysis), ultimate analysis (% C, H, N, S and O analysis) and FTIR analysis. The bio-char products obtained at different temperatures is compared and evaluated according to the fuel potential ultimate analysis and the thermal value results.

2. MATERIALS AND METHODS

2.1. Raw Samples

The raw walnut shell samples were collected from Samsun city of Turkey. The samples were rinsed with deionized water to remove surface dirt, dried in a 70 °C oven overnight, crushed, and sieved to a particle size of 63–125 µm. Functional groups of walnut shell were determined by FTIR (Fourier Transform Infrared Spectrometer) analysis techniques. Ultimate analysis (%C, H, N, and S) was performed with a CHNS-932 LECO brand analyzer while the proximate analysis (ash, volatile matter) of raw walnut shell and bio-char samples was performed in a protherm brand oven.

2.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using Simultaneous Differential Thermogravimetric Analyzer (DTA) equipped with a heat-flux type DTA and a TGA (Shimadzu, DTG-60, Japan; with a precision of temperature measurement ±0.1 K, DTA sensitivity ±0.1 µV and microbalance sensitivity ±0.1 µg) at heating rates of 20 °C min^{-1} under a nitrogen atmosphere with a flow rate of 80 mL min^{-1} with samples of approximately 10 mg.

2.3. Fluidized Bed Reactor

Experiments in the laboratory were carried out using a fluid bed test system and a specially designed heat-resistant reactor. For pyrolysis experiments, a total of 10 g of walnut shells were added to the sample chamber. The amount of sand used was determined to be 20 g and the nitrogen flow rate to be 300 mL min^{-1}. The pyrolysis experiments of the walnut shells were carried out for a reaction time of 60 minutes at 400, 450, 500, 550 and 600 °C (heating rate:10 °C min^{-1}). The temperature in the furnace was checked with the thermal couple in the reactor.

3. RESULTS AND DISCUSSION

3.1. Characterization of Walnut Shell

The proximate analysis, calorific values and ultimate analysis of the walnut shell are shown in Table 1 taken after drying the samples at 70 °C overnight. As seen from Table 1, walnut shell has about 74% and 5% volatile and ash content respectively. Volatile matter and ash contents of different biomass samples vary between 47.8-87.40 and 0.1-37.80, respectively [6]. According to these results, walnut shells have low ash content and high volatile content. The S and N values of the walnut shell are 1.851 and 1.117, respectively. It is important that N and S values are low because they cause environmental problems and reactor corrosion. The higher heating value of many biomass samples given in the literature is between 15-17 MJ kg^{-1} [7, 3]. The higher heating value of the walnut shell was found to be 16.68 MJ kg^{-1}. This calculated thermal value can be considered high when compared with the literature results [8, 9].

Table 1. Main characteristic properties of walnut shell

Characteristics	Raw Walnut Shell
Lignin (%) [9]	48.11
Hemicellulose (%) [9]	22.18
Cellulose (%) [9]	23.95
Proximate analysis	
Moisture (%)	5.43
Volatile matter (%)	74.00
Ash (%)	5.00
Fixed carbona (%)	15.57
Ultimate analysis	
C (%)	45.321
H (%)	5.538
N (%)	1.117
S (%)	1.851
Oa (%)	46.173
Higher Heating Value (MJ kg^{-1})	16.68

The FTIR spectrum of raw Walnut shell is shown in Fig 1. The large peak at 3391 cm^{-1} can be attributed to the stretching of primarily O-H groups. The symmetric and asymmetric stretching vibration associated with the peaks at 2985-2920 cm^{-1} of C single bond H are alkyl and aliphatic chains. The stretch of C=O in FTIR spectrum of raw walnut shell is 1623 cm^{-1}. C=O group is mainly from the acids, aldehydes and ketones. The 1426 cm^{-1} and 1367 cm^{-1} C-H bending bands correspond to alkyl and aliphatic bending modes. The stretching associated with the peak at 1245 cm^{-1} of walnut shell material is likely indicative of C-O stretching vibration in organic acids, ketones, ethers and alcohols groups. The absorbance peak at 1043 cm^{-1} is likely to be C-O-H deformation in secondary and primary alcohols or aliphatic ethers and, lipids [6, 11].

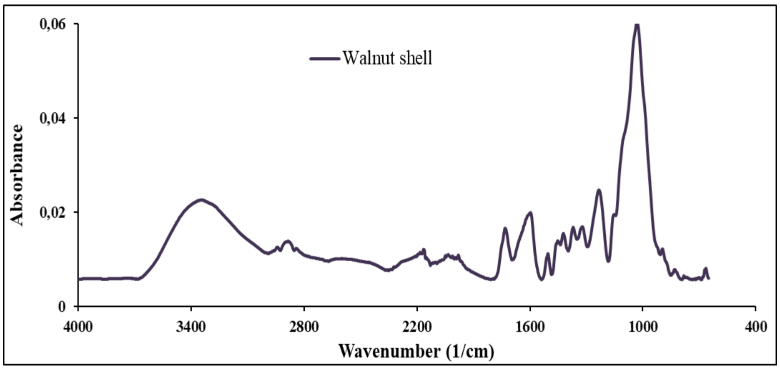

Fig 1. FT-IR spectra of raw walnut shell

3.2. Thermogravimetric Analysis

The curves of thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG) of walnut shell biomass with a heating rate of 20 °C min^{-1} are given in Fig 2.

According to the DTG curve of the walnut shell, the mass loss range can be divided into four stages due to the variable slope curves. In the first step, the decomposition of walnut shell starts at 30 °C and ends at about 110 °C. This may be due to the moisture in the structure of the walnut shell. As walnut shell biomass, all lignocellulosic materials consist of hemicellulose, cellulose and lignin. As can be seen in the DTG curve, the first decomposition starts at 199 °C and ends at 243 °C and this step indicates decomposition of hemicellulose. In the second step, the decomposition of walnut shell is between 256-311 °C, indicating that the cellulose is decomposed. The final decomposition is between 306-424 °C and the lignin component is removed from the construct. These results are consistent with the literature [10].

3.3. Characterization of Bio-char

The FT-IR analysis results of the bio-char samples obtained at different temperatures of the fluidized bed reactor are shown in Fig 3.

Aliphatic hydrocarbons belonging to alkanes in all spectra were detected at 2960-2870 cm^{-1}. It was observed that these peaks did not change as the temperature increased. The peaks at 1630 cm^{-1} were determined as C=O stretching of aldehyde, ketone and carboxylic acid compounds. These bands showed high intensity as they went out to high temperatures in the samples. The peaks seen between 2100 and 1900 cm^{-1} can be said to be Si-H stretching. These peaks showed a relatively constant density; which can be attributed to the ash content of the small sand particles that come with the char [11].

The results of the elemental analysis and the HHV value of the bio-char obtained in the fluidized bed reactor are listed in Table 2. As can be seen from the results, increasing the pyrolysis temperature increased the carbon content and reduced the oxygen value up to 600 °C. The HHV value of bio-char is the maximum value at 600 °C.

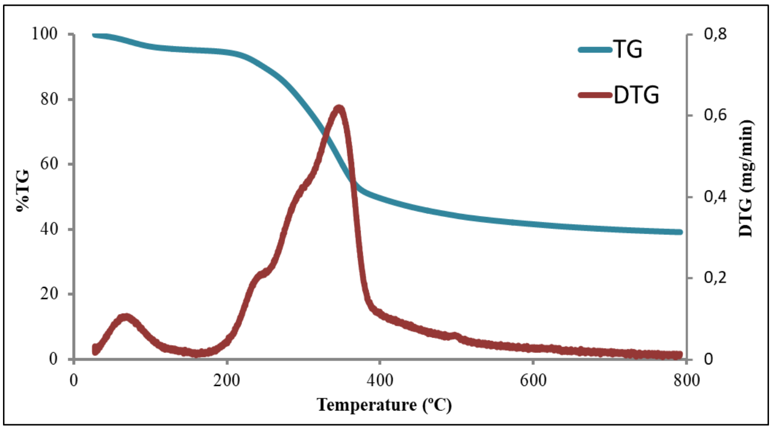

Fig 2. TG-DTG curves of walnut shell

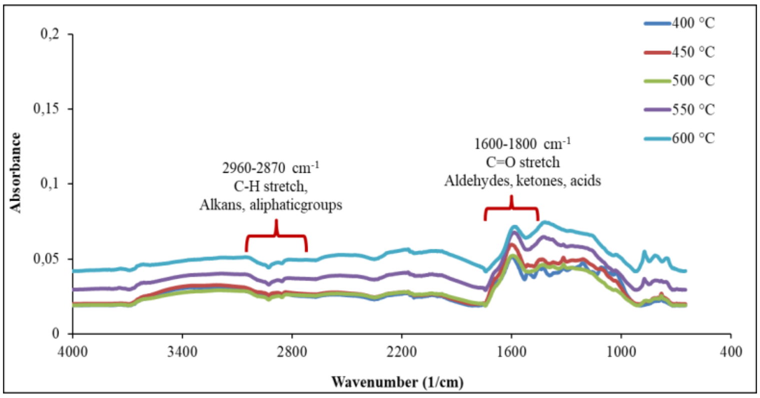

Fig 3. FT-IR spectra of bio-char samples

Table 2. Ultimate analysis of char products

Temperature (°C)	400 °C	450 °C	500 °C	550 °C	600 °C
Ultimate analysis (% wt.)					
C	57,42	59,16	62,95	64,39	73,71
H	3,95	4,42	3,63	3,09	3,02
N	1,29	1,29	1,48	1,31	1,26
S	1,86	1,85	1,98	1,93	2,03
O[a]	35,90	33,28	29,96	29,28	19,98
Higher heating value (HHV) (MJ kg^{-1}) [12]	18,65	20,38	21,13	20,96	25,68

4. CONCLUSIONS

Pyrolysis of the walnut shell biomass was carried out in the fluidized bed reactor at temperatures between 400 and 600 °C. The optimum temperature value was evaluated according to bio-char's elemental analysis and higher heating value (HHV) results. The high temperature increased the percent carbon and HHV of bio-char. With the increase in fuel properties of bio-char, the optimum temperature was determined as 600 °C.

REFERENCES

[1]. M.S. Masnadi, R. Habibi, J. Kopyscinski, J.M. Hill, X. Bi, C.J. Lim, N. Ellis and J.R Grace, "Fuel characterization and co-pyrolysis kinetics of biomass and fossil fuels," *Fuel*, Vol. 117, pp. 1204–1214, 2014.

[2]. H. Ly Vu, S.S. Kim, H.C. Woo, J.H. Choi, D.J. Suh and J. Kim, "Fast pyrolysis of macroalga Saccharina japonica in a bubbling fluidized bed reactor for bio-oil production," *Energy*, Vol. 93, pp. 1436-1446, 2015.

[3]. M. Tripathi, J.N. Sahu and P. Ganesan "Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review," *Renewable and Sustainable Energy Reviews*, Vol. 55, pp. 467–481, 2016.

[4]. Y.J. Zhang, Z.J. Xing, Z.K. Duan, M. Li and Y. Wang, "Effects of steam activation on the pore structure and surface chemistry of activated carbon derived from bamboo waste," *Applied Surface Science*, Vol. 315, pp. 279–286, 2014.

[5]. D. Czajczynska, L. Anguilano, H. Ghazal, R. Krzyzynska, A.J. Reynolds, N. Spencer and H. Jouhara, "Potential of pyrolysis processes in the waste management sector", *Thermal Science and Engineering Progress*, Vol. 3, pp. 171–197, 2017.

[6]. N. Soyler, J. L. Goldfarb, S. Ceylan and M. T. Saçan, "Renewable fuels from pyrolysis of Dunaliella tertiolecta: An alternative approach to biochemical conversions of microalgae," *Energy*, Vol. 120, pp. 907-914, 2016.

[7]. M.A. Mehmood, G. Ye, H. Luo, C. Liu, S. Malik, I. Afzal, J. Xu and M. S. Ahmad, "Pyrolysis and kinetic analyses of Camel grass (Cymbopogon schoenanthus) for bioenergy," *Bioresorce Technology*, Vol. 228, pp. 18–24, 2017.

[8]. H. Karatas and F. Akgun, "Experimental results of gasification of walnut shell and pistachio shell in a bubbling fluidized bed gasifier under air and steam atmospheres," *Fuel*, Vol. 214, pp. 285–292, 2018.

[9]. B.B. Uzun and E. Yaman, "Pyrolysis kinetics of walnut shell and waste polyolefins using thermogravimetric analysis," *Journal of the Energy Institute*, Vol. 90, pp. 825-837, 2017.

[10]. S. Abhishek, P. Vishnu and Z. Dongke, "Biomass pyrolysis—A review of modelling, process parameters and catalytic studies," *Renewable and Sustainable Energy Reviews*, Vol. 50, pp. 1081–1096, 2015.

[11]. X. Yuan, Z. Shuai, B. Robert, C.K. Atul and B. Xianglan, "Fast pyrolysis of biomass and waste plastic in a fluidized bed reactor," *Fuel*, Vol. 156, pp. 40-46, 2015.

[12]. W. Hideo, L. Dalin, N. Yoshina, T. Keiichi, K. Kunimitsu and M.W. Makoto, "Characterization of oil-extracted residue biomass of Botryococcus braunii as a biofuel feedstock and its pyrolytic behavior," *Applied Energy*, Vol. 132, pp. 475-484, 2014.

[13]. K. Açıkalın and F. Karaca, "Fixed-bed pyrolysis of walnut shell: Parameter effects on yields and characterization of products," *Journal of Analytical and Applied Pyrolysis*, Vol. 125, pp. 234-242, 2017.

[14]. Available: http://www.tuik.gov.tr/ 2018.