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Research Article

Investigation of the Effect of Temperature on the Biofuel Performance of Hydrochar Obtained from Kidney Bean Shell

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Abstract

In this study, hydrochar products were obtained from kidney bean shell biomass at different temperatures using the hydrothermal carbonization method. Hydrochar products were produced at three different temperatures (200, 220 and 240 °C) and a holding time of 90 minutes. Biomass/water ratio was taken as 1:10. Analysis techniques such as Thermogravimetric analysis, Ultimate analysis and Fourier Transform Infrared Spectroscopy were used in the characterization of raw materials and hydrochar products. In addition, the fuel properties (high heating value, energy yield and energy densification ratio) of raw KBS and hydrochar products were also investigated. As the hydrothermal carbonization temperature increases, the high heating value of hydrochar products increases. Among hydrochar products, the highest high heating value belongs to the product obtained at 240 °C. The combustion behavior of raw and hydrochar a product was examined using the thermogravimetric analysis method and combustion parameters (T_i, T_b and T_m) were determined. As a result, this study has shown that the hydrochar product produced from kidney bean shell by hydrothermal carbonization method can be used as a biofuel material.

Keywords: Hydrothermal carbonization, hydrochar, biofuel, kidney bean shell

Barbunya Kabuğundan Elde Edilen Hydrochar Ürünlerinin Biyoyakıt Performansına Sıcaklığın Etkisinin Araştırılması

Öz

Bu çalışmada, hidrotermal karbonizasyon yöntemi kullanılarak barbunya fasulyesi kabuğu biyokütlesinden farklı sıcaklıklarda hydrochar ürünleri elde edilmiştir. Hydrochar ürünleri üç farklı sıcaklıkta (200, 220 ve 240 °C) ve 90 dakika bekletme süresinde üretilmiştir. Biyokütle/su oranı 1:10 olarak alınmıştır. Ham madde ve hydrochar ürünlerinin karakterizasyonu için Termogravimetrik analiz, Elementel analiz ve Fourier Dönüşümü Kızılötesi Spektroskopisi gibi analiz teknikleri kullanılmıştır. Ham madde ve farklı sıcaklıklarda elde edilen hydrochar ürünlerinin yakıt özellikleri de (yüksek ısıl değeri, enerji verimi ve enerji yoğunlaşma oranı) araştırılmıştır. Hidrotermal karbonizasyon sıcaklığı arttıkça hydrochar ürünlerinin de ısıl değerleri artmıştır. En yüksek ısıl değere (18,19 MJ/kg) sahip hydrochar ürünü 240 °C sıcaklığında elde edilmiştir. Termogravimetrik analiz yöntemi kullanılarak ham madde ve hydrochar ürünlerinin yanma davranışları incelenmiş ve yanma parametreleri (T_i, T_b ve T_m) belirlenmiştir. Sonuçlar barbunya fasulyesi kabuğundan hidrotermal karbonizasyon yöntemiyle üretilen hydrochar ürününün biyoyakıt malzemesi olarak kullanılabileceğini göstermiştir.

Anahtar Kelimeler: Hidrotermal karbonizasyon, hydrochar, biyoyakıt, barbunya fasulyesi kabuğu

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1. Introduction

Due to the increase in energy demand and the rapid depletion of fossil fuels, the demand for new energy sources that are sustainable and more environmentally friendly is increasing. Biomass energy is a powerful energy source and is the fourth largest energy source after coal, oil and natural gas [1]. In addition, biomass is considered neutral (in terms of carbon dioxide) and is known for its low greenhouse gas emissions [2]. For this reason, research on the use of biomass as an alternative energy source has been increasing rapidly in recent years. Particularly lignocellulose biomass is known as a sustainable energy source due to its high efficiency [3]. Biological, thermochemical and physical techniques are used to convert biomass into fuels. Thermochemical processes can be classified as combustion, gasification, pyrolysis and hydrothermal carbonization [2]. Hydrothermal carbonization method, which is among the thermochemical processes, has attracted great attention in recent years [4]. Hydrothermal carbonization (HTC) is a cheap and effective method that increases the high heating value and energy density of biomass [5]. In HTC, biomass is heated in a closed system at high temperature and under self-generated pressure. Depending on the chemical properties of the raw material, different chemical reactions such as dissolution, dehydration/decarboxylation, polymerization and condensation may occur [6]. In addition, hydrothermal carbonization (HTC) occurs with water at moderate temperatures ranging from 150-300 °C [7]. Many studies have been conducted in the literature on the production of biofuel from biomass using the hydrothermal carbonization method. For example, it has been reported that the high heating values of hydrochar products obtained from turfgrass at different temperatures (180-220 °C) are in the range of 17.67–20.43 MJ/kg [9]. Hydrochar products were obtained from macadamia nut shell by hydrothermal carbonization method at different temperatures (170, 200 and 230 °C) and different biomass/water ratios. [8]. It has been reported that the high heating values of hydrochar products vary between 22.22–27.29 MJ/kg. In another study, the high heating values of hydrochar products produced from wheat straw biomass at different temperatures (180, 220 and 260 °C) and for different times (10, 20 and 30 min) were measured. It has been reported that hydrochar with the highest high heating value was obtained in 30 minutes and at 260 °C [10].

In this study, hydrochar products were produced from kidney bean shells (KBS) at different temperatures (200, 220 and 240 °C) using the Hydrothermal carbonization (HTC) method. The effect of temperature on the fuel properties of hydrochar products was investigated. For this, first the raw material was characterized using different techniques (Thermogravimetric analysis, Ultimate Analysis, Fourier Transform Infrared Spectroscopy). Then, the fuel performance (mass yield, energy yield, and High heating value) of the obtained hydrochar products was investigated. The hydrochar product with the highest high heating value was obtained at 240 °C and the high heating value was calculated as 18.19 MJ/kg. According to the results, the fuel properties of KBS were improved with HTC and the resulting hydrochar products can be used as biofuel materials.

Studies on the investigation of fuel potentials of hydrochar samples obtained from kidney bean shells and the determination of fuel potential values are insufficient in the literature. Determining the fuel properties of hydrochar products obtained from this type of raw material adds innovation and originality to this study. In addition, considering the issues such as climate change and global warming that have occurred in recent years, the fact that hydrochar products enable the production of more sustainable biofuels reveals another unique aspect of the study.

2. Materials and Methods

2.1 Preparation of raw materials

Raw KBS was purchased from local markets in Samsun, Turkey. Before starting the experiments, the raw materials were dried at 70 °C for 12 hours. After the KBS was dried, it was ground using a blender. The ground samples were used in experiments.

2.2 Hydrothermal carbonization

After mixing 0.5 g KBS and 5 mL deionized water, the mixture was placed in a 40 mL steel reactor. The samples were kept in the oven at different temperatures (200, 220 and 240 °C) for 90 minute. At the end of the carbonization process, the reactor was cooled and the solid product was collected and the yield was calculated. The hydrochars obtained from the KBS was labeled as HC_{200}, HC_{220} and HC_{240}.

2.3 Characterization of KBS and hydrochars

Fourier Transform Infrared Spectroscopy (FT-IR), Ultimate Analysis and Thermogravimetric (TG) Analysis techniques were used for the characterization of raw KBS and hydrochars produced at different temperatures. Fourier Transform Infrared Spectrometer (Mattson 1000) device was used for FT-IR analysis. FTIR spectra of KBS and hydrochars were drawn in the wavenumber range of 650 cm^{-1} and 4000 cm^{-1}. The % C, N, H and S amounts were measured simultaneously, and the oxygen content was calculated from the percentage difference. High heating value (HHV), energy and mass yields and energy densification ratio of raw KBS and hydrochar products were calculated using the equations given below [11,12].

$$HHV=0.338\times C+1.428\times(H-O/8)+(0.095\times S) \quad (1)$$

$$\text{Energy densification ratio} = (\text{HHV of hydrochar}) / (\text{HHV of KBS}) \quad (2)$$

$$\text{Energy yield (\%)} = \text{Mass yield} \times \text{Energy densification} \quad (3)$$

2.4 Thermogravimetric analysis

Combustion analysis of the products was carried out in air atmosphere using a thermogravimetric analyzer (DTG-60). Approximately 10 mg of material was used in each measurement. Samples were heated from 20 °C to 800 °C at a constant heating rate of 20 °C/min. S determines the quality of combustion. Within the scope of this study, the combustibility index S was determined using the following equation [21].

$$S = (R_{max} \times R_{mean})/(T_i^2 \times T_b) \tag{4}$$

where T_i is the ignition temperature, T_b is the burnout temperature, R_{max} and R_{mean} are maximum and mean decomposition rate.

3. Results and Discussion

3.1 Characterization of KBS and hydrochars

Ultimate analysis results of raw KBS and hydrochar product are shown in Table 1. In the characterization of raw biomass, ash determination was first made. In the literature, the ash content is between 0.2-22.5% [13]. As can be seen from the results, it can be said that the ash amount of KBS is compatible with the literature. Ultimate analysis and HHV analysis results of some biomass wastes have been reported in the literature. According to the results of ultimate analysis, Nitrogen (N) and Sulfur (S) values of biomasses vary between 0-8.14% and 0-0.86%, respectively [14]. Sulfur (S) and Nitrogen (N) values in biomass are expected to be low in order not to create greenhouse gases. As can be seen from the results, there is no sulfur (S) in the structure of KBS. The amount of Nitrogen (N) is compatible with the literature. The HHV of KBS was calculated as 13.05 MJ/kg. In addition, the fuel properties of the hydrochars (especially the HHV value) are calculated. When Table 1 is examined, the elemental analysis results of KBS have changed significantly after the HTC process. With the increase of HTC temperature, there was a significant increase in the %C content. The hydrochar product with the highest carbon content was obtained at 240 °C temperatures. The %C value of raw KBS and HC_{240} samples was measured as 41.26% and 51.69%. Increasing carbon value allows hydrochar products to increase their high heating value and be used as an alternative fuel material [19, 20]. HHV is a crucial parameter of solid biofuels, such as biomass and its derived hydrochars, as it embodies the total attainable energy in the biomass [22]. As a result, the product with the highest HHV among hydrochar products is HC_{240}. The mass yield values of HC_{200}, HC_{220} and HC_{240} hydrochar products were determined as 75.7%, 71.6% and 68.4%, respectively. As seen in Table 1, energy yield increased significantly with increasing temperature and reached 95.08% for HC_{240}.

Hydrothermal carbonization method and process conditions (temperature, time, biomass water ratio etc.) are very important to obtain hydrochar products with high energy value. In particular, temperature is a critical factor in determining the reaction intensity and has a decisive effect on the transformation pathways of the raw material [23].

Studies in the literature show that as temperature increases, yield decreases and high heating value increases [24]. As the temperature increases, the Hydrogen (H) and Oxygen (O) content in the hydrochar structure decreases, while the Carbon (C) content increases. A high carbon value causes an increase in high heating value (Pauline, 2020). For example, it has been reported in the literature that the high heating value of hydrochar products obtained from tobacco stem biomass at 260 °C reaches from 26.1 MJ/kg to 27.2 MJ/kg [25]. In addition, the HHV results of hydrochar samples obtained from lignocellulosic biomass such as walnut shell, tea stalk, olive pomace were reported as 21.46, 22.53, 25.56 MJ/kg, respectively [26].

Table 1. Characterization of KBS and hydrochars

Materials	**Ultimate Analiz (%)**					**Ash (%)**	**HHV (MJ/kg)**	**Energy densification**	**Energy yield (%)**
	C	**H**	**N**	**S**	**O**				
KBS	41.26	5.91	0.52	-	52.31	5.97	13.05	-	-
HC_{200}	45.51	5.87	0.39	-	48.23	2.78	15.16	1.16	87.81
HC_{220}	48.82	5.74	0.63	-	44.81	5.23	16.70	1.28	91.65
HC_{240}	51.69	5.76	0.50	-	42.05	3.42	18.19	1.39	95.08

FT-IR spectra of KBS and hydrochar products were examined and presented in Figure 1. The vibration peak seen at 3362 cm^{-1} in the raw KBS is the O-H stretching of water. However, as the HTC temperature increases, the O-H bond in the structure of hydrochar products gradually weakens. This is due to dehydration and decarboxylation reactions during the HTC process [17]. The peaks observed around 2960-2872 cm^{-1} in raw and hydrochar samples are C-H stretching vibrations arising from aliphatic hydrocarbons. C=O asymmetric stretching vibrations are seen at approximately 1650 cm^{-1} in all products. This peak may belong to compounds derived from ketones, aldehydes, esters and carboxylic acids, for example [17]. The peaks seen in the spectra at approximately 1000-1500 cm^{-1} may belong to C-O, C-C stretching vibrations [15,18].

Hydrochar is a low-cost adsorbent used to adsorb pollutants in water due to the rich functional group structure on its surface [28]. It has been reported in the literature that hydrochar products obtained from different biomass are used in adsorption applications. For example, it has been reported in the literature that hydrochar products obtained by HTC are used as adsorbents in the removal of heavy metals and antibiotics after modification [27]. As another example, it has been reported in the literature that hydrochar products obtained from oak sawdust biomass by hydrothermal carbonization method at different temperatures (175, 200, 225 °C) and times (12, 24, 48, 60, 72 h) contain oxygen-rich functional groups [16].

According to literature results; It can be said that the hydrochar samples obtained in this study can be used in adsorption studies because they contain oxygen-rich functional groups (C=O, C-O).

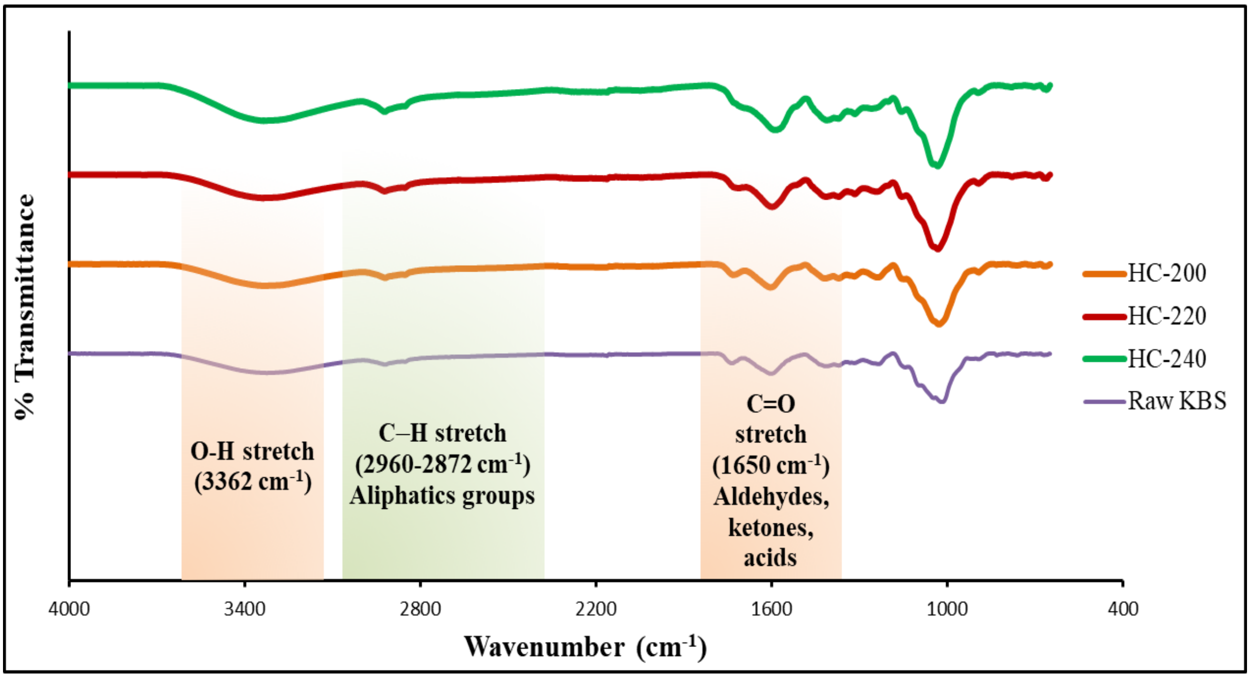
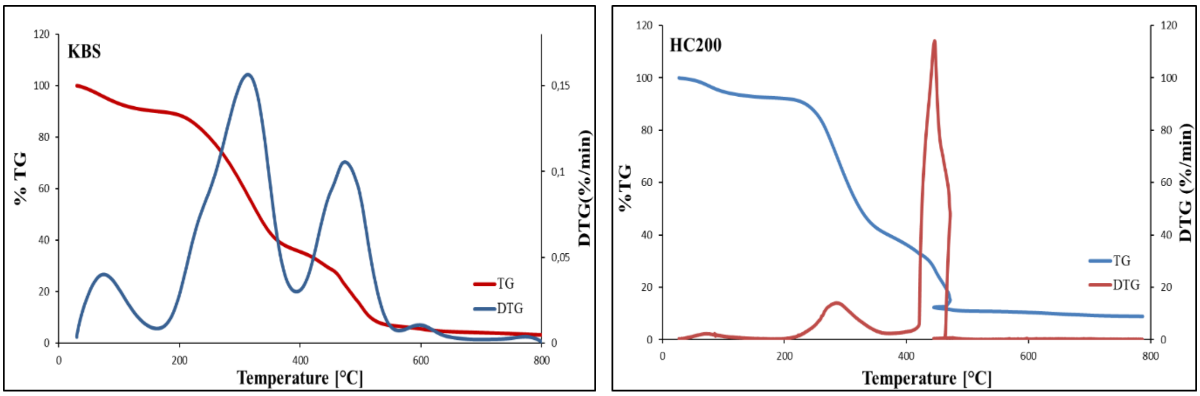


Figure 1. FT-IR spectra of raw KBS and hydrochars

3.2 Thermogravimetric analysis and combustion characteristics

TG and DTG curves of the thermal decomposition of raw KBS and hydrochars are shown in Figure 2. According to the DTG curve; the decomposition of the crude KBS product occurs in 3 steps. The first decomposition is in the temperature range of 31-152 °C and volatile components are separated from the structure. This step is a decomposition that represents moisture loss in KBS. (It appears as a small peak on the DTG curve). The second decomposition is in the temperature range of 163-384 °C and the weight loss is 53.62%. The final decomposition is in the temperature range of 392-793 °C and the weight loss is 32.78%. Similar thermogravimetric curves were observed in studies reported in the literature. For example; according to the thermogravimetric analysis results of KBS biomass, decomposition occurred in three steps [1].



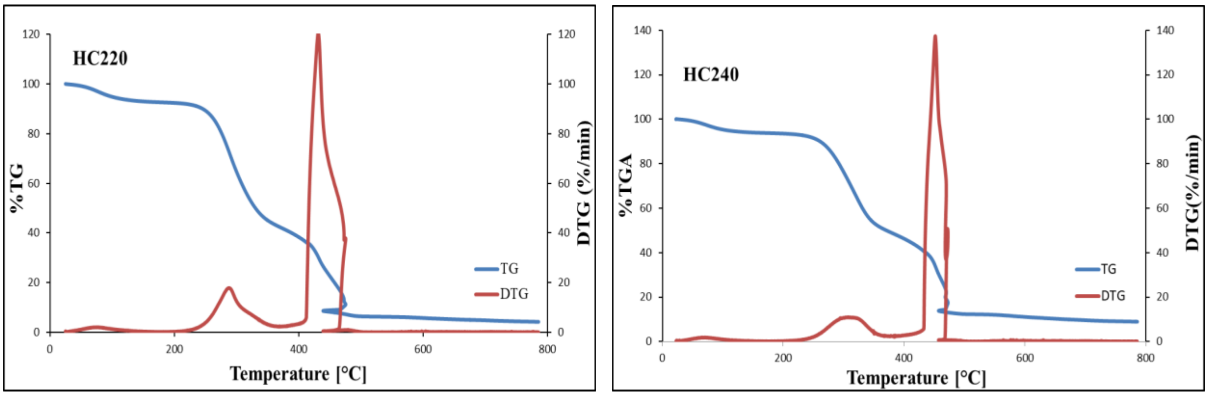


Figure 2. TG-DTG curves of KBS and hydrochars

When the DTG curves of the hydrochar samples were examined, two stages were observed for thermal decomposition in the temperature range of 25-800 °C under the air atmosphere. In the first stage, all hydrochar samples decompose at approximately 220-350 °C. In the second stage, the degradation of the samples is in the temperature range of 400-450 °C. At this stage, a weight loss of 66.91, 80.57 and 71.49% is observed in HC_{200}, HC_{220} and HC_{240} samples, respectively. Compared to HCs, raw KBS has the highest weight loss and shows less stability.

Table 2. Combustion parameters of KBS and hydrochars

Sample	T_i (°C)	T_b (°C)	T_m (°C)	$-\Delta TG_{max}$ (%/min)	$-\Delta TG_{mean}$ (%/min)	S ($\%^2/°C^3.min^2$)
KBS	163	793	305	0.154	0.03	2.19×10^{-10}
HC_{200}	231	478	444	112.19	2.35	1.03×10^{-5}
HC_{220}	232	492	431	120.63	2.47	1.12×10^{-5}
HC_{240}	243	484	451	137.45	2.34	1.13×10^{-5}

Combustion parameters (T_i, T_b, and T_m) of KBS and hydrochar products were estimated using TG and DTG curves. A high T_i of the solid fuel can avoid the potential fire hazard which is favor for the safe handling, storing and transportation [20]. The combustion parameters of KBS and hydrochars are presented in Table 2. The T_i values of KBS, HC_{200}, HC_{220} and HC_{240} products are 163, 231, 232, and 243 °C, respectively. As can be seen, the T_i value of the HC_{240} product is higher than raw biomass and other hydrochar samples. For example, similar to our study, it has been reported that the T_i value of hydrochar produced from waste ginkgo leaf residues is higher than that of raw biomass [21]. T_b (depletion temperature) values of KBS, HC_{200}, HC_{220} and HC_{240} products were determined as 793, 478, 492 and 484 °C, respectively. This result showed that the combustion process of KBS was longer than that of hydrochar products. As the hydrothermal temperature increased, the combustibility index S values showed a clear increasing trend. Compared with raw KBS, the S values of HC_{200}, HC_{220}, and HT_{240}

samples increased to 1.03×10^{-5}, 1.12×10^{-5} and 1.13×10^{-5} respectively, indicating superior combustion performance.

4. Conclusions

It is noteworthy that the fuel properties of hydrochar products obtained using KBS biomass was improved using the HTC method. All hydrochar products have higher carbon content and high heating value compared to the raw material. HTC method significantly increased the high heating value of hydrochar products. Among the hydrochar samples, the product obtained at 240 °C has the highest carbon value (51.69%) and HHV (18.19 MJ/kg). FT-IR results of hydrochar products showed that there are oxygen-rich functional groups in the structure. In a different study, the fuel properties of hydrochar products obtained from KBS at different times using the hydrothermal carbonization method can be investigated. As a result, The HC_{240} product is rich in %C, has a higher HHV value and a higher energy yield, and is suitable for green energy and biofuel applications.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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