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Research Article

Effect of torrefaction pretreatment on combustion behaviour of different agricultural wastes

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ABSTRACT

In this study, which was carried out to investigate the effect of the torrefaction process on the combustion behaviour of agricultural wastes, almond hulls and shells, olive seeds and corn stalks were used. The samples, dried in a laboratory atmosphere, were torrified at 300±5 °C for 41 minutes. The change in fuel properties was determined by making proximate analyses of the solid product obtained after the process and compared with the raw sample. The effects of the torrefaction process on the combustion behaviour of agricultural wastes of different structures were investigated by burning the 1±0.15 g weighted raw and torrefied samples at 700 °C furnace initial temperature in a fixed bed system. Biochars containing higher fixed carbon were obtained with the torrefaction process applied to agricultural waste, and it was determined that this caused biochars to burn more efficiently and for a longer time than raw biomass. As a result, it was determined that biochar with better properties was produced by the torrefaction process applied to agricultural wastes and it was suitable for burning in solid fuel combustion systems. Thus, biochar obtained will both contribute to the country's economy and add value to agricultural wastes that cause problems during storage, transportation, loading into the burning system, and combustion.

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INTRODUCTION

The increase in greenhouse gas emissions, caused by the burning of fossil fuels, and the resulting increase in global average temperatures, has become a very important problem with its impact on human health, the environment, and climate conditions. The fundamental cause of this is the overuse of fossil fuels. When setting the goals for 2030, it was underlined by the United Nations that providing eco-friendly and green energy was one of the top priorities. Using green energy will help reduce over-reliance on fossil fuels and create an eco-friendly environment. Additionally, studies have shown that conventional energy sources (such as coal and fossil fuels) tend to run out, so it is necessary to investigate alternatives to ensure that customers have access to energy at all times [1]. Hydro, geothermal, tidal, solar, wind and biomass energy are examples of current renewable energy sources. One source of renewable energy, biomass, has dependable and promising qualities. This is due to the abundance of biomasses in both woody (forest wood) and non-woody forms (agricultural). In terms of primary energy sources, biomass ranks fourth behind oil, coal, and natural gas [2, 3].

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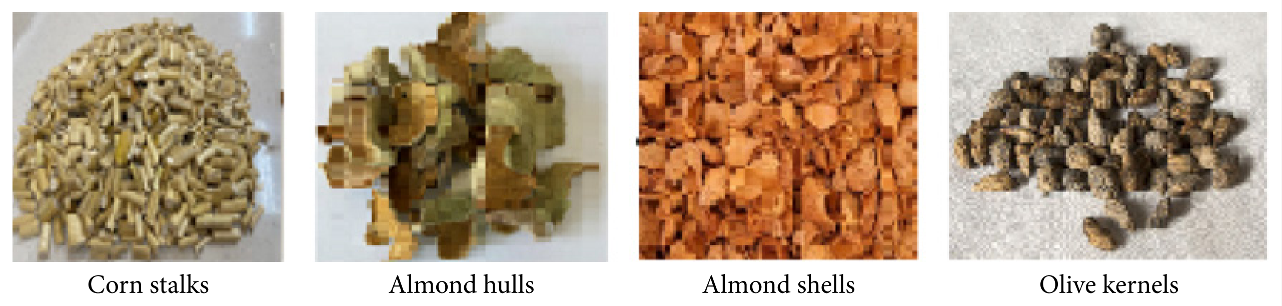

Figure 1. Agricultural waste samples.

Agricultural biomass is defined as energy crops grown and residues/wastes from agricultural production (such as straw, vineyard pruning waste, and vegetable and fruit production waste). It is thought that the residues obtained from agricultural activities will soon be one of the most important energy sources. It is reported in the literature that the annual agricultural waste produced globally is approximately 2000 billion tons [1]. This waste is mostly formed in regions with intensive agricultural activities. Usually, these wastes are dumped in the fields or burned [4]. Conversion of these wastes into usable energy will make an important contribution to the protection of the environment. For agricultural wastes to be used effectively and efficiently in energy production, pre-treatment is required. These processes are carried out to reduce problems such as low calorific value and bulk density, high moisture content, transportation, and storage, which limit the use of agricultural waste as a direct fuel. Various processes are applied to eliminate the disadvantages of biomass to be used in energy production. These are thermal, physical, biological, and mechanical processes [4, 5]. Thermal processes are generally the process of heating biomass in an inert or oxygen-deficient environment. Examples of heat treatment are gasification, pyrolysis, carbonization, and torrefaction [5]. These methods differ in operating temperatures. Torrefaction is a thermal pretreatment technique that operates at temperatures as low as 200–300 °C, usually under inert conditions and at a heating rate not exceeding 50 °C/min. Waste recycling by torrefaction is an important alternative for the sustainable management of both waste and energy and improves the undesirable properties of agricultural wastes that hinder their thermal treatment. As a result of this process; a hydrophobic solid with increased energy density is produced that can be easily ground, processed, and transported. Unlike conventional pyrolysis coal, which is characterized by an energy efficiency of 55–65%, torrefied solid typically retains 90% of the initial energy contained in the main fuel and is suitable for combustion, co-combustion, and gasification applications [1, 6, 7].

In this study, the effect of torrefaction applied to agricultural wastes of different structures on solid fuel combustion stages such as ignition, volatile matter and carbon combustion periods was investigated. For this purpose, almond shells and shells, corn stalks, and olive kernels were used as agricultural waste.

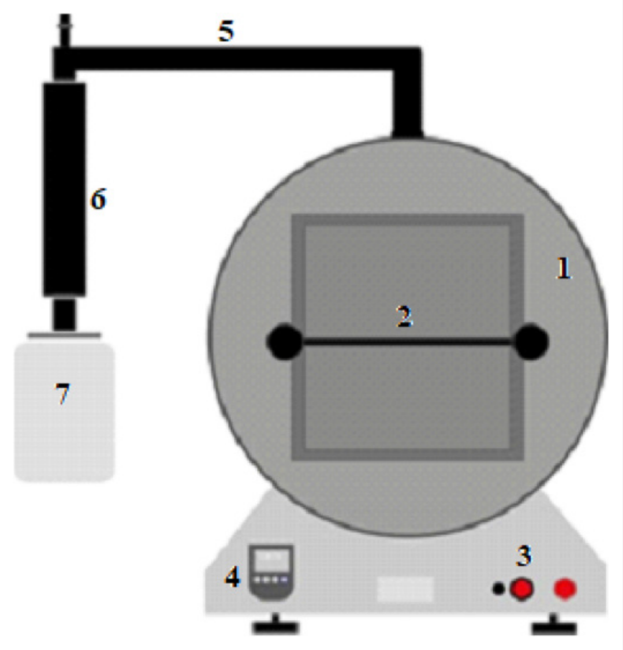

Figure 2. Torrefaction system: 1- Cylindrical tube furnace 2- Furnace cover 3- On/off button 4- PID control system 5- Gas and condensable liquid product output system 6- Double condenser 7- Liquid product container.

MATERIALS AND METHODS

Preparation of Samples

In the experiments, corn stalks, almond hulls, almond shells and olive kernel residues were used as agricultural waste (Fig. 1). Corn stalks, almond hulls and almond shells were obtained from producers in Elazığ, while olive kernels were obtained from producers in İzmir. The samples were dried in the laboratory atmosphere. Some of the dried samples were cut down (e.g., corn stalk) and ground shredded for use in the proximate analysis.

Torrefaction Experiments

Torrefaction experiments were performed in a laboratory-scale torrefaction system given in Figure 2. The torrefaction system consists of a PID-controlled, 40 cm outer diameter and 30 cm long cylindrical tube furnace (18 cm x 18 cm x 20cm inner volume) and a double condenser for collecting the liquid product. In condensers, cooling was done with water. After the system was prepared, 10 g of biomass

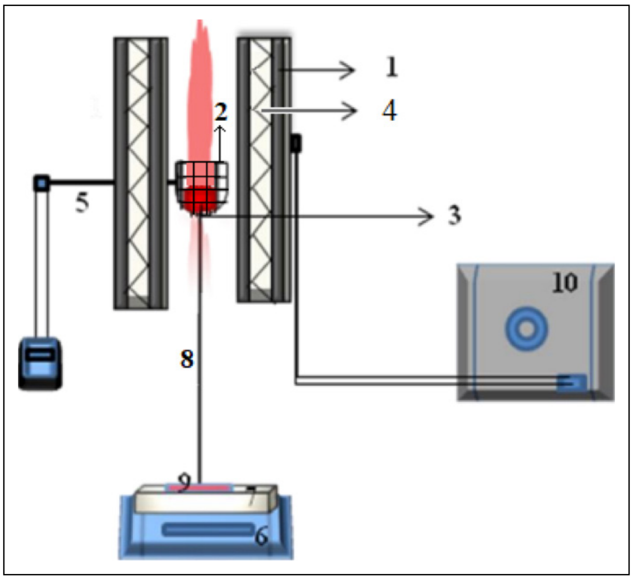

Figure 3. Combustion system: 1-Refractory brick 2-Wire mesh basket 3-Burning pellet 4-Heating elements 5-Thermocouple 6-Top balance 7-Support plate 8-Basket rod 9-Mirro 10.Voltage transformer.

sample was placed in the furnace and heated to the operating temperature with a heating rate of 10 °C/min. When the operating temperature reached 300±5°C, it was torrefied at constant temperature for 41 minutes (working temperature and residence time were determined by preliminary experiments and response surface methodology (RSM)).

The torrefaction process was carried out in volatile matter atmosphere released from the biomass as a result of heating, without passing air or inert gas through the system. At the end of the residence time, the heating was stopped and the system was cooled for 30 minutes. The biochar samples removed from the furnace and completely cooled were weighed and the solid product yield was calculated according to Equation 1. The liquid+gas product yield was calculated from the difference according to Equation 2. Here, m_{bc} and m_{raw} denote the weights of biochar and raw biomass, respectively.

$$\text{Solid product yield (\%)} = \frac{m_{bc}}{m_{raw}} \times 100 \tag{1}$$

$$\text{Liquid+Gas yield (\%)} = 100 - \text{Solid product yield (\%)} \tag{2}$$

Proximate Analysis

Proximate analysis, in which the volatile matter and ash ratios were determined, was performed in the muffle furnace according to ASTM D 1782–84 standards [8]. Proximate analysis was performed on both the original sample and the torrefacted samples (-100 mesh particle size).

The moisture content of the samples was determined in a Mettler LJ16 moisture analyzer (0.01% sensitivity), by keeping them at 105 °C for 2 hours.

For volatile matter analysis, approximately 1 g of the sample was put into the crucible brought to constant weight. The lid of the crucible was closed and put into the muffle furnace (preheated to 950 °C). After the crucible was kept in the furnace for 7 minutes, the covered crucibles were removed and left to cool in the desiccator for 1 hour and then weighed. The volatile matter content of the sample was calculated using Equation 3.

$$\textit{Volatile matter (\%w/w)} = \frac{m_{cs} - m_{cs,950℃}}{m_{cs} - m_c} \times 100 \tag{3}$$

Here, m_c, m_{cs} and $m_{cs,950oC}$ are the weights of the crucible, the sample with the crucible, and the sample with the crucible after 950 °C, respectively.

After determining the volatile matter content to determine the ash content, the open crucibles containing the samples were kept in a muffle furnace heated to 750 °C for 6 hours. The crucibles removed from the furnace were cooled in a desiccator for one hour before being weighed. The ash content of the sample was calculated using Equation 2.

$$\textit{Ash (\%w/w)} = \frac{m_{cs,750℃} - m_c}{m_{cs} - m_c} \times 100 \tag{4}$$

Here, m_c, m_{cs} and $m_{cs,750oC}$ are the weights of the crucible, the sample with the crucible, and the sample with the crucible after 750 °C, respectively.

To check the accuracy of the experimental data, the analyses were repeated several times. Results of parallel studies with deviations of less than ±5% were averaged.

Combustion Experiments

The effects of the torrefaction process on the combustion behaviour of agricultural wastes were investigated by burning the 1g±0.15 weighted samples of the raw and torrefied biomass particles at the starting temperature of the furnace at 700 °C in the fixed bed system.

The setup depicted in Figure 3 was used for combustion studies. It is made of a vertically grooved refractory chamber with an interior diameter of 35 mm, an outside diameter of 82 mm, and a height of 122 mm that holds electrical heating elements. The chamber's top was closed with a round refractory material. A 30 mm diameter stainless steel mesh basket is placed vertically in the chamber, attached to the upper end of a 1.4 mm diameter and 250 mm long stainless steel rod. The lower end of the rod was placed on a scale with a 1 mg precision while being fastened to a square stainless steel plate. The combustion behaviour of the sample in the chamber was observed with the help of a mirror. Heating of the chamber was accomplished using a variable output voltage transformer and temperature control using a NiCr thermocouple placed just above the basket in the chamber. Before the experiments were carried out, the chamber was first heated up to the operating temperature with transformer control. The sample was then thrown into the basket, the time recording was started and the initial weight of the sample was read. The mass of the samples was recorded at 5s intervals during the volatiles and char burning periods. At the same time, the onset and disappearance times of the volatile flame and the extinction times of the glowing char were also observed with the mirror and recorded. Volatile matter and carbon combustion rates were calculated according to Equation 5 using the corresponding mass loss curves.

$$R = \frac{1}{W_0} \times \frac{dW}{dt} \tag{5}$$

Table 1. Torrefaction yield (300±5 °C for 41 min.)

Sample	Solid %	Liquid and gas %
Almond hull	53.4	46.6
Almond shell	80.8	19.3
Olive kernel	78.4	21.7
Corn stalk	43.7	56.4

Wo is the volatile matter or fixed carbon amounts of the sample determined by proximate analysis and dW/dt is the slope calculated from the graph for the volatile matter or carbon combustion period. Experimental data are given as the average result of at least three experiments.

RESULTS AND DISCUSSIONS

Torrefaction Results

In Table 1, the product distribution of agricultural wastes that were torrefaction treated is given. It was determined that hard woody wastes such as almond shells and olive kernels had higher solid product yields. It was observed that the solid product yields of almond hull and corn stalk, which are more flexible and fibrous, were lower. This result shows that the torrefaction yield depends on the type of biomass. It was determined that harder agricultural wastes were more difficult to decompose when thermal treatment was applied, and therefore the amount of solid product was high, while the fibrous biomass was broken down faster when thermal treatment was applied, and more liquid + gaseous products were obtained. This is because the compounds forming the lignocellulosic structure have different decomposition temperatures. It has been stated that hemicellulose, which forms the lignocellulosic structure, decomposes in the temperature range of 225–325 °C, cellulose at 305–375 °C, and lignin at 280–500 °C [9].

When the biomass is heated, hemicellulose starts to decompose first and the amount of liquid and gas product increases as the amount of hemicellulose in the structure of the biomass increases.

Proximate analysis results of raw and torrefied biomass are given in Table 2. As a result of the applied torrefaction process of all samples, it was determined that while the volatile matter amount decreased, the ash and fixed carbon amounts increased. It was determined that the volatile matter amount of almond shell and olive kernel with a high solid product yield decreased by 9% and the fixed carbon amount increased in the range of 30–55% after the torrefaction process.

As a result, it can be said that the volatile components of agricultural wastes, which have a harder (woody) structure, are slowly separated from the biomass during the torrefaction process and the volatile compounds remaining in the biochar increase the solid product yield. On the other hand, it was determined that the volatile matter contents of corn stalk and almond hull (which yields low solids) decreased by 42% and 32%, respectively, and the fixed carbon contents increased by 309% and 96%, respectively. The results of the proximate analysis show that the structure of the raw biomass affects the composition of the products formed after torrefaction. As a result, it is estimated that the corn stalk is fibrous and decomposes faster as a result of thermal treatment, and therefore the hemicellulose content is higher than the other samples. When these separated compounds reach a certain concentration around the fuel, they ignite with the effect of oxygen in the environment. This time, until the flame appears, is called the ignition time.

Table 2. Proximate analysis data of raw and torrefied samples

Sample	Volatile matter %	Ash %	Fixed carbon %*
Almond hull	76	6.5	17.5
Torrefied almond hull	52	13.7	34.3
Almond shell	85	0.3	14.7
Torrefied almond shell	77	0.4	22.6
Olive kernel	80	1.0	19.0
Torrefied olive kernel	73	1.7	25.3
Corn stalk	85	4.2	10.8
Torrefied corn stalk	49	6.8	44.2

*: Determined from the difference.

Combustion Results

The combustion times of raw and torrefied biomasses determined in the fixed bed combustion system at 700 °C are given in Table 3. It was determined that the combustion times of the four biomass increased after the torrefaction process, although they had different structures. When the fuel is heated, first moisture and then low molecular weight compounds begin to separate.

It was determined that the critical ignition concentration was reached later and the ignition times increased because the volatile matter ratio decreased after the torrefaction process [10, 11]. The time from the appearance of the flame to its disappearance is defined as the volatile matter combustion time. With the spread of volatile compounds around the heated particle, the hydrocarbon concentration increases, and the visible flame volatile combustion event occurs [12, 13]. Volatile matter burning time was also found to be longer in torrefied biomass. This result shows that there is less volatile matter on the surface of the biochar and the volatile compounds remaining in the interior are released slowly from the biochar. This is in agreement with the proximate analysis data. Because the volatile matter burning time around the sample (the period during which the visible flame is observed) depends on the hydrocarbon concentration [13, 14].

The time required for carbon combustion is calculated as the interval between the disappearance of the visible volatile flame and the fading of the burning char. It was determined that the carbon burning period of the torrefied samples was longer and more stable.

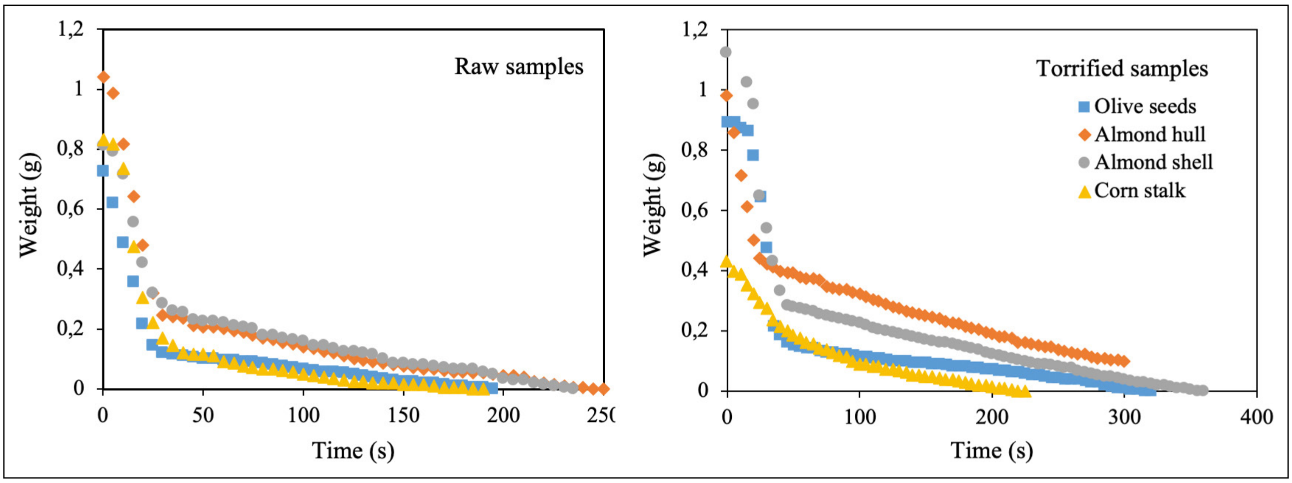

Figure 4. Mass loss curves of raw and torrefied samples.

Table 3. Combustion times of raw and torrefied biomass (700 °C)

Sample	Ignition (flame onset) time (s)	Volatile combustion (flame) time (s)	Carbon combustion time (s)
Almond hull	3.3	29.6	180.1
Torrefied almond hull	5.2	36.2	325.1
Almond shell	5.0	12.5	141.1
Torrefied almond shell	11.5	52.0	385.5
Olive kernel	3.1	29.2	180.2
Torrefied olive kernel	11.0	46.2	381.0
Corn stalk	5.0	26.7	111.2
Torrefied corn stalk	2.4	11.8	208.0

Table 4. Combustion rates of raw and torrefied biomass (70 °C)

Sample	Volatiles combustion rate $(s^{-1})x10^3$	R^2	Carbon combustion rate $(s^{-1})x10^3$	R^2
Almond hull	33.2	93	5.8	98
Torrefied almond hull	21.2	76	4.5	99
Almond shell	26.8	89	5.7	99
Torrefied almond shell	15.6	80	3.5	99
Olive kernel	34.3	95	5.9	99
Torrefied olive kernel	23.2	88	3.3	97
Corn stalk	35.4	95	10.0	94
Torrefied corn stalk	22.8	91	6.9	92

Mass loss curves of raw and torrefied samples during combustion are illustrated in Figure 4 for four samples. All these curves have two distinct regions recognized as volatiles and char combustion periods with different slopes from which respective volatiles and carbon combustion rates can be estimated. Volatile matter combustion and carbon combustion period are seen in both graphs. Although the carbon burning period of the raw samples was close to each other, it was determined that the torrified samples behaved differently in the carbon burning periods.

Numerical values of volatile matter combustion rates represented by the slopes of the first regions of mass loss curves for raw and torrefied samples are given in Table 4. The magnitudes of the correlation coefficients (R^2) for linear fit indicate that the results are acceptable. It was determined that the volatile matter burning rates of the torrefied samples were lower than the raw samples. This result explains the increased volatile burning time after torrefaction. The obtained data show that the volatile compounds near the surface are separated from the biomass during torrefaction and when the biochar formed is burned, the volatile compounds remaining in the interior leave the particle more slowly and for a longer time. In this case, it can be said that the energy of the volatile matter, which constitutes 50–75% of biochar, can be utilized in a more controlled manner during combustion than raw biomass

The carbon combustion rates calculated from the second part of the mass loss curves are also given in Table 4. It is seen that the correlation coefficients (R^2) showing linear fit in the carbon combustion period are quite high and the results are acceptable. It was determined that the carbon of the biochar obtained after torrefaction burned more slowly and for a long time [15]. This is expected behaviour. Because the times required to burn coals practically depend on the rate of combustion and the amount of carbon, as well as the type and relative amounts of other components and their morphology [8]. As a result, it was determined that the biochar obtained after torrefaction burns more slowly and for a longer time under the same conditions when compared to raw biomass [16].

CONCLUSIONS

The results on the effect of the torrefaction process applied to agricultural wastes of different structures on the combustion behaviour of the wastes lead to the following conclusions.

It was determined that while the volatile matter ratio decreased with the applied torrefaction process, the ash and fixed carbon content increased. Proximate analysis data show that the structure of the raw biomass (woody or fibrous) affects the composition (volatile matter and fixed carbon amounts) of the biochar formed after the applied torrefaction process.

Although agriculture wastes have different structures, it was determined that the four biomasses burned more stable and longer after the torrefaction process.

The obtained results showed that biochar with better properties than raw biomass was produced by the torrefaction process applied to agricultural wastes and it is suitable for burning in solid fuel combustion systems. The solid product (biochar) obtained will both contribute to the country's economy and add value to agricultural wastes that cause problems during storage, transportation, loading into the burning system and combustion.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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