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Thermal Decomposition and Combustion Characteristics of Pistachio Pruning Residues

Mohadese Arefi[1], Ahmad Ghazanfari Moghaddam[1], Mohsen Ostadhoseini[1]

[1] Biosystems Engineering Department, Agriculture Faculty, Shahid Bahonar University of Kerman.

Corresponding author: aghazanfari@uk.ac.ir

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ABSTRACT

Due to different reasons, such as the destructive effects of fossil fuel consumption, climate changes, global warming, and threats to human health, biomass is considered as alternate fuel. This biofuel is the most widespread source of renewable energy, and its scientific exploitation is increasing. In this research, pistachio pruning residues including leaves and stems were separately used as a source for biomass and their combustion and heat characteristics were investigated. A TGA device was used for thermal analysis and the combustion properties including enthalpy of combustion, high heating value (HHV) and low heating value (LHV) were measured experimentally and by using regression equations. The amounts of cellulose, hemicellulose, and lignin in stem were 48%, 16%, and 15%, respectively, and the same materials for leaves were 35%, 19%, and 32%, respectively. The high calorific value was calculated using regression equations, which were calculated as 17.5 MJ/kg for stem and 14.5 MJ/kg for leaves. The results showed that the two methods for determining the HHV and LHV were in good agreement with each other. The TGA analysis of the samples showed that the thermal decomposition of stem and leaves starts at a temperature of about 220°C, but during the initial stage of decomposition, the decomposition rate for stem is more severe than the decomposition rate of leaves.

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INTRODUCTION

Biomass is a reliable renewable energy source for producing biofuels such as biodiesel, bioethanol, biogas and biohydrogen (Sharma & Arya, 2019). Converting biomass into higher value energy is a developing sustainable industry (Khademi & Masomi, 2022; Shi et al., 2023). Thermal decomposition and thermochemical conversion processes are the main two methods for converting biomass into heat or producing electricity, as well as converting into solid, liquid and gaseous biobased fuels. The most abundance sources of biomass are agricultural and forestry residues and waste of stem processing industries and aquatic biomass. Some municipal solid and kitchen wastes also contain significant amount of biomass (Kaltschmitt, 2019).

Cellulose, hemicellulose and lignin are the main components of plant and stemy biomass. Many researches have been done in the field of determining the amount of lignin, cellulose and hemicellulose in different biomass materials. The percentages of these combination affect the heating properties of these materials. For hardstem the percentages of cellulose, hemicellulose and lignin are 45%-75%, 10%-35% and 15%-20% respectively, and 30%-51%, 25%-40% and 24%-35%, respectively, for softstem (Van Thuijl et al., 2003).

The heating and decomposition behaviors and mechanisms of the three components of different biomass have been investigated by different researchers. Different types of analytical instruments, such as thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectrometry (GC/MS) analysis are used for these studies. A study on thermogravimetric characteristics of cellulose, hemicellulose and lignin using a TGA indicated that the interaction among three biomass components was trivial and decomposition of these components obey different path (Zhu & Zhong, 2020).

Heating value is a good indication for energy content of biomass materials. Heating value indicates the energy per kilogram of a substance and shows its potential to be use as fuel. For plant biomass the heating value is stated in term of high heating value (HHV) and low heating value (LHV) (Gorensek et al., 2019). Another indicator to evaluate the energy of biomass materials is enthalpy of combustion, which is the heat released by burning one kilogram of biomaterial.

Currently, in Iran more than 360 thousand hectares of orchards are under pistachio cultivation, and considered amount of residues are obtained from pruning these trees (Ostadhosseini et al., 2016). According to available statistics, 135 thousand tons of waste related to harvesting and approximately 180 thousand tons of waste related to pruning are produced annually from pistachio trees, which have no specific consumption and are mostly burned. Therefore, a suitable solution for proper use of these wastes should be planned and implemented by a scientific investigation into energy value of these wastes and residues as a source of bioenergy.

The purpose of this research was to investigate thermal decomposition and combustion properties of pistachio tree leaves and stem. Thermal analysis was performed using a TGA device and combustion properties including combustion enthalpy (H_C), high heating value (HHV) and low heating value (LHV) were obtained. In this research, the heat of combustion of pistachio leaves and stem was measured by theoretical methods and with a bomb calorimeter device.

MATERIALS AND METHODS

Sample preparation and composition analysis

The stem and leaf samples used for the experiments were obtained from the pistachio orchards of Shahid Bahnar University, Kerman, Iran. The collected samples were first spread in front of the sun for a week to dry. To perform the experiments, leaf and stem samples were ground separately and made into powder. Since the components of plant materials can be effective in calculating the calorific value of biomass, therefore, the amount of moisture, volatile substances and ash in the samples were measured separately. To determine the moisture content, 100 grams of each pistachio leaf and stem sample was placed in an oven at 105°C for 24 hours. An electric furnace with a temperature of 550°C was used to measure the percentage of volatile substances and ash. Also, the amount of fixed carbon (residual solids) was calculated from the total difference of moisture percentage, percentage of volatile substances and ash from the mass of the original sample. The percentages of elements present in a biomass sample including oxygen, carbon, hydrogen, nitrogen, oxygen and sulfur has a major impact on its calorific value. In this research, these percentages were determined using an elemental analysis instrument (vario MACRO CHN/CHNS elemental analysis device, Germany).

Calculation of HHV and LHV

Several regression relationships are mentioned in the sources to determine the release value of biomass materials using constituent elements. In this research, the value of HHV was calculated using relations 1 and 2 (Channiwala & Parikh, 2002):

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (1)$$

$$HHV = 0.3536FC + 0.1559VM - 0.0078A \quad (2)$$

where C, H, S, O, N, A, FC and VM respectively represent the percentage of carbon, hydrogen, sulfur, oxygen, nitrogen, ash, fixed carbon and volatile substances in the samples.

Having high calorific value (HHV), low calorific value (LHV) for pistachio leaves and stem was calculated with equation 3 (Sheng & Azevedo, 2005).

$$LHV = HHV - 21.82 \times (H/100) \quad (3)$$

Determination of lignin, cellulose and hemicellulose

To determine the percentage of lignin, a sulfuric acid solution was used according to the TAPPI T2220M-83 standard method. One gram of the sample was placed in 15 ml of 72% sulfuric acid for 60 minutes at 30°C and the mixture was thoroughly stirred and then 560 ml of distilled water was added to it. The solution was placed in an oven with a temperature of 105°C for 105 minutes and finally the solution was passed through filter paper. The mass of the dry material remaining on the filter paper was the amount of lignin in the desired material (Ghafarzadeh, 2009).

The amount of cellulose and hemicellulose was measured using the DIN 2403 standard method. For this purpose, some leaf and stem samples were ground using a hammer mill and poured into a laboratory sieve machine and this machine was operated for one minute. Then one gram of the desired sample powder was poured into a 125 ml Erlenmeyer flask and the Erlenmeyer flask was placed in a water bath with a temperature of 20°C. Then 5 ml of 17.5% caustic soda solution was slowly added to Erlen for 3 minutes, and then this operation was performed more intensively for 2 minutes (5 minutes in total). Again, 2.5 ml of 17.5% soda solution was added to Erlen for 5 minutes. This step was repeated twice (total 12.5 ml in 20 minutes). Then, the solution was poured on a large hole porcelain sieve whose dry mass was previously determined and filtered using a vacuum. In the next step, the contents of the strainer were washed with 50 ml of 9% soda solution and vacuum filtered. The contents were washed in two steps and each time with 10 ml of distilled water. In the next step, 10 ml of 10% acetic acid was added to the filter (no vacuum) until the content of the filter was completely filled. The solution was left for 3 min to remove excess acid by vacuum. The contents were washed several times with distilled water until the water resulting from the washing did not turn the blue litmus paper colorless or red. Then the strainer was placed in the oven with a temperature of 105°C for 24 hours. Finally, the difference in the strain mass in these two cases was the amount of cellulose and hemicellulose of the sample. Holocellulose is the sum of cellulose and hemicellulose.

To determine the amount of cellulose, hemicellulose, relationships (4), (5), (6) and (7) were used (Zare Mirkabad, 2010).

$$\%HC = \frac{M_h}{M_p} \quad (4)$$

$$\%HMC = \frac{M_h - M_c}{M_h} \quad (5)$$

%Cellulose = %HC×%C (6)

%Hemicellulose = %HMC×%HC (7)

That %HC was the percentage of total holocellulose, M_h was mass of holocellulose on the strainer, M_c was the mass of completely dry cellulose on the strainer, M_p was mass of completely dry stem powder, %Cellulose was the percentage of cellulose compared to the whole sample, %HMC was percentage of hemicellulose compared to holocellulose, % Hemicellulose was The percentage of hemicellulose compared to the whole sample, %C was percentage of cellulose compared to holocellulose, %Hemicellulose was percentage of hemicellulose compared to the whole sample.

Determining combustion enthalpy

In this research combustion enthalpies of leaves and stems of pistachio trees were determined by two methods of a) using the percentages of their chemical components and b) experimentally. In the first method the combustion enthalpy was calculated using the following equation (8) (Pulidori et al., 2023):

$$H_c = \frac{\sum_i^3 (\%i \ \frac{H_i}{MW_i})}{100} \quad (8)$$

Where $\%i$ is the percentage of hemicellulose, cellulose and lignin. To calculate equation 8, the enthalpy of combustion and the mass of each component (hemicellulose, cellulose and lignin) must be determined. The following chemical equations for combustion of each components were used to obtain the enthalpy of combustions (Gorensek et al., 2019):

Lignin : $C_{15}H_{14}O_4 + 33.5\ O_2 \rightarrow 15\ CO_2 + 7H_2O$ (9)

Cellulose : $C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O$ (10)

Hemicellulose : $C_5H_8O_4 + 5O_2 \rightarrow 5CO_2 + 4H_2O$ (11)

In order to experimentally determine the burning enthalpy of pistachio stem and leaves, oxygen a bomb calorimeter (C2000, IKA Germany) was used. In this measurement, 15 grams of both leaf and pistachio stem samples were ground and turned into tablets. The tablet samples were burned in the bomb calorimeter and the amount of released heat energy (kJ/g) was read for each sample.

Thermogravimetric analysis (TGA)

The method of thermogravimetric analysis or TGA is the common method of thermal decomposition and analysis of biomass. This method is based on measuring the mass loss of biomass during a controlled heating process. This method provides useful information about decomposition of a substance during heating or its reaction with its surrounding gaseous. In these experiments about 20 mg of sample was heated in a TGA analyzer (USA TG Analyzer Model -7 Perkin Elmer) with a heating rate of 10°C/min, from 30 to 1100°C under nitrogen gas. The obtained graphs were analyzed at different stages and the decomposition of leaves and pistachio stems were investigated.

RESULTS AND DISCUSSION

Table 1 shows the results of determining the percentage of materials obtained from the thermal decomposition of pistachio stem and leaf samples. Higher moisture content in the sample has reduced its heating value. The higher amount of fixed carbon in the sample showed that this sample needs more time to burn. Also, the higher number of volatile substances indicated that this sample ignited more easily and has a higher reactivity in combustion applications. Pistachio leaf has a higher percentage of moisture and fixed carbon and a lower percentage of volatile substances, so it has a lower heating value than pistachio stem. Research has been done in relation to determining the ash content of coal for different organisms such as cotton stalk (Chen et al., 2012) and orange peel (Chen & Chen, 2009). The higher amount of ash indicates the lower calorific value of the target sample. As a result, the higher ash content of leaf powder compared to the stem powder sample indicated its lower calorific value compared to stem (James et al., 2012).

Table 1. The results related to the determination of the percentage of materials obtained from the thermal decomposition of the samples

Sample	Fixed carbon (%)	Ash (%)	Volatile matter (%)	Humidity (%)
Leaf	11.8	8	72.1	8.1
Stem	10.5	5.5	76.1	7.9

The results of Table 2 show that the percentage of oxygen, sulfur and nitrogen is higher in the leaf sample and hydrogen and carbon in the stem sample. Considering the fact that fuel energy is produced from the combination of two elements carbon and hydrogen together with oxygen, and the lower the amount of oxygen and the higher the amount of carbon and hydrogen, it indicates that the amount of biomass energy is higher, Therefore, the energy in pistachio stem was more than pistachio leaf. Table 2 shows the results of elemental analysis for both samples.

Table 2. The results related to determining the percentage of carbon, nitrogen, oxygen, hydrogen and sulfur using the CHNOS device

Sample	%N	%C	%H	%O	%S
Leaf	1.55	42.07	5.49	48.33	0.37
Stem	0.53	46.51	6.11	44.58	0.16

The results of thermal analysis are given in Table 1 and elemental analysis in Table 2. According to the percentage of each component of the samples, high and low heating values were determined for both leaf and pistachio stem samples. Accordingly, relations 1, 2 and 3 were used to determine HHV and LHV. The results of determining these two parameters for each of the samples are reported in the table below.

Table 3. The results of calculating the calorific value using formulas 1 and 2 for each of the pistachio stem and leaf samples.

Sample	Formula 1 HHV	Formula 2 HHV	Formula 1 LHV	Formula 2LHV
Leaf	16.13	15.35	14.93	14.15
Stem	18.79	15.53	17.45	14.19

The results of Table 3 show that each of the high and low calorific values for the stem sample is higher than the leaf sample. This result indicates that the energy released from the stem due to complete reaction with oxygen is more than the leaf.

In this research, the structural composition of the samples (percentage of cellulose, hemicellulose and lignin) was determined using the instructions and relationships mentioned in 3 to 6 in materials and methods. These values can be seen in Table 4. The results of Table 4 show that the amount of cellulose in stem and the amount of lignin and hemicellulose in leaves is higher. The higher amount of cellulose in the stem sample is related to its greater strength compared to the leaf.

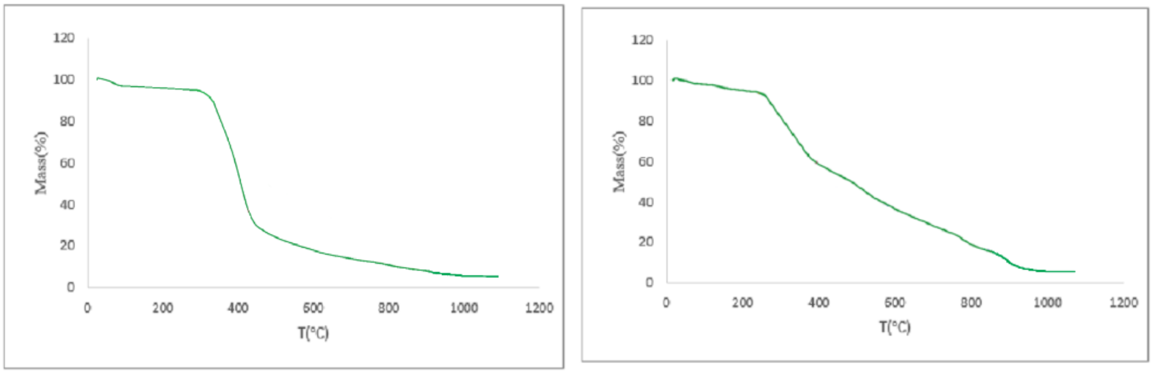
Table 4. The percentage of cellulose, hemicellulose and lignin of the samples

Sample	Lignin (%)	Hemicellulose (%)	Cellulose (%)
Stem	15	16	48
Leaf	32	19	35

Table 5 shows the comparison of the enthalpy of combustion obtained from the experimental method and using the formula, which shows that the method based on the calculation of energy estimation of the samples is in good agreement with the values obtained from calorimetry. In general, the values obtained were in agreement with the values reported by Polidri et al (2023) which were performed on the skin lesions of citrus fruits, aromatic plants, and poultry feathers.

Table 5. Comparison of combustion enthalpy obtained from the experimental method and using formula 7

Sample	Experimental (Calorimetric Bomb)	Using formula 7
Leaf	17.82	18.25
Stem	15.76	15.25



a b

Figure 1. Thermal weighing of pistachio stem (a) and pistachio leaf (b)

The thermogravimetric graphs (Fig. 1) obtained from the TGA tests show the curves of mass change with respect to temperature for stems (a) and leaves (b). This TGA chart shows the amount of mass loss for each stage of mass change written as a percentage. The horizontal axis always shows the temperature in degrees Celsius and the vertical axis shows the mass change. The starting and ending temperatures of each thermal event in the TGA curves depend on the conditions of the experiment. One of the most important factors affecting these temperatures is the heating rate, the characteristics of the sample, and the gas flow rate. As the heating speed increases, because the thermal decomposition is delayed, these temperatures are transferred to higher temperatures. As shown in diagram 1.a (according to the data recorded during the TG test, the thermal decomposition of pistachio stem starts from the very beginning at a temperature of about 30°C and continues with a slight slope up to a temperature of 110°C. This low mass loss is related to the evaporation of moisture in the sample. From 111 to 260°C, mass stability was observed in the sample, and mass loss occurred again in the sample. The main thermal decomposition of the stem powder sample occurred from a temperature of 260 to a temperature of about 970°C and at a high rate. This significant mass loss is related to the removal of volatile substances in the sample. From this temperature onwards, the mass loss rate of the sample became much lower and continued with a gentle slope until the end of the test (up to 1100°C) until the sample reached mass stability.

Fig. 1.b shows the thermal measurement of the pistachio leaf, which begins at 30°C and continues up to 150°C with a gentle slope, which is related to the evaporation of moisture in the sample. In the temperature range of 151 to 290°C, approximate mass stability was observed in the sample. Then, from the temperature of 290 to 980, a rapid mass loss was observed in the sample, which was related to the removal of some of the volatile substances of the sample. From the temperature of 980°C onwards, the mass loss rate of the sample decreased slightly and continued at a constant rate until the end of the test.

CONCLUSIONS

- Based on the research done the following conclusions are made:
- The volatile matter in in stem is higher in the stems (76.1%) while the ash content of the leaves was higher (8.0%).
- The higher percentage of C and H and lower amount of O should contribute to higher heating value for stems.
- The results related to the percentage of carbon, nitrogen, oxygen, hydrogen and sulfur obtained using the CHNOS device showed that the thermal energy of pistachio stem was higher than that of pistachio leaves.

- The results of determining the structural components of the sample indicated that the amount of cellulose in stem and the amount of lignin and hemicellulose in leaves were higher.
- The values of enthalpies of combustion obtained by bomb calorimeter and calculated by theoretical formula were close to each other.
- In the absence of oxygen, the degradation of stem take place faster than the leaves residues.

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