Thermogravimetric Evaluation for the Pyrolysis Process of Pellets Produced from Quinoa and Amaranth Harvest Residues

Abstract

In this study, the combustion properties of pellets produced from quinoa (C3 plant) and amaranth (C4 plant) harvest residues were evaluated by Thermogravimetric Analysis (TGA) and Differential Thermogravimetry (DTG) methods. Pelletizing was carried out at 25% moisture content and at a material temperature of 70 °C. 7.5% molasses was used as the adhesive. The pellets were heated from 25 °C to 1000 °C in a thermal analyzer at a tracking rate of 10 °C min⁻¹ and in N₂ gas environment. The mass loss and mass loss rate occurring in this temperature range were recorded simultaneously and expressed in thermograms. Combustion stages are observed as a peak in the DTG curve and these peaks represent the mass losses in the combustion stages. According to the analysis results, the highest mass loss rate in the evaporation zone of water in the quinoa plant was 2.12% at 96.65 °C, and in the amaranth plant at 2.34% at 101.7 °C. However, in the next step, the mass loss rate decreased in both pellets. At this stage of the analysis, the water in the pellets completely evaporated and the mass loss was 12.43% in quinoa and 13.38% in amaranth, according to the initial mass. With the increase of volatile matter output, the mass loss rate increased again, and the highest mass loss rates were realized as 6.42% and 4.96%, respectively, at 320 °C for quinoa and 315 °C for amaranth. The rate-determining stage in the combustion kinetics of coal and biomass is the semicoke combustion stage. At this stage, the lowest mass loss (0.89%) occurred in both pellet samples. TGA and DTG results showed that there were no significant differences between the combustion stages of quinoa and amaranth pellets, and their combustion behaviors were generally close to each other.

Key words: Biomass, Biofuel, Agricultural residues, Thermogravimetry, Differential Thermogravimetry.

1. INTRODUCTION

Fossil resources, known as "conventional", have met most of our energy in the process up to the present. However, since fossil resources cannot be found in every country, their access and transportation require high costs, their reserves are decreasing day by day and they cause great harm to the environment, studies on energy production from renewable sources, which are alternatives to these fuels, have become the focus of attention of researchers. Therefore, it would not be wrong to say that the use of renewable energy will increase in the near future (Çıtak and Kılınç Pala, 2016). In this context, one of the solutions to reduce the release of pollutants harmful to the environment and human health in recent years is the production of bioenergy from biomass (Küsek et al., 2015). It positions biomass as an interesting alternative source to fossil fuels, due to the renewable character of bioenergy as a resource, its wide distribution in the world, and its near-neutrality of carbon dioxide emissions, (Saxena et al., 2009; Shen et al., 2011). The sources that can be within reach to obtain energy from biomass are very diverse by their nature. They can generally be found at sea, on land, or both. These resources are wood residues, oilseed crops, carbohydrate crops, fiber crops such as flax, kenaf, hemp, sorghum, branches, stems,
straw, roots, bark, etc. plant residues, animal wastes, and urban and industrial wastes (Karaosmanoğlu, 2006; Kuş et al., 2016).

It is possible to obtain bioenergy from biomass sources in two ways, conventional (classical) and modern (technical) methods. The classic method can be expressed as the direct use of agricultural residues and wastes. The use of forest products and dried dung produced from plant and animal wastes as fuel can be given as an example. In the modern method, the energy forms of biomass can be grouped as solid (wood, pellet, etc.), liquid (ethanol, biodiesel, etc.), and gas (biogas, hydrogen, etc.). The conversion of biomass to these energy forms and various energy sources is realized by means of thermal, biological, physical etc. techniques (Üçgül and Akgül, 2010).

The thermal technique is one of the most widely used methods today. The first method that comes to mind in the thermal decomposition of biomass is pyrolysis. Pyrolysis is the decomposition by means of the heat of biomass material in the absence of oxygen. Pyrolysis has been used to produce products such as liquid biofuels (Pütün et al., 2005), syngas (Kaewluan and Pipatmanomai, 2011), chemicals (Orecchini and Boci, 2007), and biochar (Prins et al., 2006) for direct energy production from biomass (Kazagic and Smajevic, 2007; Soria-Verdugo et al., 2015). The variety and properties of new products obtained by the pyrolysis process depend on the process parameters and biomass type. In other words, the products obtained as a result of pyrolysis are not only by operating parameters such as temperature, heating rate, and ambient gas, but also they are affected by physical properties such as particle size and porosity of the material used, and chemical properties such as moisture content, organic and inorganic content, carbon content, elemental composition. In addition to these parameters, another important issue to be considered in the pyrolysis process is the kinetic mechanism determined by the thermogravimetric analysis method. With this method, the components of biomass can be examined, the combustion behavior of the material can be modeled depending on the temperature increase during pyrolysis, and the actual mass losses can be expressed with thermograms (Yaman, 2004; Collard and Blin, 2014).

Every country in the world has resources that can be used in alternative energy production depending on its own ecological conditions. Turkey is an extremely convenient country in terms of biomass production (sunbathing, area availability, water resources, climatic conditions, etc.), considering its ecological conditions (Topal and Arslan, 2008). Therefore, it has a huge potential for residues left over from agricultural products after harvest. These product residues, which pose a problem, can be mixed with the soil, burned, or idle at the harvest site by conventional methods after harvest. If agricultural wastes and residues are used as a biomass source with modern methods, they can both be disposed of more safely and economically benefit from the energy to be obtained from these wastes (Acar, 2015). However, the rate of using the mentioned biomass wastes in energy production is very low (Başçetinçelik and Öztürk, 2005).

Within the scope of this study, harvest residues of two different products such as quinoa and amaranth were taken into account. Amaranth, which is a group of annual plants in the family Amaranthaceae, is classified as a cereal, vegetable, ornamental plant, forage plant, or weed (Ergun et al., 2014). Since Amaranthus sp. species have a C4 carbon sequestration mechanism, organic matter production per unit area is quite high (Durak, 2015). Quinoa (Chenopodium quinoa Willd.), a plant of the Andes Mountains, is an annual herbaceous C3 plant, propagated by seed (therophyte), used in human and animal nutrition. It has a drought-resistant, developed, and branched pile root structure. The height of the plant can vary between 40-150 cm (Bhargava et al., 2007; Tan and Yöndem, 2013).

The stalk parts of quinoa and amaranth are left in the field, as in many other field crops, after these products are harvested as grains. These residues are generally either mixed with the soil and evaluated
as organic matter, or they are destroyed by burning. Another alternative is to burn these stalks directly and use them as an energy source. The special purpose of this study is to evaluate the crop income from quinoa and amaranth cultivation, as well as the possibilities of using the stalks, which do not have any usage area, as biomass fuel, both to provide economic return and to be used as an energy source. In addition, by determining the thermal properties of the pellets produced from these residues, it is to obtain a renewable and efficient energy source.

2. MATERIALS AND METHODS

In the study, amaranth (Amaranthus caudatus) and quinoa (Chenopodium quinoa) harvest residues were used as pellet primary materials. Red pine shavings and powdered pomace were used to prepare different mixtures, and sugar beet molasses was used as an adhesive material. Quinoa and amaranth harvest residues were obtained from plant stalks grown in Iğdır University Agricultural Application and Research Center. After harvest, quinoa (C3 plant) and amaranth (C4 plant) harvest residues were left to dry in the laboratory environment for 10 days. It was then ground with a hammer mill followed by a flour mill (Grover and Mishra, 1996) to obtain the appropriate particle size. Red pine shavings (PS) was obtained from a beehive fabricating enterprise and powdered pomace (PP) was obtained from the olive processing factory, of the other materials. No drying process was applied to the powder pomace while the red pine shavings was dried in outdoor conditions. Ground quinoa and amaranth materials were mixed with red pine shavings and powdered pomace, and 6 different ingredients were obtained for pelleting (Table 1).

Table 1. Contents of pellet samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Proportional Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>Chenopodium Quinoa Harvest Residues (100%)</td>
</tr>
<tr>
<td>Q2</td>
<td>Chenopodium Quinoa Harvest Residues (50%) + Red Pine Shavings (50%)</td>
</tr>
<tr>
<td>Q3</td>
<td>Chenopodium Quinoa Harvest Residues (50%) + Powdered Pomace (50%)</td>
</tr>
<tr>
<td>A1</td>
<td>Amaranthus Caudatus Harvest Residues (100%)</td>
</tr>
<tr>
<td>A2</td>
<td>Amaranthus Caudatus Harvest Residues (50%) + Red Pine Shavings (50%)</td>
</tr>
<tr>
<td>A3</td>
<td>Amaranthus Caudatus Harvest Residues (50%) + Powdered Pomace (50%)</td>
</tr>
</tbody>
</table>

Moisture, ash, and volatile matter contents of the materials were determined before the mixtures were prepared. Approximately 25 grams of each material In order to determine moisture content was taken and kept in a drying oven at 105 °C for 3 hours and moisture contents were calculated on a wet basis. Accordingly, the moisture contents of quinoa (Q0), amaranth (A0), red pine shavings (PS), and powdered pomace (PP) were determined as 9.6%, 9.6%, 12.4%, and 11.9%, respectively. Ash contents for Q0, A0, PS and PP were determined as 6.4%, 10.8%, 2.0%, and 3.3%, respectively, and volatile matter contents were determined as 74%, 66%, 75%, and 65%, respectively. The material was heated up to 70 °C and the moisture content was increased to 25% In order to obtain shapely pellets (Figure 1) (Atay et al., 2016). In the pressing process, a circular row perforated type pelleting machine with a power of 3 kW, a capacity of 50-60 kg h⁻¹, and a speed of 96 min⁻¹ were used. The pellet mold inlet and outlet hole diameters of the pelleting machine were 11 mm and 6.8 mm, and the length was 19 mm, respectively.

Thermogravimetric measurements were performed with a Thermogravimetric Analyzer SDT Q600 of TA company with a weighing accuracy of ±0.01%. Thermal analyzes were carried out at a temperature range of 25 to 1000 °C, at a heating rate of 10 °C min⁻¹, and in an N₂ gas environment (TS
The samples were prepared to weigh 20-25 mg by grinding large particles in a mortar and sieving. The thermal degradation behaviors during pyrolysis were investigated from the data obtained by heating the prepared samples (20 - 25 mg) with alumina crucibles up to 1000 °C in TGA. TGA is a technique in which the loss of mass that occurs in a sample heated in a controlled environment is measured against time or temperature. The mass loss of the sample is recorded with an electronic precision balance depending on the furnace temperature increasing linearly and adjusted by the intensity of the heat flow in the TG analyzer. The crucible temperature, which shows the actual temperature of the solid, is measured simultaneously with the help of thermocouples (Branca and Blasi, 2004; Fang et al., 2006; Shen et al., 2011). DTG, on the other hand, is the first derivative of TGA and shows the mass loss rate in the sample per unit time. The mass loss rate (DTG curve) is calculated by differentiating the TGA curve with temperature without any smoothing correction on the data (Liu et al., 2002; Shen et al., 2011). The mass loss and the mass loss rate due to the temperature increase were recorded simultaneously by the TGA apparatus and reflected on the thermograms (thermal decomposition graph). The initial, maximum, and final decomposition temperatures and mass loss rates of the samples, with the help of these thermograms, were determined and the combustion behavior of the pellets were examined.

![Figure 1. Pellets obtained as a result of pressing](image)

3. RESULTS AND DISCUSSION

Sungur et al. (2018) stated that the combustion of pellet fuel, as in all solid fuels, takes place in four stages (Figure 2). The first stage is drying by evaporation of water, the second stage is separation of volatile components by gasification (pyrolysis), the third stage is the combustion of volatile (gas) components, and the fourth stage is the combustion of coke (fixed carbon). However, Berkowitz (1985) and Açma (1999) reported three stages for combustion in biomass. These stages are the output of volatile matter as a result of the heating of the biomass, the combustion of the volatile matter in the gas phase and the combustion of carbon-rich semi-coke. First of all, the volatile matter is released, with the temperature continues to rise and the outflow of moisture. The organic matters in the fuel begin to
decompose and the volatile matter that comes out burns by combining with the oxygen in the environment. The porous solid portion enriched in carbon, depleted in oxygen and hydrogen, and containing most of the mineral matter is called semi-coke. When the volatile matter exit and combustion are completed, the oxygen in the surroundings reaches the semi-coke surface and makes a transition into the particle (Berkowitz, 1985). The output and combustion of volatile matter are very fast, while the combustion rate of semi-coke is quite slow. That's why, the rate-determining step in the combustion kinetics of coal and biomass is the semi-coke combustion step (Williams et al., 2000). Even though Sungur et al. (2018) stated four stages in the combustion of biomass, Berkowitz (1985) reported the first two of these stages as the first stage.

![Diagram](image)

**Figure 2. The combustion stages of the pellet (Sungur ve ark., 2018)**

The thermal decomposition curves (thermograms) of the mass loss (TGA) and differential mass loss (DTG) obtained during the pyrolysis of pellets produced from quinoa and amaranth harvest residues are shown in Figure 3. The TGA and DTG curves of each sample are given as an integrated figure. In thermograms, the green (descending) curve (TGA) indicates the decrease in sample mass in % due to the increase in temperature, while the blue (wavy) curve (DTG) expresses the proportional mass loss (%) per unit time (one minute) due to the temperature increase. The mass loss due to moisture output is seen in the TGA curves, while the DTG curves show the change in the mass loss ratio due to the moisture output depending on the temperature. It is understood that in addition to three peaks, a fourth peak appeared in the DTG curves. Although the fourth peak is not taken into account, it suggests that it may have originated from molasses used as the adhesive material. However, taking into account the combustion stages of the biomass according to Berkowitz (1985), evaluations were performed over three peaks. The first peak represents the mass loss due to the moisture output depending on the temperature increase, the second peak refers to the mass loss due to the output of volatile matter by the decomposition of cellulose and hemicellulose, and the third peak represents the mass loss occurring depending on the combustion of semi-coke.
Figure 3. TGA and DTG curves for quinoa and amaranth pellets
Caballero et al. (1997) reported that at least two different processes took place and a long tail was formed in the DTG curves formed by the pyrolysis of agricultural residues. Shafizadeh and McGinnis (1971), Williams and Besler (1992), and Maschio et al. (1992) hypothesize that these peaks correspond to the thermal decomposition of lignin and cellulose, and hemicellulose, respectively. However, Caballero et al. (1997) reported that the next peak in the TGA-DTG diagrams is an extension of the previous one, and that lignin begins to decompose at low temperatures similar to hemicellulose decomposition, and the thermal decomposition temperature is much higher, and so this peak can be considered as the last stage of lignin.

According to the thermograms in Figure 3, the mass loss (DTG curve) of the pellet samples together with the increase in temperature is seen. The mass loss in the first peak region of the DTG curve occurs with the evaporation of the moisture in the pellet. The mass loss in the first peak region occurred in the temperature range of 50 – 150 °C for all pellets, by heating the biomass to 1000 °C. The highest mass losses in this range arose at a temperature close to the boiling temperature of water in the pyrolysis process for each pellet. The highest mass loss rates occurring for the Q1, Q2, and Q3 pellets in the first peak region were obtained at pyrolysis temperatures of 97, 104, and 99 °C as 2.12%, 1.87%, and 2.41%, respectively. Mass loss rates for A1, A2, and A3 pellets at the same stage were at 2.34%, 1.62%, and 1.59%, respectively, at 102, 101, and 99 °C pyrolysis temperatures. Although the temperature increase continued with the completion of the first stage, the mass loss rate decreased. This is because the evaporation process of the water in the pellet has been finished. Although this change in mass loss rates was lower in quinoa pellets, it was between 0.15 - 0.25% in the temperature range of 151 - 161 °C.

The greatest mass losses in the pyrolysis of quinoa and amaranth pellets occurred in the second peak region of the thermograms. This region is called the active pyrolysis region. The mass loss rate value tended to increase again as the volatile matter release started in the active pyrolysis zone. With the effect of the temperature exceeding 300 °C with this stage, the highest mass losses occurred in all pellets for both this stage and the 3 stages. The highest mass loss rates occurring at this stage for the Q1, Q2, and Q3 pellets, were at pyrolysis temperatures of 320, 327, and 322 °C as 6.42%, 7.31%, and 6.12%, respectively; for A1, A2, and A3 pellets, were at 4.96%, 6.41%, and 5.47%, respectively, at 315, 325 and 322 °C temperatures. There was a second-time decline in the mass loss rate towards the completion of the stage. These declines were between 0.75%-0.88% for quinoa pellets and 0.72%-0.94% for amaranth pellets in the temperature range of 393-417 °C. When the mass loss rates in the active pyrolysis range are compared with the inception mass, were 47.7%, 51.7%, and 46.9% for the Q1, Q2, and Q3 pellets, respectively; it was 43.6%, 50.4%, and 48.6% in A1, A2, and A3 pellets. Özsin (2018) reported that more than 50% of the material mass is lost in the active pyrolysis range. Similarly, losses close to or exceeding 50% were observed in the current study.

After this stage, the decomposition stage of the semi-coke is the third stage of the reaction, known as the passive pyrolysis range began. The combustion stage of semi-coke is the stage in which the fixed carbon is burned, and is the final stage of combustion. At this stage, the mass loss rate occurring due to the increase in temperature is generally at the lowest level. The mass loss rate increased again with the temperature exceeding 400 °C in the third stage of pyrolysis, and the analysis was completed at 1000 °C, which is the final temperature, by down as the temperature passed the peak. The highest mass loss rates realized in the final stage for the Q1, Q2, and Q3 pellets, were 0.89%, 0.81% and 0.93%, respectively at pyrolysis temperatures of 417, 427 and 429 °C; in A1, A2, and A3 pellets, they were 0.89%, 0.90% and 1.03%, respectively, at 426, 428 and 428 °C pyrolysis temperatures.
In the pyrolysis process, the mass losses caused peaks in the DTG curves with the increase in temperature in the experiments carried out at constant heating rate, and these curves became stable in the passive pyrolysis region. As a matter of fact, Özsin (2018) reported that the temperature changes linearly with time in the experiments performed with a constant heating rate in the thermal analysis method. It is generally possible to see this linearity after 700 °C, when the thermograms are examined.

Although there are differences in decomposition temperatures and mass loss rates, they were generally close to each other, when the stages in the pyrolysis of the pellets obtained from both naked quinoa and amaranth residues and a mixture of red pine shavings and powder pomace were evaluated together. It can be said that the addition of red pine and powder pomace increases the maximum decomposition temperature and mass loss rate (except for Q1) (Table 2). However, the total mass losses in amaranth pellets were generally higher. Maximum decomposition temperature and maximum mass loss rates were obtained in red pine shavings mixed pellets (Q2 and A2). It is assumed that the high loss rate in these pellets is due to the high volatile matter content of the red pine shavings. The lowest maximum mass loss rate was determined in A3, while the pellet with the lowest maximum decomposition temperature was A1. However, the lowest mass loss value belongs to Q1 pellet, while the highest mass loss value belongs to A1 pellet.

**Table 2. Maximum decomposition temperatures and total mass losses of pellets**

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Maximum decomposition temperature (°C)</th>
<th>Maximum mass loss rate (% min⁻¹)</th>
<th>Total mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>320.2</td>
<td>6.42</td>
<td>72.70</td>
</tr>
<tr>
<td>Q2</td>
<td>327.5</td>
<td>7.31</td>
<td>73.12</td>
</tr>
<tr>
<td>Q3</td>
<td>321.9</td>
<td>6.12</td>
<td>72.01</td>
</tr>
<tr>
<td>A1</td>
<td>315.2</td>
<td>4.96</td>
<td>74.78</td>
</tr>
<tr>
<td>A2</td>
<td>324.9</td>
<td>6.41</td>
<td>73.27</td>
</tr>
<tr>
<td>A3</td>
<td>322.2</td>
<td>5.47</td>
<td>73.70</td>
</tr>
</tbody>
</table>

It is understood that the temperature ranges in which the three peak regions occur in the pyrolysis of bio-pellets produced from quinoa and amaranth harvest residues and the mass loss rates due to these temperatures reflect the lignocellulosic structure of the biomass. Indeed, Caballero et al. (1997) and Paniagua Bermejo et al. (2020) stated that lignocellulosic materials consist of three main fractions, hemicellulose, cellulose, and lignin, and that content of these fractions and the interactions between them are so important and that there is a harmonious relationship between the peaks in the TGA-DTG diagrams and the decomposition of hemicellulose, cellulose, and lignin.

4. CONCLUSION

Two different types of biomass (quinoa and amaranth) were analysed experimentally in a TGA at a 10 °Cmin⁻¹ heating rate. The mass losses of quinoa and amaranth pellets depending on the temperature and the mass loss rates per unit time were determined. For quinoa and amaranth pellets, the highest mass losses rates were in the active pyrolysis region, while the lowest losses were occurred in the passive range. Three peaks were formed in the thermograms and a decomposition similar to the previous studies on organic materials occurred. Although the temperature ranges and mass loss rates of the pyrolysis stages of quinoa and amaranth pellets were different, they were close to each other.
5. ACKNOWLEDGEMENTS

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6. AUTHOR CONTRIBUTIONS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. CONFLICT OF INTEREST

There are no conflicts of interest between the authors.

REFERENCES


