Properties of bio-pellets obtained from walnut and peanut shells

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Abstract: Energy is considered a measure of development in today's world. In recent years, the increasing global population has led to a growing demand for energy. Due to the limited availability of fossil fuels and the environmental harm they cause, there has been a shift towards renewable energy sources worldwide. Among these renewable energy sources, biomass technology is clean, eco-friendly, and highly energy-efficient. Its implementation not only contributes to energy production but also plays a significant role in rural development. Within the realm of biomass, the production of bio-pellets is essential for the sustainable utilization of healthy, eco-friendly, and organic waste materials for energy purposes. The pelletization process offers several advantages, including an increase in the volumetric heat value of the material, reduced transportation and storage costs, improved combustion characteristics, and a decrease in particle emissions into the atmosphere. This study focuses on the production of bio-pellets by mixing walnut shell (WS) and peanut shell (PS) materials in five different ratios (100% WS, 50% WS+50% PS, 75% WS+25% PS, 25% WS+75% PS, 100% PS). The moisture content, ash content, volatile matter content, fixed carbon content, and drop resistance of the obtained pellets have been determined.

Keywords: walnut shell, peanut shell, bio-pellet, energy

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1 Introduction

In today's world, with the increasing development of technology and rising living standards, the demand for energy has also grown. Energy production and consumption have become indicators of development[1]. Energy is derived from two sources: fossil and renewable energy[2-4]. Fossil energy sources consist of non-renewable and limited resources such as coal, oil, and natural gas. The need for energy shifted to coal-based sources after the Industrial Revolution and later to oil and natural gas with the rapid advancement of technology. However, confidence in fossil resources was shaken by the oil crisis in 1973, leading developed countries to seek new energy sources[5]. Additionally, the rapid depletion of fossil energy sources not only contributes to economic crises but also exacerbates ecological issues due to increased greenhouse gas emissions[6]. Therefore, there is a need for clean, reliable, and environmentally friendly renewable energy sources, and investments are being made in this regard.

Renewable energy sources include hydro, solar, wind, geothermal, and biomass sources[7,8]. Among renewable energy sources, biomass holds a significant place due to its environmentally friendly nature, waste management capabilities, and energy sustainability. Biomass is converted into energy by being utilized as biofuel. From biomass, various liquid, solid, or gaseous biofuels are obtained through physical processes (size reduction, crushing and grinding, drying, filtration, extraction, and briquetting) and conversion processes (biochemical and thermochemical processes)[9].

In the production of biofuels in solid form, one of the most effective methods is pelletization. Pelletization involves compressing organic materials into pellets with a diameter of 6-12 mm under the pressure of flat and circular-shaped presses[10]. Knowing the physical, chemical, thermal, and flue gas emission properties of pellets is crucial, especially for transportation, storage, handling processes, and combustion systems. Pellet physical properties include diameter, length, mass, density, hardness, durability, and porosity[11].

The pellet density affects transportation costs, transportation, and storage efficiency. More densely produced pellets reduce transportation costs and enhance transportation and storage efficiency[12,13]. Pellet durability is essential for ensuring that the pellets remain intact until they reach the end user. High-durability pellets offer advantages in transportation, handling, and storage[12]. Pellet durability is categorized as high quality when it exceeds 80%, medium quality when it falls between 70% and 80%, and low quality when it is below 70%[13,14].

In pelletization, the optimal moisture content is crucial because it strengthens the inter-particle bonds. Materials with high moisture content tend to pass easily through compression holes, resulting in low-quality pellets. Conversely, materials with low moisture content require high pressure during pelletization, leading to material jamming in the die holes, resulting in time and material loss[12]. Particle size in pelletization plays a significant role in pellet quality. Reducing particle size increases the surface area, pore size, and the number of contact points for particle adhesion during compression. For high-quality pellets, the particle size should be between 6 and 8 mm, with a significant portion (10%-20%) comprising very small particles[15]. Small particles fill the gaps between larger particles, creating dense and durable pellets. To produce high-quality pellets, organic materials should be ground in sieves with a diameter range of 3.2-4.0 mm[16].

Pellets produced from the pelletization of organic materials have several advantages compared to fossil fuels. They are more cost-effective, renewable, and compliant with the Kyoto Protocol in terms of CO emissions. They provide the cleanest combustion

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system among solid fuel systems, are easy to transport and handle, consist of readily available materials, and have long-lasting burning characteristics[17].

In this study, bio-pellets were produced by mixing WS and PS materials in five different ratios (100% WS, 50% WS+50% PS, 75% WS+25% PS, 25% WS+75% PS, and 100% PS). After bio-pellet production, the physical and mechanical properties were determined, including durability, breaking resistance, compression resistance, moisture absorption resistance, dimensions, length, weight, and density. The chemical characteristics of the bio-pellets, including nitrogen, carbon, fixed carbon, moisture, ash content, water absorption resistance, and volatile matter content, were determined. The thermal and thermogravimetric values of the obtained bio-pellets were determined to demonstrate the suitability of organic materials with high energy efficiency for energy production. The use of organic materials as bio-pellets demonstrates their potential for conversion into energy and can also contribute to addressing environmental issues.

2 Materials and methods

Walnut shells were obtained from the Kahramanmaraş Hard-Skinned Fruits Application and Research Center (SEKAMER), and peanut shells were acquired from peanut processors in Osmaniye. The materials used in pellet production were initially naturally dried under the sun and then ground using an industrial grinder (CMY Machine, Corum, Turkey) (Figure 1). The materials were left in the sun for three weeks. After grinding, the particle size was 2 mm and the final moisture content was 8.67% for WS and 10.18% for PS.

Figure 1 The ground materials (walnut and peanut shells)

The ground materials were pelletized using a laboratory-type pelletizing machine (CMY Machine, Corum, Turkey) with a motor power of 6 kW and a processing capacity of 70-90 kg/h. This machine had a circular, sequentially perforated flat die for pellet production (Figure 2).

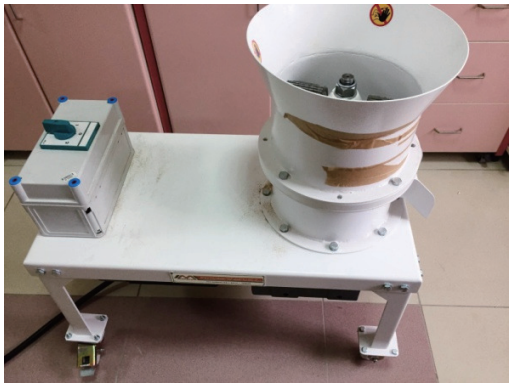

Figure 2 The pelletizing machine

In this study, five different mixtures of materials were created for pellet production (Figure 3), and the dry mass-based mixing ratios (%) and the names of these mixtures are presented in Table 1.

Figure 3 Obtained pellets

Table 1 Mixing ratios (%) of the materials used for pellet production on a dry mass basis and the nomenclature of the mixtures

Material	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5
WS/%	100	0	50	75	25
PS/%	0	100	50	25	75

The pelletization process involved taking each mixture type and creating a homogenous mixture with 5% liquid molasses. This mixture was poured into the pelletizing machine using a container. The machine's die holes gradually narrowed, resulting in a continuous pellet output. This process was repeated for each mixture type. Before switching from one mixture type to another, the pelletizing machine and its die holes were cleaned.

To determine the pellet bulk density, 40 randomly selected pellets were taken from each mixture type, and the diameter, length, and weight values of each pellet were measured. The pellet diameters and lengths were measured with a digital caliper with a precision of 0.01 mm, and their weights were determined through weighing on a precision scale. The pellet bulk density was calculated in kg/m^3.

The analysis of the pellets included:

1) Ash content analysis, following TS ISO 1171 standards.

2) Moisture content analysis, based on ASTMD 3173 standards.

3) Volatile matter content analysis, following TS ISO 562 standards.

4) Fixed carbon content analysis, according to ASTMD 3172 standards.

5) Total carbon and nitrogen content analyses, conducted using the AOAC (1990)[18].

6) To determine the pellet breakage resistance, four pellets were randomly selected from each of the five mixtures. The weight of these pellets was measured and recorded, and they were dropped from a height of approximately 1.80 m onto a hard surface four times. Subsequently, they were sieved through a sieve with a 3.15 mm hole diameter. Weight measurement was performed again. The breakage resistance was calculated as a percentage by comparing the post-test pellet weight to the pre-test pellet weight.

The higher heating value (HHV) was determined using Equation (1).

$$HHV = 0.312FC + 0.154VC \quad (1)$$

where, HHV is higher heating value, MJ/kg; FC is fixed carbon content, %; VC is volatile matter content, %.

For vertical compression resistance, three pellets were randomly selected from each mixture. These pellets were individually placed in a compression unit, and a steadily increasing compression force was applied until the pellet fractured. The compression resistance was measured in Newtons (N), and Equation (2) was used for calculation.

$$\sigma x = 2F/\pi \cdot d \cdot l \quad (2)$$

where, σx is vertical compression resistance, N; F is maximum applied fracture force, N; d is pellet diameter, m; l is pellet length, m.

For the moisture absorption resistance test, five pellets were randomly selected from each mixture. These pellets were stored in an oven at approximately 105°C for about 24 hours, and their initial weights (weight before going into the oven) were measured and recorded. Subsequently, they were conditioned in a climate chamber at 27°C with 90% humidity, and their final weights were measured and recorded. The moisture absorption resistance was calculated as a percentage using Equation (3).

$$P_a = \left(m_f - m_i\right) / (m_i) \times 100\% \quad (3)$$

where, P_a is moisture absorption resistance, %; m_f is final weights of the pellets, g; m_i is initial weights of the pellets, g.

To determine the combustion characteristics of the pellets, thermogravimetric analyses were conducted under a nitrogen atmosphere. Powdered samples of grounded pellets were placed in ceramic crucibles, and analyses [differential thermogravimetric analysis (DTGA) and thermogravimetric analysis (TGA)] were performed with a heating rate of 10°C/min from 30°C to 920°C. Instantaneous data were recorded by a computer during the analysis. After the analysis, the results were presented graphically as differential thermogravimetric analysis (DTGA) and thermogravimetric analysis (TGA) curves. The mass loss rates, initial degradation temperature, maximum degradation temperature, and final degradation temperature of the pellets were determined using the TGA and DTGA curves.

All data in the research were measured in triplicate, and average values were calculated. The obtained values were transferred to figures and tables and interpreted.

3 Results and discussion

3.1 Physical and chemical analysis of raw materials

The moisture, ash, volatile matter, fixed carbon, and C, N, S values of WS and PS raw materials were determined. In the WS raw material, the moisture content after staying under the sun was 8.67%, ash content was 1.66%, volatile matter was 83.02%, and fixed carbon was 6.63%. In the PS raw material, the moisture content was 10.18%, ash content was 7.19%, volatile matter was 77.74%, and fixed carbon was 4.88%. The higher heating values were 14.80 MJ/kg for WS and 13.44 MJ/kg for PS (Table 2).

3.2 Pellet analyses

Physical, thermal, durability, abrasion resistance, moisture absorption rate, bulk density, vertical compression resistance, diameter, length, weight, and particle density analyses were conducted on the pellets. The results of these analyses are presented below.

3.2.1 Pellet physical and thermal properties

The moisture content of the pellets ranged from 4.06% to 6.52%. As the peanut ratio increased, the moisture content also increased. These values are lower than the value specified in the EN14774-1 standard (≤10%), indicating that the pellets meet the standard moisture requirements. Ash content ranged from 3.30% to 7.93%, with the lowest in WS and the highest in PS pellets. Ash content increased with increasing PS ratio. The ash content is significantly lower compared to coal, resulting in minimal ash residue after combustion. The volatile matter content was the lowest in PS pellets and the highest in WS pellets. Increasing the WS ratio led to an increase in volatile matter content. Fixed carbon values ranged from 7.74% to 12.60%, and increasing the WS ratio led to higher fixed carbon values. The higher heating values ranged from 14.35 to 16.21 MJ/kg, with an increase in thermal values as the WS ratio increased (Table 3).

Table 2 Raw material physical and thermal properties

Analysis	WS	PS
Short analysis/%		
Moisture	8.67	10.18
Ash	1.66	7.19
Volatile matter	83.02	77.74
Fixed carbon	6.63	4.88
Elemental analysis/%		
C (Carbon)	50.9	46.9
S (Sulfur)	0.13	0.01
Other analysis		
Higher heating value/MJ·kg^{-1}	14.80	13.44

Table 3 Pellet physical and thermal properties

Analysis	100% WS	75% WS+ 25% PS	50% WS+ 50% PS	25% WS+ 75% PS	100% PS
Short analysis					
Moisture	4.06	4.70	5.20	5.64	6.52
Ash	3.30	4.26	6.35	7.02	7.93
Volatile matter	80.04	79.43	78.82	78.24	77.79
Fixed carbon	12.60	11.58	9.61	9.09	7.74
Other analysis					
Higher heating value/MJ·kg^{-1}	16.21	15.80	15.09	14.83	14.35

3.2.2 Durability and abrasion resistance

The selection of tests related to pellet quality (durability resistance, abrasion resistance, and compressive stress resistance) varies depending on the forces encountered during production and use. Durability resistance or abrasion testing is a parameter used to assess the extent of wear encountered in the pneumatic and mechanical transport of pellets. In this study, durability resistance ranged from 96.15% to 98.49%, and abrasion resistance ranged from 98.96% to 99.94%. As the PS ratio increased among the pellets, an increase in both durability and abrasion resistance was observed (Table 4).

Table 4 Durability and abrasion resistance

Pellets	Durability resistance/%	Abrasion resistance/%
100% WS	96.15	98.96
75% WS+25% PS	96.74	99.39
50% WS+50% PS	97.67	99.58
25% WS+75% PS	98.08	99.90
100% PS	98.49	99.94

3.2.3 Moisture absorption rate

The moisture absorption resistance of the pellets was determined through changes in pellet weight. Exposure to rainy weather or high relative humidity conditions during transportation

or storage can diminish pellet quality[19]. The moisture absorption resistance of pellets is related to determining the equilibrium moisture content of the pellets under specific relative humidity and temperature conditions. Generally, a higher equilibrium moisture content in pellets indicates their hygroscopic nature[20]. Moisture absorption during the storage phase can negatively affect the strength properties of pellets[21,22]. The moisture absorption rates of the pellets ranged from 12.80% to 18.38%. An increase in the PS ratio resulted in higher moisture absorption rates (Table 5).

Table 5 Moisture absorption rate (%)

Pellets	Moisture absorption rate/%
100% WS	12.80
75% WS+25% PS	13.47
50% WS+50% PS	15.54
25% WS+75% PS	17.26
100% PS	18.38

3.2.4 Bulk density

The bulk density of the pellets ranged from 537.64 to 565.96 kg/m^3. An increase in the WS ratio resulted in an increase in bulk density. WS pellets are heavier per unit volume (Table 6).

Table 6 Bulk density

Pellets	Bulk density/kg·m^{-3}
100% WS	565.96
75% WS+25% PS	560.14
50% WS+50% PS	555.80
25% WS+75% PS	549.30
100% PS	537.64

3.2.5 Vertical compression resistance

The compression resistance of pellets is defined as the maximum load a pellet can withstand before breaking without using a compression test[20]. The vertical compression resistance of pellets ranges from 88.16 to 220.60 N. An increase in the PS ratio results in an increase in compression resistance, indicating an increase in the strength against the measured stress force during the vertical compression of the pellets (Table 7).

Table 7 Vertical compression resistance

Pellets	Vertical compression resistance/N
100% WS	88.16
75% WS+25% PS	144.70
50% WS+50% PS	155.50
25% WS+75% PS	180.66
100% PS	220.60

3.2.6 Pellet diameter, length, weight, and particle density

The average pellet diameter, length, weight, and particle densities are provided in Table 8. The pellet diameters range from 6.81 to 6.92 mm, pellet lengths range from 22.26 to 31.16 mm, and pellet weights range from 0.89 to 1.32 g. These pellet diameters fall within the limits specified for wood pellets for heating purposes (6-8 mm) as outlined in the handbook used for the certification of wood pellets for heating purposes by the European Pellet Council (EN16127)[23]. Pellet lengths also fall within the boundaries defined in the EN16127[23] standard for pellet lengths (3.15-40.00 mm). The pellet particle densities range from 1077.19 to 1159.91 kg/m^3, and an increase in the PS ratio results in higher pellet particle densities (Table 8).

Table 8 Pellet diameter, length, weight, and particle density

Pellets	Diameter/mm	Length/mm	Weight/g	Particle density/kg·m^{-3}
100% WS	6.90	22.26	0.89	1077.19
75% WS+25% PS	6.92	27.97	1.18	1124.78
50% WS+50% PS	6.81	29.34	1.22	1133.23
25% WS+75% PS	6.88	31.16	1.32	1142.40
100% PS	6.87	27.51	1.18	1159.91

3.2.7 Thermogravimetric analysis (TGA) applied to pellets

One of the best methods used to determine the combustion characteristics of pellets is thermogravimetric analysis (TGA). Differential thermogravimetric analysis (DTG) is a method used to determine the energy change resulting from a chemical reaction. TGA indicates the decrease in sample mass as a percentage with temperature increase, while DTG indicates the mass loss as a percentage occurring with temperature increase.

Figure 4 presents the TGA decomposition curves for pellets of all mixture types formed at temperatures ranging from 30°C to 1000°C and at a heating rate of 10°C/min. Similarly, Figure 5 shows the DTG decomposition curves for pellets of all mixture types. Table 9 also provides the initial decomposition temperature (T_i), maximum decomposition temperature (T_{max}), and final decomposition temperature (T_f).

When looking at the DTG curves, the maximum mass loss rate related to the combustion time was observed at 356°C in the 100% WS sample. The differences in decomposition temperatures in the samples may be due to variations in reactivity between the components (Figure 4).

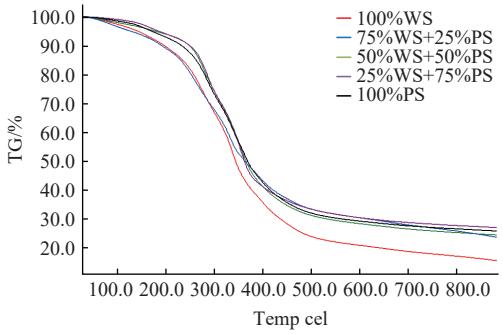

Figure 4 TGA curves of pellets

As the samples are further heated, the temperature range shifts to higher values, and the final decomposition temperatures were observed in the following order: 480°C for 100% WS, 520°C for 100% PS, 537°C for 75% WS+25% PS, 543°C for 25% WS+75% PS, and 547°C for 50% WS+50% PS. In this temperature range, the maximum mass loss rate is observed to be 2.20%/min for the 100% WS sample, while the minimum mass loss rate is 1.19%/min for the 100% PS sample (Figure 5, Table 9).

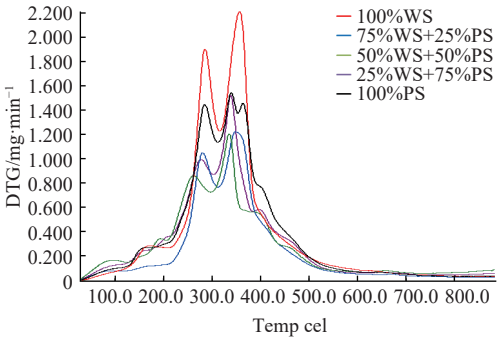

Figure 5 DTG curves of pellets

Table 9 Thermal decomposition temperatures of pellets

Pellets	T_i/℃	T_{max}/℃	T_f/℃	Mass loss rate/%·min^{-1}
100% WS	135	356	480	2.20
75% WS+25% PS	125	339	520	1.53
50% WS+50% PS	135	337	537	1.51
25% WS+75% PS	130	348	543	1.22
100% PS	120	335	547	1.19

4 Conclusions

The results obtained from the analyses can be summarized as follows:

1) In terms of the higher heating value of the raw material, WS was found to be higher than PS material.

2) The higher heating values range from 14.35 to 16.21 MJ/kg, and an increase in WS content results in an increase in heating values.

3) Pellet durability resistance ranges from 96.15 to 98.49, and pellet fracture resistance ranges from 98.96 to 99.94. An increase in PS content leads to increased durability and fracture resistance in pellets.

4) The pellets' moisture absorption rates range from 12.80 to 18.38, with an increase in PS content leading to increased moisture absorption.

5) Pellet bulk densities range from 537.64 to 565.96 kg/m^3, and an increase in WS content results in increased bulk density.

6) Vertical compression resistance in pellets ranges from 88.16 to 220.60 N, and an increase in PS content leads to increased compression resistance.

7) Pellet particle densities range from 1077.19 to 1159.91 kg/m^3, and an increase in PS content results in increased pellet particle densities.

8) When looking at the DTG curves, the maximum mass loss rate due to combustion is observed at 356°C in the case of 100% WS.

In this study, a solution was developed using pellets made from walnut and peanut waste, which are abundantly produced in the region. The findings revealed that the calorific value of WS was higher than that of PS, but PS exhibited greater durability and abrasion resistance compared to WS. Conversely, PS had a higher moisture absorption rate, vertical compression ratio, and particle density than WS. Additionally, the mass loss rate of WS was higher than that of PS. Therefore, the high calorific value alone does not determine the quality of the pellet. Factors such as low moisture content, low mass loss rate during combustion, and low moisture retention capacity are also crucial. Given the differences observed in the properties of the two mixtures, a ratio of 50% WS+50% PS is recommended for optimal pellet quality.

Recommendations for the subject

To reduce energy dependence and make use of local resources, agricultural biomass resources can be converted into pellets to produce alternative energy. Establishing pellet production facilities can provide employment opportunities in rural areas. Entrepreneurs involved in pellet production can be supported and incentivized by the government to increase interest in alternative energy sources.

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