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Biogas potential of hazelnut shells and hazelnut wastes in Giresun City

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ABSTRACT

In recent years, the world's natural energy resources unable to meet the increasing energy needs. In Turkey and in the world, there is an increasing need for renewable energy. One of the renewable energy sources is biogas energy. In this study, the biogas potential of Giresun, which is also known as coastal city, can be formed from 2 different organic wastes are experimentally calculated. Organic wastes included in the calculation; hazelnut shells (HS) and hazelnut wastes (HW). Production experiments were investigated in two ways: untreated and thermal pretreatment. In addition, biogas yield was examined at room temperature (23 °C), at mesophilic temperature (39 °C), and at thermophilic temperature (60 °C). As a result, the highest biogas yield was found at temperatures of 60 °C and under thermal pretreatment conditions. Under these conditions, annual biogas production potential of Giresun city was found as 38.21 GW h/yr.

1. Introduction

The Earth has mostly used natural energy sources until the 21 st century. However, it is understood that these energy sources are the depleting, and that the reserves remain in limited quantities. For this reason, a trend towards renewable energy sources has begun [1]. Biogas energy is among the renewable energies and it is a flammable gas. Biogas is obtained as a result of biomass processing. It is the difference from other combustible gases (eg natural gas), derived from only animal or vegetable, such as organic raw materials. Biological wastes, organic wastes from food industry, organic kitchen wastes, animal plants such as corn or sugar beet, and animal feces from animal feed can be used as substrates in biogas plants. Biogas is a kind of gas which must be mixed with water at certain ratios and can be obtained in oxygen-free environment. In biogas content contains approximately 50–70 % methane (CH_4), 30–50 % carbon dioxide (CO_2), 0.1–1 % nitrogen (N_2), 0.01-0.2% oxygen (O_2) and 10–4000 ppm hydrogen sulphide (H_2S). The biogas flammability feature is derived from the CH_4 gas, which is similar with natural gas [2].

The raw materials and properties used in the biogas production have a significant effect on the energy efficiency. Biogas production from organic materials depends on the substances that can decompose into CH_4 and CO_2. Therefore, the composition and decomposability of animal fodder and energy plants are the most important parameters in methane yield [3]. Crude protein, crude oil, fiber, cellulose, hemicellulose, starch and sugar are quite effective in the formation of methane. Feeding animals also affects methane production and biogas production, as the majority of the substances that convert to carbon in cattle are digested in the rumen and intestines. For this reason, cattle manure, pigs and poultry have lower potential for biogas production compared to fertilizer. Biogas which is derived from cattle manure has the lowest CH_4 concentration. It has been reported that higher protein levels of manure during anaerobic digestion (AD) have higher methane yield [4,5].

AD and biogas production depend on many important parameters. These parameters are temperature, pH, dry matter rate, organic matter rate, C/N ratio, hydraulic retention time and organic loading rate [6]. In addition, organic components of biogas production like lignocellulosic components limit the biogas production [7]. The dissociation of lignocellulosic materials into anaerobic environments is very difficult [8]. The hydrolysis of cellulose and hemicellulose is very long. Lignin has no hydrolysis under anaerobic conditions [9]. For this reason, pretreatment technologies have been developed to provide biogas production from these lignocellulosic materials [10]. These pretreatments are; thermal pretreatments, chemical pretreatments, biological pretreatments, and solvent addition pretreatments [11].

In recent years, studies revealed that biomass energy potential is 9.5 GW in Turkey [12]. In the study which is done in Erdil and Erbıyık, it has defended that Turkey has rich biomass energy and this biomass energy potential will be evaluated [13]. In another study, Turkey's renewable and yearly energy potential of biomass was estimated at respectively 17.2 and 32.6 Mtoe [14].

In this study, biogas energy potential, considering 2 types of waste that are found in Giresun, it calculated as a result of

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experimental studies. These wastes are HS and HW. In AD, these wastes were examined under three different temperature conditions and thermal pretreatment. Turkey has similar studies. For example, Özer calculated the organic waste resources of Ardahan, in a similar way to this study it has found that the city has a total potential of 323 GW h/year biogas [15]. Similarly, Turker and Avcioğlu have found biogas potential of 49 PJ (1170.4 ktoe) which could be produced from animal wastes in Turkey [16]. Giresun is a coastal city and the lack of flatness causes to low settlement. For this reason, area required for disposal of waste is insufficient. It is desired to draw attention to the amount of organic waste with this work. The aim of this work was to raise awareness of the opening of a biogas foundation in Giresun, emphasizing the energy potential of Giresun.

The main wastes of Giresun are hazelnut shells and hazelnut wastes. Giresun is not adequately assessed in terms of organic wastes. Giresun has no systematic settlements and it is a coastal city. So there are some problems for organic wastes. One of the most important problem is that the wastes are poured into the sea and cause to pollution. The disposal of these waste is not adequate in solid area. Similarly, there is no storage for hazelnut wastes. The same situation is necessary to cattle manure. CM waste is abandoned to nature and not adequately assessed. Biogas production is the most appropriate method for evaluating organic wastes [17]. However, there is no biogas foundation in Giresun.

Fig. 1 shows the fresh hazelnuts collected from Giresun. After hazelnut has collected, it enters the hazelnut thresher and separates the hazelnut and hazelnut waste. The so-called hazelnut waste is a lignocellulosic compound that is greenish around the hazelnut. The hazelnut from the Patos machine is decomposed. This is a by-product and it are given in Fig. 2.

Giresun has an important place both in Turkey and in the world with hazelnut production. According to the latest research, the annual amount of nuts produced 652,800 t in the world, while 412,000 t of hazelnut produced in Turkey [18]. In Giresun, 88,392 t of hazelnuts are produced annually. Giresun's hazelnut production is about 13.54% of world hazelnut production [19]. Considering these values, Giresun has a considerable potential for hazelnut shell and hazelnut wastes. Hazelnut shells are used in the production of hazelnut coal. It is an alternative assessment method that hazelnut shells can be used as biogas production besides coalification.

The aim of this study is to emphasize the biogas potential of bacillus organic wastes in the province of Giresun. Biogas production is variable and complex according to the pretreatment technologies applied. Therefore, in this study, biogas production process was investigated by untreated and thermal pretreatment. Thus, methane production in Giresun province under untreated conditions and under thermal pretreatment conditions was determined experimentally. In this way, the biogas potential of the province of Giresun was emphasized.

Fig. 1. Unblended hazelnut image (raw hazelnuts).

Fig. 2. Blended hazelnut image (Hazelnut wastes).

2. Materials and methods

C and N values of organic wastes were determined using a costech Elemental Analyzer. The dry substance content was determined by drying for 48 h at 105 °C. The volatile solids ratio was obtained by burning the dried material in an ash furnace at 550 °C for 2 h [20]. The ash was found by subtracting the starting mass from the known mass. Hemicellulose, cellulose, and total lignin were determined from yzed CS with 72% H_2SO_4, using 0.3 g of the dried sample processed with 3 ml of 72% H_2SO_4 (v/v) for 1 h at 30 °C in a thermostatic bath. The filtrate was analyzed for carbohydrate contents in a chromatographic system [21].

Giresun province has an important place in the world in terms of hazelnut production. According to recent records, 102,000 t of hazelnuts are produced annually in Giresun [19]. In the laboratory work, 48 g of 100 g shell nut was weighed as shell. According to this account, 48.25% of hazelnut is crust in Giresun. According to the laboratory work has done, this study was conducted to determine the hazelnut waste rate, which is considered as hazelnut blend. According to this study, dried hazelnut weighing 100 g was weighed and removed without hazelnut (blend part) and weighed again. According to this account, hazelnut blending ratio was measured as 41.20%.

2.1. Laboratory and thermal pretreatment studies

Some organic wastes contain lignocellulosic components in their structures [22]. Evaluation of lignocellulosic components under anaerobic conditions takes a long time but yields low [23]. Thus, the biogas yields of organic wastes vary considerably with the applied pretreatment technologies [24]. In this way, the potential preliminary work to be carried out when the potential calculations are carried out or the work which is valid under the temperature conditions must be specified. Due to the thermal pretreatment, some of the cellulose and hemicellulose present in the lignocellulosic components are broken up into smaller monomers. This facilitates the dissolution of these monomers in water, resulting in increased biogas production yield and shortening of AD time [22].

All thermal pretreatments used in the experiments were carried out at 120 °C for 1 h. Pretreatments were performed in the autoclave. The pretreatment was carried out in autoclave bottles as the triple sample to applied repeatedly. Total 10% solids were produced. Prior to the start of AD, the pH value of all aqueous mixtures was adjusted to 7 with buffer solutions. This was done for 2 different organic waste samples used in the experiments.

HS and HW were taken from Giresun Boztekke village. Experimental studies for total biogas potential calculations were performed in 500 ml glass bottle. The heating temperature was provided by a magnetic stirrer heater from the bottom layer. Due to the sensitivity of anaerobic bacteria to light, the system is covered with aluminum foil. To determine the methane content of biogas, a 500 ml liquid special design experiment bottle is shown in Fig. 3. In the experiments, fresh wastewater sludge was used as inoculum. In all experiments, the inoculum/substrate ratio was taken as 1/10 (w/w). AD was maintained with 0.5 L gas collection bags. When the gas sample was desired to be taken, the biogas sample was drawn with the pump, which is an equipment of the biogas measuring device at the end of the valve. In this example, the CH_4 ratio in the portable biogas measuring device has been determined. The amount of biogas measured was determined as the total ml biogas per g of organic waste (ml/g total solids). The amount of biogas was measured every 4 days during the AD phase. As a result of all the measurements, biogas production was cumulative. The CH_4 contents of the collected gases after AD were analyzed by IRCD4 Multi-Gas Detecting Alarm Manual Instruction. The infrared sensor contained in the portable gas meter has a CH_4 and CO_2 content of (v/v) 0–100 %.The pH was measured every week.

2.2. Calculation of theoretical electricity power potential from organic waste

The total biogas potential of each organic waste was calculated according to Eq. (1).

$$TBP_i = \sum AAOM_i \times ER_i \quad (1)$$

where; TBP is total biogas potential (m^3/yr),

AAOM is annual amount of organic matter (t/yr),

ER is experimental results (m^3/t)

where; ER is experimental results determined by the amount of biogas

i: Organic matter type

$$AAOM_i = AOM_i \times C_i \quad (2)$$

where APOM is annual organic matter. C_i is organic matter coefficient (the total number of animals per yr for cattle breeding, the number of people for urban solid wastes, the weight of crust in hazelnuts for hazelnut shells and the weight ratio of hazelnut harvested for hazelnut wastes)

for HS = 0.4825 (experimentally determined ratio)

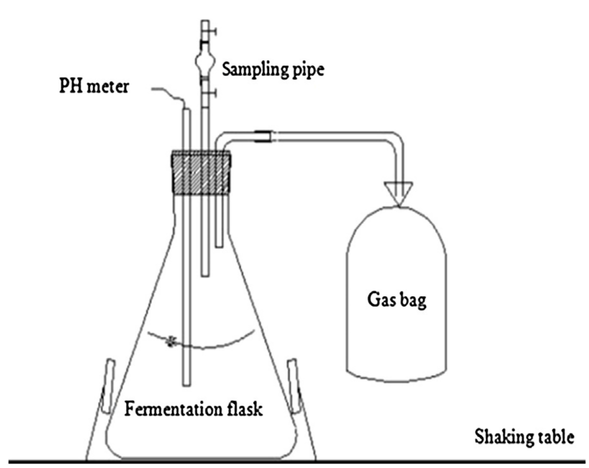

Fig. 3. Experimental setup image.

for HW C_i = 0.4120 (experimentally determined ratio)

$$TEE_i = TBP_i \times MO_i \times ECM \quad (3)$$

where TEE: total electrical energy potential, MO: Methane ratio, ECM: Energy content of methane.

10 kW h/ m^3 CH_4 is assumed according to Ref. [26]. But, the potential of electricity generation from the biogas was calculated according to Eq. (4):

$$e_{biogas} = E_{biogas} \times \eta \quad (4)$$

where e_{biogas} is the quantity of generated electricity (kWh/ yr), E_{biogas} is the unconverted raw energy in the biogas (kWh/yr) and the η denotes the overall efficiency of the conversion of biogas to electricity (%). The amount of η is varied depending on the power generation plants. In a study of η value was equal to 40%. In this study, the value was 0.4.

3. Results and discussion

Organic substances used for biogas production in this study; HS and HW, the experimental analysis of these wastes is shown in Table 1.

The anaerobic digestion process of 2 different organic wastes was provided by gas measurement taken every 4 day. Each measurement was provided on untreated conditions for each organic waste and on thermal pretreatment conditions.

In Fig. 4, A and B 10 show that HS in the AD at different temperature conditions, respectively, without pretreatment and thermal pretreatment. The maximum biogas production for RT was found as 71 ml/g $_{solid\ waste}$, 87 ml/g $_{solid\ waste}$ for MT and 91 ml/g $_{solid\ waste}$ for TT. The maximum biogas production for RT was found to be 89 ml/g $_{solid\ waste}$, 113 ml/g $_{solid\ waste}$ for MT and 123 ml/g $_{solid\ waste}$ for TT. The pH change is suitable for anaerobic digestion (change 6.8–7.3). Total anaerobic digestion time was determined as 140 for pretreatment and 196 days for untreated. The anaerobic digestion was terminated when the gas production was at the same value for 7 days on top. In this study, production untreated took a very long time. However, when thermal pretreatment is applied, the production time is reduced by 56 days. Probably the reason is that some of the cellulose molecule contained in the lignocellulosic component breaks down into small components. In a study was conducted with reed biomass, biogas production was studied without thermal pretreatment and with thermal pretreatment In this study, the amount of the hemicellulose macro molecule in the lignocellulosic component almost disappeared as a result of thermal pretreatment applied at 200 °C for 10 min. At this rate, the production yield was almost doubled. [28].

In Fig. 5 (C), the maximum biogas production was found to be 108 ml/g $_{solid\ waste}$ for RT, 149 ml/g $_{solid\ waste}$ for MT and 178 ml/g $_{solid\ waste}$ for TT. In Fig. 5 (D) the maximum biogas production for RT was found to be 168 ml/g $_{solid\ waste}$,

Table 1
Physical and chemical parameters of organic wastes.

Parameters	HS	HW
% C (% w/w)	45.98	41.28
% N (% w/w)	1.06	0.88
C/N (% w/w)	43.37	46.91
% dry matter (% w/w)	90.91	80.12
% Volatile Solid (% TS)	95.68	84.02
pH	–	–
% Moisture (% w/w)	9.09	19.88
Cellulose (% w/w)	26.11	47.78
Hemicellulose (% w/w)	29.80	33.20
Lignin (% w/w)	42.48	18.07

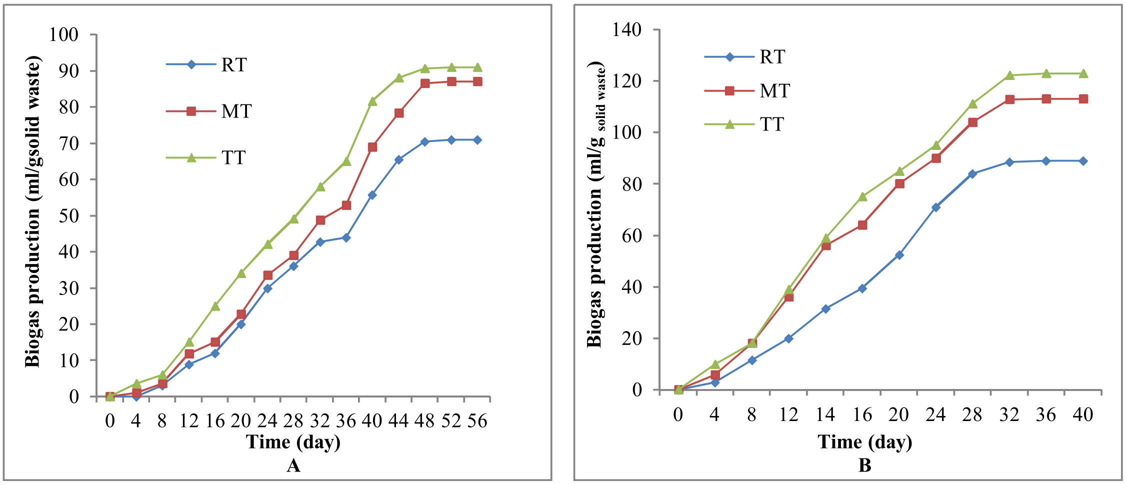

Fig. 4. Biogas production under untreated conditions (A), and thermal conditions (B) for hazelnut shell.
(RT: room temperature, MT: mezophilic temperature, TT: thermophilic temperature).

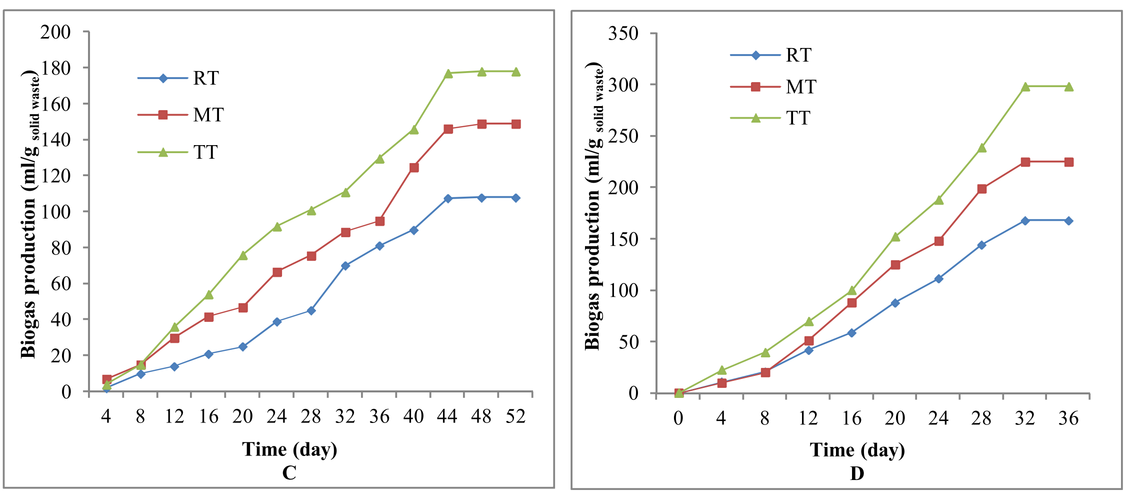

Fig. 5. Biogas production under untreated conditions (C) and thermal pretreatment conditions (D) for hazelnut waste.
(RT: room temperature, MT: mezophilic temperature, TT: thermophilic temperature).

225 ml/g $_{\text{solid waste}}$ for MT and 298 ml/g $_{\text{solid waste}}$ for TT. During the anaerobic digestion process the average pH varied from 6.1 to 7.8. The pH change is suitable for anaerobic digestion. The total anaerobic digestion time was determined as 52 for thermal untreated and 36 days for pretreatment. The anaerobic digestion was terminated when the gas production was at the same value for 48 h. The anaerobic digestion time was shortened by about 76 days due to applied thermal pretreatment.

Generally the biogas production is the mesophilic temperature with the optimum temperature of 39 °C. At higher temperatures than room temperature, lower yields are obtained than thermophilic temperature conditions. Despite this, the optimum temperature in terms of economic and cost costs is known as mesophilic conditions of 39 °C [1]. In this study, the biogas value produced for untreated conditions and thermophilic conditions for HS was close to the biogas value carried out at room temperature for thermal pretreatments. Therefore, instead of keeping the reactor under thermophilic conditions for 52 days at 60 °C, waiting for 36 days after 1 h of thermal pretreatment requires less cost.

Previously, biogas production studies on hazelnut waste have not been found in the literature. It is a straw-like plant containing lignocellulosic components in the hazelnut blend structure. For this reason, the literature comparison was made with wheat straw. In one study, thermal pretreatment was applied to wheat straw at 150–220 °C for 1–15 min and biogas production was increased by 20% [29].

Table 2 shows the AD studies in the literature of substances similar to organic substances made in this study and energy values calculated from 2 different organic wastes based on thermal

Table 2
Comparison of study results with literature.

Organic waste	Production conditions	Thermal pretreatment condition	% incremental biogas yield	References
HS	mesophilic temperature (39 °C)	120 °C, 1h	33.70	this study
HW	mesophilic temperature (39 °C)	120 °C, 1h	67.40	this study
Pistachio Shell	mesophilic condition (35 °C)	121 °C, 15 min	66.0	[30]
Wheat straw wastes	mesophilic condition (35 °C)	200 °C, 10 min	20.0	[31]

Table 3
Biogas yields of Giresun province organic wastes at room temperature (about 23 °C).

Untreated				Thermal pretreatment		
Organic waste	total biogas potential (m^3/ yr)	average CH_4 ratio (% v/v)	total energy value (MWh/ yr)	total biogas potential (m^3/ yr)	average CH_4 ratio (% v/v)	Total energy value (MWh/ yr)
HS	3,176,636	59.70	7,585.8	3,981,980	59.60	9,509.0
HW	3,636,319	62.80	9,134.4	5,656,497	62.50	14,209.0

Table 4
Biogas yields of organic wastes at mesophilic temperature (39 °C).

Untreated				Thermal pretreatment		
organic waste	total biogas potential (m^3/ yr)	Average CH_4 ratio (%)	Total energy value (MWh/ yr)	total biogas potential (m^3/ yr)	average CH_4 ratio (%)	total energy value (MWh/ yr)
HS	3,937,239	59.10	9,307.6	5,055,773	59.30	11,951.8
HW	5,016,774	62.70	12,582.0	7,575,666	62.60	19,000.0

Table 5
Biogas yields of organic wastes at thermophilic temperature.

Untreated				Thermal pretreatment		
organic waste	total biogas potential (m^3/ yr)	Average CH_4 ratio (% v/v)	total energy value (MWh/ yr)	total biogas potential (m^3/ yr)	average CH_4 ratio (%)	total energy value (MWh/ yr)
HS	4,116,205	58.90	9,697.8	5.503.186	58.9	12,965.2
HW	5,993,193	62.90	15,078.8	10.033.549	62.8	25,244.4

Table 6
Electricity potential generated by organic waste.

	Untreated			Thermal pretreatment		
	23 °C	39 °C	60 °C	23 °C	39 °C	60 °C
total energy value (GWh/yr)	16.70	21.89	24.78	23.72	30.95	38.21

pretreatment and untreated production results are given. The maximum increase was achieved in HW (67.4%).

Table 3 gives the biogas production potential of Giresun calculated according to experimental results at room temperature of HS and HW. The average CH_4 content in production experiments was changed from 0 to 55 in the first 15 days. 15 after the day the average ratio was fixed. The highest rate of methane was 62.8% for HW. The highest biogas energy value was found as HW under thermal pretreatment.

Table 4 shows the biogas production potential of HS and HW at the temperature of 39 °C, calculated according to experimental results. The average CH_4 content in production experiments was changed from 0 to 52 in the first 14 days. 14 after the day the average was fixed. The highest methane rate was 62.7% for HW. The highest biogas energy value was again found as HW under the thermal pretreatment conditions.

Table 5 gives the biogas production potential of HS and HW, at the temperature of 60 °C, calculated according to experimental results. The average CH_4 content in production experiments was changed from 0 to 58 in the first 18 days. 14. After the day the average was fixed. The highest rate of methane was 62.9% for HW. The highest biogas energy value was found as HW under the thermal pretreatment conditions. As a result of experimental studies, small changes in methane content values (0-0.7%) was observed since thermal pretreatment. This change was estimated to be due to the sensitivity of the biogas measuring instrument.

Table 6 summarizes the energy values of 2 different organic wastes at each temperature value untreated and thermal pretreatment conditions. According to this, the highest biogas energy value was estimated as 38.21 GW h/yr under the thermal pretreatment and 60 °C conditions. 0.107 dollars worth of electricity in Turkey for 1 kW h for 2018 [32]. Starting from this value, the energy income that can be produced from organic wastes of Giresun is 4,088,470.0 dollars/yr. Costs and labor costs was excluded from these calculations. Only the amount of biogas energy value of the organic wastes generated by the city of Giresun was to be emphasized.

CO_2 emissions increase significantly owing to the fossil fuel based power generation. The highest contribution to total CO_2 emissions in Turkey comes from energy sector with about 85% [33]. This is an important occasion for all the renewable energy potential of Turkey should be used. Biogas utilization with AD for organic waste, particularly the animal manure contributes to the mitigation of GHG emissions via CH_4 emission offset by converting manure into biogas displacing with coal [34].

In a study, determined the biogas potential of Ardahan city to be produced from animal wastes and an annual energy value of 322.6 GW h of organic waste was determined [15]. This emphasized that resulted in 2,312,951 t of CO_2 emissions to reach this energy value. If the finds calculated for Giresun province was proportional to these findings; The total CO_2 emission rate in Giresun province will be reduced by 273,954 t of CO_2. Until 2030, Turkey has an aim of reducing greenhouse gas (GHG) emissions up to 21% [35]. All the activities taking on the reducing GHG emissions will contribute to this aim. This biogas energy potential will be a good chance to be able to accomplish the CO_2 emission reduction and renewable energy use aims of Turkey. Besides, this study could also have contribution to the aim of increasing the renewable energy sources in all over the world.

4. Conclusions

In this study, the energy value which will occur in the case of 2 kinds of organic waste types in Giresun was evaluated in AD. The saving of this energy value and the emission reduction of carbon dioxide are considerable. Other countries or in Turkey, there are many theoretical studies account for biogas potential. However, unlike the theoretical studies, this study was supported by experimental calculations. Furthermore, the anaerobic process of each organic waste was monitored. All processes are provided in the form of cumulative biogas formation. In experimental studies the anaerobic duration is prolonged by the long course of the hydrolysis step of the lignocellulosic components. However, the time was shortened by the applied thermal pretreatment. Feasibility report of a zone or biogas production potential calculations should be supported with experimental studies. Because the anaerobic yield of organic waste varies depending on whether pretreatment is applied or not.

Declaration of Competing Interest

There is no interest relation of my article named **'Biogas potential of hazelnut shells and hazelnut wastes in Giresun City'**.

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