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Increasing the biomethane yield of hazelnut by-products by low temperature thermal pretreatment

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Abstract: Biomethane energy, which has the status of renewable energies, has the potential to be produced from all kinds of organic wastes, as well as from lignocellulosic materials, which are the most common in nature. In this study, hazelnut shells (HS), one of the hazelnut by-products, were used for biomethane production. In order to obtain higher yields from HS, thermal pre-treatments were applied at temperatures of 60°C, 80°C and 100°C. Pretreatment effects were controlled by lignocellulosic substance amount determinations. As a result of thermal pretreatment at 100°C for 2 h, cellulose and lignin removals occurred approximately 15% and 30%, respectively. While the cumulative biomethane yield of raw HS was 32.3 mL•g total solids $(TS)^{-1}$, the cumulative biomethane yields of 100°C pretreated HS were measured as 132.3 mL•gTS^{-1}. As a result of different pretreatment temperatures, different cumulative biomethane yield curves were successfully simulated with the Modified Gompertz equation and R^2 values were found to be between 0.9962 - 0.9985.

Key words: Renewable energy, sigmoidal models, hazelnut shells, biogas

1. Introduction

As countries grow rapidly in terms of industry and population, the energy needs of industrially developed and developing countries are increasing day by day. Energy need has become an important problem in the world today. The demand for energy leads to the decrease of fossil fuels (natural gas, coal, lignite, etc.) [1]. Depleting natural energy resources have led the world to search for new energy. One of the renewable energies is biogas/biomethane energy, which replaces depleting natural gas [2].

Biogas can be produced from organic materials by the anaerobic digestion (AD) method. AS treatment of wastes with high water content has been a generally preferred method in recent years due to its advantages such as high performance, low cost and energy production. Especially, AD applications are common in the treatment of domestic and industrial wastewater, animal manure and solid waste. AD method requires less energy and nutrient resources compared to other commonly used purification techniques [3]. Biogas content contains approximately 50 - 80% CH_4, 20-50% CO_2, 0.1-1% N_2, 0.01 - 0.2% O_2 and 10-4000 ppm H_2S is present [4-6, 8].

Biogas can be produced from different organic substances as well as lignocellulosic components [5]. Lignocellulosic organic matter refers to structures containing cellulose, hemicellulose and lignin in its structure and forms the structure of plant-derived biomass. Biogas production from lignocellulosic biomass without pretreatment is quite inefficient [6]. For this purpose, several innovative pretreatment technologies have been developed [7]. One of these is thermal pre-treatment methods, which were developed both for the environment and for their ease of applicability [8]. Thermal pretreatment is a type of physical pretreatment in which lignocellulosic biomass is subjected to heating at a certain temperature and pressure, and accordingly, the temperature range for thermal pretreatment can be 50–240°C [9].

One of the most underrated lignocellulosic components in AD is hazelnut by-products. In previous studies, hydrothermal and ultrasonic pretreatment of hazelnut shells (HS), one of the hazelnut by-products, was applied before AD [10]. In another study, thermal pretreatment optimization was performed on HS at high temperatures (50, 100 and 150°C) [11]. Apart from these studies, the biomethane yield of HS without pretreatment was investigated and the biomethane yield was obtained as 40.03 ± 4.30 mL/g volatile solids (VS) [12]. Apart from these studies, to the best of the authors' knowledge, there is no study that increases the biomethane/biogas yield of HS, one of the hazelnut by-products. Thus, there is a need to apply thermal pre-treatments to HS at lower temperatures (especially below 100°C) and longer application times and to conduct more in-depth research.

In this context, the aim of this study was to examine the lignocellulosic change in the structure of the HS and the differences in biomethane potential by applying thermal pre-treatment to raw HS at temperatures below 100°C for 2 hours. In this context, total solids (TS), VS, cellulose, hemicellulose and lignin analyzes of HS were performed before pre-treatment. Similar analyzes were performed after thermal pretreatment and the results were compared.

2. Material and Method

2.1. Substrate and inoculum

HS, one of the hazelnut by-products, was chosen as the substrate for AD. Sewage sludge from the wastewater treatment plant was used as inoculum. Raw materials were stored at 4°C before use.

2.2. Thermal pre-treatments

Thermal pretreatments were applied to HS at 60, 80 and 100°C [10]. Pre-treatments were applied in the oven. Thermal pretreatment time for each sample was kept constant as 2 hours. For each reactor, 2 g of dry reactor residue was added to the autoclave flask. 5 g of distilled water was added to prevent dry biomass from burning during thermal pretreatment. As a result of the pre-treatment, solubility was determined by filtering the slurry with glass cotton [11].

2.3. Anaerobic digestion tests

AD experiments were carried out in 500 mL conical flasks. 400 mL of these AD bottles was used as the effective volume and 100 mL was set as the head space. The TS ratio was chosen as 10% for all anaerobic bottles [13]. The inoculum/substrate ratio was taken as 1.0 on the basis of organic matter in the effective volume of 400 mL [14]. After the inoculum-substrate ratio was completed, N_2 gas was purged for 5 minutes to eliminate oxygen in the head space [15]. In the established setup, 5 types of reactors were prepared: 60°C, 80°C and 100°C pre-treatment reactor, control reactor and the reactor containing only the inoculum. A total of 10 reactors were prepared, each with two floors. In order to ensure AD conditions, the top was closed with a cork stopper and a mechanism containing gas bags was installed. The outer surface temperature (AD temperature) in the water bath was set at 37 ± 1.5°C. After AD conditions were achieved, the system was left to produce biogas, and during this process, each reactor was manually stirred every 24 hours. During the anaerobic process, gas volume was measured every 3 days and CH_4 content analyzes were performed. The AD test lasted approximately 39 days, and as a result of this period, the gases accumulated in the reactors were collected. Then, the net biomethane yield of the HS was calculated by subtracting the biomethane yield of the inoculum from the biomethane efficiency of the reactor containing the inoculum and HS. These gases were then saved for content analysis [15].

2.4 Analytical methods

TS and VS values of HS were analyzed according to APHA standards [16]. Cellulose, hemicellulose and lignin contents were measured using fiber analyzer (ANKOM A2000i, USA) [17]. Content analysis of the biogas obtained from AD experiments was performed with a portable biogas measuring device called IRCD4 Multi-Gas Detecting Alarm Manual Instruction. For this purpose, an average of 10-50 mL was taken from each biogas sample and the CH_4, CO_2, H_2S and O_2 values were determined with an average sensitivity of 1%. Scanning electron microscopy (SEM) images were acquired at x350 magnification values using a SU–1510 SEM (Hitachi, Japan), after preparing the raw and pretreated HS samples [14].

2.5 Kinetic study

In AD, the proliferation rate of microorganisms and the CH_4 gas production rate are directly proportional [14]. For this reason, the gas volumes determined cumulatively in the AD process were simulated with the modified Gompertz equation. MATLAB® (R2021a) program was used to obtain kinetic parameters in cumulative measurements. Then, the estimated values of the modified Gomperz equation were found. The modified Gompertz equation is given in Eq. (1) [8].

$$y = Ae^{\left(-e^{\left[\frac{\mu m e(\lambda - t)}{A} + 1\right]}\right)} \quad (1)$$

Where, A: Maximum biogas production amount (mL/g VS), e: 2.71828, λ: Delay time (days), t: Time and μ_m: Defined as specific biogas production rate (mL/g VS. day).

3. Results

3.1. Physicochemical properties of substrate and inoculum

The physicochemical properties of HS, which are hazelnut by-products, and wastewater treatment sludge used as inoculum are given in Table 1. In Table 1, the TS value of the

HS was reported as 92.4%, while the TS value of the inoculum was reported as 14.06%. While there is a significant potential in the VS rate of HS (90.87%), the VS rate of the inoculum is quite low (66.12%). In one study, the TS and VS values of HS were determined as 85.45 and 76.96, respectively [18]. In another study, TS and VS values were found to be 91.58 and 89.94, respectively [19]. As a result, previous studies support the values in Table 1.

Table 1. Physicochemical properties of raw hazelnut shell and inoculum used in the study

Parameters	Raw hazelnut shell	Inoculum
(TS) (%w/w)	92.40	14.06
(VS) (%TS)	90.87	66.12
pH	-	7.29
Cellulose (%w/w)	19.51	-
Hemicellulose (%w/w)	18.48	-
Lignin (%w/w)	36.07	-

Note: O content was found by subtracting the sum of C, H, N and S content from 100%

3.2. Effect of pretreatments on lignosulosic structure

In addition to the elemental content of HS, the lignocellulosic content in HS was determined. Accordingly, the cellulose, hemicellulose and lignin contents in raw HS were determined as 19.51%, 18.48% and 36.07% by weight, respectively. A literature search was conducted to test the consistency of the results of the analyses, and the results of lignocellulosic analyzes in HS were compared with the results reported by Bianco et al. [10]. Cellulose, hemicellulose and lignin values were found to be 26.11%, 29.8%, 42.48% by weight, respectively. The reason for this difference may be due to measurement error or sample difference. In another study, the cellulose, hemicellulose and lignin values of HS were 27.55%, 28.92%, 39.91% by weight, respectively, showing similar results with the amount of lignocellulosic substance declared in this study [11].

Table 2. Physicochemical properties of pre-treated hazelnut shells.

		Thermal pre-treatments conditions		
Parameters	**Control**	**60°C and 2 h**	**80°C and 2 h**	**100°C and 2 h**
Cellulose (%w/w)	19.51	18.5	16.8	15.39
Hemicellulose (%w/w)	18.48	17.8	16.5	15.0
Lignin (%w/w)	36.07	35.0	33.3	29.9

Cellulose is considered the main lignocellulosic component for biogas production. The amount of cellulose plays a vital role in any biochemical process. In one study was stated that the maximum degradation of glucan was only 2.8% at 160°C and increased to 14.7% after pretreatment at 200°C for 120 min [20]. In this study, looking at the values in Table 2., the cellulose value of raw HS is 19.51%; As a result of pre-treatment at 60°C and 2 hours, 1.1% cellulose was dissolved and reached 18.5% by weight. As a result of pre-treatment at 80°C and 2 hours, 2.7% cellulose was dissolved and reached 16.8% by weight. As a result of pre-treatment at 100°C and 2 hours, 4.1% cellulose was dissolved and reached 15.39% by weight. Cellulose removal as a result of pretreatment at 80°C increased by 1.7% compared to the pretreatment result at 60°C; Cellulose removal as a result of pretreatment at 100°C increased by 1.41% compared to the pretreatment result at 80°C. When the results are compared, the highest cellulose removal occurred as a result of the pre-treatment at 100°C.

Hemicellulose is a type of heterogeneous polysaccharide and contains hexoses, pentoses, uronic acid sugars. In the hemicellulose structure, the hydroxyl group of the sugars is partially replaced by the acetyl group [21]. While the hemicellulose value of raw HS in this study was 18.48%; As a result of pre-treatment at 60°C and 2 hours, 0.6% hemicellulose dissolved and reached 17.8% by weight. As a result of pre-treatment at 80°C and 2 hours, 1.9% hemicellulose dissolved and reached 16.5% by weight. As a result of pre-treatment at 100°C and two hours, 3.4% hemicellulose was dissolved and reached 15.0% by weight. Hemicellulose removal as a result of pretreatment at 80°C increased by 1.3% compared to the pretreatment result at 60°C; Hemicellulose removal as a result of pretreatment at 100°C increased by 1.5% compared to the pretreatment result at 80°C. When the results are compared, the highest hemicellulose removal occurred as a result of pre-treatment at 100°C.

The presence of lignin is a vital factor that limits the extent and rate of hydrolysis by enzymes during the biochemical reaction of lignocellulosic biomass. Studies have shown that lignin removal from lignocellulosic biomass increases cellulose digestibility [22]. In this study, the degradability of lignin was tested after thermal pretreatment in order to test the high yield of HS in the AD process. While the control value of lignin was 36.07%; As a result of 60°C and 2 hours of pre-treatment, 1% lignin was dissolved and reached 35% by weight. As a result of 80°C and 2 hours of pre-treatment, 2.7% lignin was dissolved and reached 33.3% by weight. At 100°C and As a result of 2 hours of pre-treatment, 6.1% lignin was dissolved and reached 29.9% by weight. Lignin removal as a result of pretreatment at 80°C increased by 1.7% compared to the pretreatment result at 60°C; Lignin removal as a result of pretreatment at 100°C increased by 3.4% compared to the pretreatment result at 80°C. When the results are compared, the highest lignin removal occurred as a result of pre-treatment at 100°C.

3.3. Effect of pretreatments on biomethane yields

The cumulative biomethane yields obtained in the AD process as a result of thermal pre-treatments applied to HS are calculated in (mL•gTS^{-1}) and are given in Table 3. Accordingly, the biomethane yield of raw HS was found to be 32.3 mL gTS^{-1}. This very low value shows us that biomethane production from lignocellulosic material is very low. In order to increase this value, a thermal pre-treatment was applied at temperatures of 60°C, 80°C and 100°C and application times of 2 hours. As a result of these pre-treatments at 60°C, the biomethane yield reached from 32.3 mL•gTS^{-1} to 88.3 mL•gTS^{-1}. Biomethane yield; 1.73 times as a result of pretreatment at 60°C compared to the control reactor; 2.53 times as a result of pre-treatment at 80°C; It increased 3.09 times as a result of pre-treatment at 100°C. The biogas production amount of the pretreated reactor at 80°C increased by 29.3% compared to the biogas production amount of the pretreated reactor at 60°C. The biogas production amount of the pre-treated reactor at 100°C increased by 15.8% compared to the biogas production amount of the pre-treated reactor at 80°C. According to these results, it is clear that the highest biomethane yield occurs in the reactor with 100°C and 2 hours pretreatment.

Table 3. Cumulative biomethane yields of inoculum, control and thermally pretreated hazelnut shells

Pretreatments conditions	Cumulative biomethane yields (mL·gTS^{-1})
Inoculum	15.5
Control	32.3
Thermal (60°C)	88.3
Thermal (80°C)	114.2
Thermal (100°C)	132.3

Biomethane measurements were made every 3 days in AD and the anaerobic process was completed in 39 days (Figure 1). Since biomethane yield could not be obtained in the last 3 consecutive days, the AD process was stopped and gas volumes were calculated.

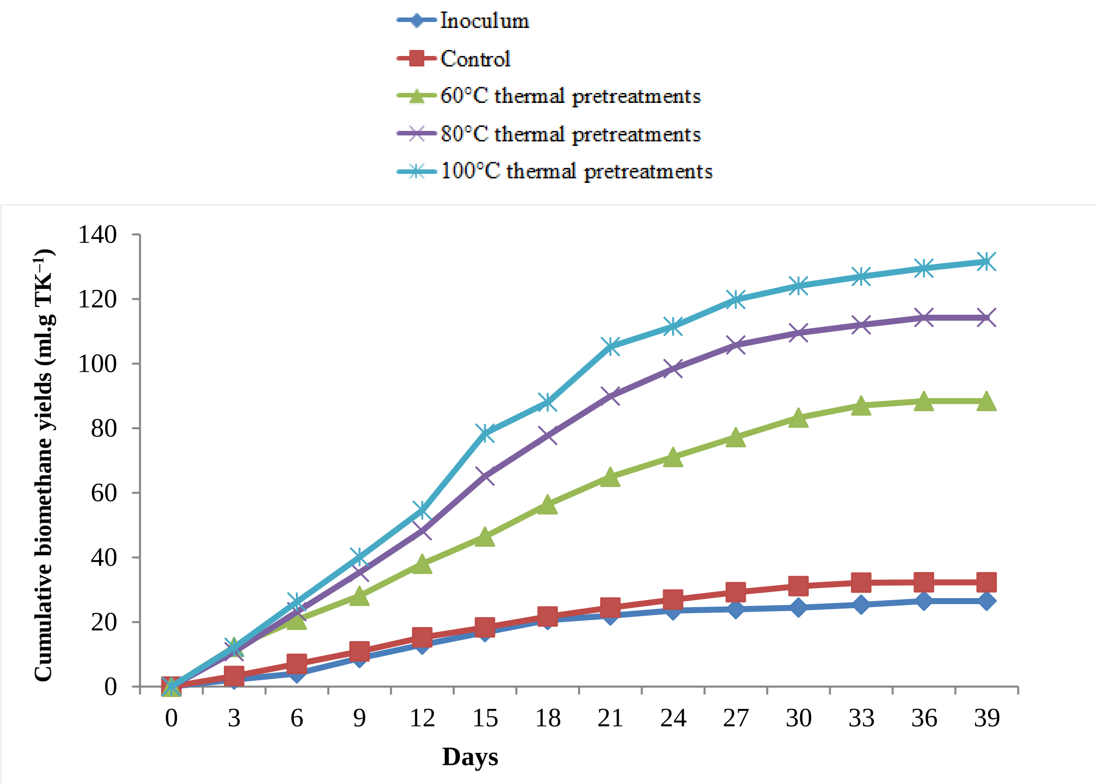

Figure 1. Cumulative biomethane yields of inoculated, control and thermally pretreated hazelnut shells

3.4. Effects of pretreatments on surface morphology

SEM images were taken to evaluate the effects of thermal pretreatments on HS. Surface images of unpretreated and pretreated HS are given in Figure 2. It is observed that the sample without pretreatment has surface hardness and crystallinity and does not contain pores (Figure 2 (a)). When the pretreatment temperature is 60°C (Figure 2 (b)), a slightly porous structure is observed. After 80°C pre-treatment (Figure 2 (c)), it appears that the surface crystallinity is broken and cracks are formed. In the SEM images of 100°C pre-treated HS, the cracks on the surface appear to increase and become extremely wide. It is clearly seen that the cracks increase and widen as the pre-treatment temperature increases. Therefore, it can be said that the reactor with a higher pretreatment temperature is more suitable for anaerobic microorganisms in AD.

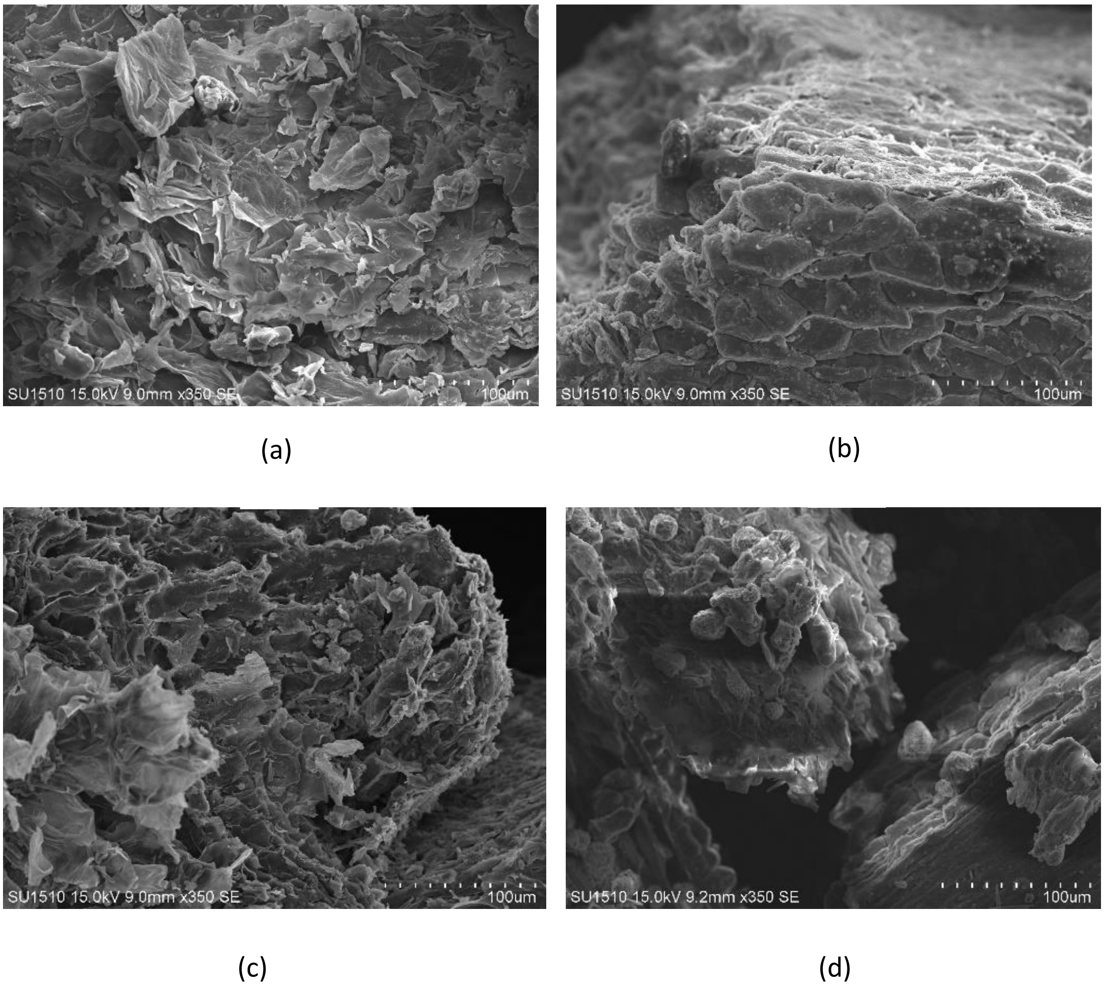

Figure 2. SEM images of hazelnut shells after thermal pre-treatment (a; no pre-treatment, b: 60°C pre-treated, c: 80°C pre-treated and d; 100°C pre-treated hazelnut shells).

3.5 Kinetic study results

Mathematical models describe the interactions of operating parameters of anaerobic microorganisms and the improvement of technical properties; It is a tool used to explain the impact on biogas production and to predict system performance [23]. In AD, the biogas production rate and proliferation rate of microorganisms are directly proportional. Thus, MATLAB® (R2019b) program was used to calculate the kinetic parameters of sigmoidal curves. Estimated biomethane values were found for the modified Gompertz model by entering the cumulative biogas production rate measured every three days into the program.

Table 4. Kinetic Parameters of the Modified Gompertz Model

Kinetic parameters	Unit	Inoculum	Control	60°C	80°C	100°C
λ	(day)	3.163	1.51	0.8901	2.371	2.424
μ_m	(mL·gTS^{-1}.gün)	1.481	1.393	3.405	5.258	6.11
A	(mL·gTS^{-1})	26.3	34.25	96.88	120.2	136

R^2	-	0.9977	0.9973	0.9962	0.9985	0.9979

Delay time: λ ; Specific biomethane yields: µm ; Max. biogas production amount: A; coefficient of determination: R^2

According to Table 4, A value indicates maximum biomethane yields [18]. According to the modified Gompertz model, the maximum biomethane yield is 136 mL gTS^{-1} in the 100ºC pre-treated reactor. The experimental biomethane yield of the reactor with 100ºC thermal pretreatment is 132.3 mL·gTS^{-1}. The estimated maximum biomethane yield and experimental biomethane yield are consistent. Specific biomethane yields (µm) vary between 1.393 mL•g TS^{-1} and 6.11 mL•gTS^{-1}. Experimental biomethane yields and specific biomethane yields appear to be linearly consistent.

Lag times (λ) express the time required for anaerobic bacteria to start multiplying (reproducing) [24]. Since statistically significant biomethane/biogas is produced after the delay period in biogas reactors, it is desirable that the delay times be minimum in terms of cost [13]. In this study, the delay times of the vaccine, control and pre-treatment reactors obtained according to the modified Gompertz model were calculated and given in Table 4. The lowest λ value is 0.8901 days in the reactor with 60°C thermal pretreatment. When the delay times of all reactors are evaluated, the reactor with 60°C thermal pretreatment is the most suitable reactor since the delay time is desired to be minimum. If other pre-treated reactors are taken into consideration (for 80°C and 100°C pre-treated reactors, respectively), λ values were obtained as 2.371 and 2.424 days, and the closeness of the values to each other is remarkable. However, the delay period of the vaccine was found to be 3,163 days. In a study, the cumulative biomethane curves obtained as a result of AD treatment of HS, a lignocellulosic waste, were modeled with the modified Gompertz equation. As a result of the thermal pretreatment (100°C) they found in their study, the λ values (0.8956 days) are close to the values in this study [25].

Model compatibility (model performance) for reactors is determined by R^2 values [11]. R^2 value is desired to be closest to 1; The closer it is to 1, the higher the model compatibility [26]. The R^2 value closest to 1 is 0.9985 in the reactor with 80°C thermal pretreatment. Considering the highest biomethane yield, the most compatible reactor is the reactor with 80°C thermal pretreatment. According to Table 4, the R^2 value varies between 0.9962 and 0.9985. According to the results of the modified Gompertz model in a study, R^2 values vary between 0.975 and 0.993 [27]. Therefore, it can be seen that the kinetic constants obtained here are compatible with those previously given in the literature. In a study conducted to increase biomethane yield as a result of co-fermentation of cattle manure and canola waste, the R^2 value was calculated as 0.9983 in the curves obtained with the Modified Gompertz model [28]. The values of the kinetic parameters found in this study are compatible with the literature.

4. Conclusion

In this study, HS, one of the hazelnut by-products, were used as raw material for biomethane production. Since HS is a lignocellulosic substance, thermal pre-treatments have been applied so that anaerobic microorganisms can better benefit from organic substances. Biomethane measurements were made every 3 days in AD and this process was completed in 39 days.

Raw HS samples were subjected to thermal pretreatment separately at temperatures of 60°C, 80°C and 100°C for 2 hours. While the biomethane yield of raw HS is 32.3

mL•gTS^{-1}, after thermal pre-treatment, the biomethane yields for temperatures of 60°C, 80°C and 100°C are 88.3 mL•gTS^{-1}, 114.2 mL•gTS^{-1}, respectively. It was measured as 1 and 132.3 mL•gTS^{-1}. The effects of pretreatments on HS were checked by cellulose, hemicellulose and lignin analyses. Cellulose, hemicellulose and lignin values in raw HS were found to be 19.51%, 18.48% and 36.07%, respectively.

In this study, for the first time, low-temperature thermal pretreatments were applied to hazelnut by-products and successful biomethane production was achieved. The fact that biomethane yields are higher in pre-treated reactors compared to the control shows that the pre-treatment method used is appropriate. It is recommended that future experimental studies apply biomethane yields with alkaline, acid and thermochemical pretreatments of HS. Moreover, it is recommended to use raw HS in full-scale anaerobic reactors in future studies.

Authorship contribution statement

H. Şenol: Conceptualization, Original Draft Writing Methodology, Supervision;
M. Oyan: Data Curation, Original Draft Writing; Visualization,
E. Görgün: Data Curation, Original Draft Writing; Visualization,

Declaration of competing interest

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.

Ethics Committee Approval and/or Informed Consent Information

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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