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ORIGINAL ARTICLE

Anaerobic digestion of sugar beet pulp after acid thermal and alkali thermal pretreatments

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Abstract

In this study, biogas production was investigated in mesophilic conditions from sugar beet pulp (SBP). In untreated conditions, water dissolution rate was 15.5% and biogas production rate was 168.7 mL/g TS (total solid). Alkaline thermal pretreatments were applied at 100 °C with 3 N NaOH and KOH solutions. Amounts of alkaline and acid were added in an amount equal to 5%, 10%, 15%, 20%, and 30% of the solids in the reactor. Acid thermal pretreatments were applied at 100 °C with 5% (v/v) H_2SO_4 and HNO_3 solutions. The anaerobic digestion (AD) time was shortened by approximately 10 days after pretreatment. The highest biogas yield was 458.4 mL/g TS as a result of KOH thermal pretreatment. In this reactor, soluble chemical oxygen demand (sCOD) removal was 87.1%, and cellulose, hemicellulose, and lignin removals were 32.4%, 28.6%, and 33.5% w/w, respectively. It was observed that the cumulative biogas production (CBP) successfully fitted the modified Richards (MR) model and modified Gompertz (MG) model.

Keywords Biogas · Anaerobic digestion · Alkaline thermal pretreatment · Acid thermal pretreatment · Modified Richards model · Modified Gompertz model

1 Introduction

In the current century, confidence in energy is decreasing and environmental pollution is increasing. It is necessary to reduce carbon dioxide emissions and reduce the demand for fossil fuels. Therefore, in the current situation, the use of bioenergy is beneficial for economic development and nature [1]. Globalization has created a rapid increase in industrialization to meet the needs of society. The largest areas of growth are the agricultural industries [2].

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Anaerobic digestion (AD) is called a decomposition of various organic substances in an anaerobic environment and is a complex system depending on the activities of various microorganisms. The main components of AD are carbohydrates, lipids, and proteins. AD generally consists of the stages of hydrolysis, acidogenesis, acetogenesis, and methanogenesis [3]. Biogas produced by AD has the status of renewable energies. In the production of biogas, besides the energy production, organic wastes are also eliminated [4]. SBP is a by-product of sugar production. At least 350 kg of sugar is obtained from 1 ton sugar beet [5–7].

Pretreatment technologies developed for biogas production provide hydrolysis of lignin, cellulose, and hemicellulose in lignocellulosic components. Thus, incremental biogas is produced in AD [8]. Acid pretreatment provides the most hydrolysis of hemicellulose from lignocellulosic components [9]. This pretreatment is useful for converting energy plants into energy [10]. Alkaline pretreatments provide the most lignin hydrolysis. In addition, it increases the internal surface area of the lignocellulosic material [11]. SBP is an energy biomass with lignocellulosic content. Pretreatment is needed for the content of cellulose, lignin, and hemicellulose in waste such as sugar beet pulp to become attractive in AD [12].

As a result of AD of SBP untreated, methane yield was 122.86 mL/g volatile solids (VS) [13]. In the literature, it has been emphasized that AD efficiency of SBP can be increased by many pretreatment methods [14]. As a result of enzymatic pretreatment, methane yield was 295.2 mL/g VS [15] and methane yield at 160 °C thermal pretreatment was reported as 502.50 mL/g VS [14]. It has been emphasized that AD efficiency of SBP can be increased by many pretreatment methods [14]. The AD efficiency of SBP has been increased in the literature by co-fermentation or pretreatment [13, 15]. Incremental biogas yields resulting from the application of innovative pretreatment methods developed for biogas production vary according to the type and structure of organic samples [8]. However, the effects of different pretreatment technologies of SBP have not been studied sufficiently in the literature. Therefore, in this study, acid thermal pretreatment and alkali thermal pretreatment were compared with SBP and the difference of these pretreatments from other chemical, physical, and thermal pretreatments was demonstrated.

Researchers used modified Gompertz model to predict biogas yield rate with given that biogas yield rate convenience to anaerobic bacteria growth rate in AD. It was reported that modified Richards model was the most suitable one to describe the experimental data of several sigmoidal curves [16]. Therefore, it was compared with the modified Gompertz model and modified Richards model which is an alternative model.

The aim of this study was to compare the results of untreated, thermal alkali pretreatment, and thermal acid pretreatment for SBP. Under constant pretreatment temperature (100 °C), certain concentrations of acid and alkali were added to the SBP. There is no comparison of alkali thermal and acid thermal pretreatments for SBP in the scientific literature. Thus, the difference between the alkali thermal and acid thermal pretreatments applied to sugar beet pulp was compared with the other pretreatments in the literature.

2 Materials and methods

2.1 Organic raw material and anaerobic inoculum

SBP was collected from Samsun province (Turkey). It was distinguished from foreign materials such as soil, dust, and straw. After drying, the particle size was milled to 1 mm. Thus, it was made ready for AD. Fresh cattle manure (CM) was used as an inoculum. Fresh CM was added to all reactors up to 10% (w/w) of the solids content (S/I = 10). Table 1 shows the characterization of SBP and CM.

Table 1 Characteristics of organic raw materials

Parameters	Inoculum	SBP
TS (% w/w)	18.70 ± 1.0	74.55 ± 1.0
VS (% TS)	82.10 ± 0.5	86.10 ± 0.5
Moisture (% w/w)	81.30 ± 1.0	25.45 ± 1.0
Ash (% w/w)	3.20 ± 0.1	11.25 ± 0.1
sCOD (mg O_2/L_{slurry})	26580.0 ± 122	4660.0 ± 5.0
pH	6.81 ± 0.03	4.09 ± 0.03
Cellulose (% w/w)	20.30 ± 0.5	29.90 ± 0.5
Hemicellulose (% w/w)	18.92 ± 1.0	25.92 ± 1.0
Lignin (% w/w)	12.85 ± 0.5	3.91 ± 0.5
% C (% w/w)	32.12 ± 0.50	43.25 ± 0.50
% N (% w/w)	1.65 ± 0.15	15.90 ± 0.15
C/N	19.46 ± 0.3	27.03 ± 0.3

2.2 Analytical methods

Volatile solids (VS), TS, ash, moisture, carbon (C), nitrogen (N), soluble chemical oxygen demand (sCOD), pH, cellulose, hemicellulose, and lignin analyses were performed before starting AD to organic waste. TS and VS analyses were analyzed according to APHA standards [17]. The lignocellulosic contents (cellulose, hemicellulose, and lignin) were measured using a fiber analyzer (Giresun, Turkey) [18]. The carbon to nitrogen ratio (C:N) of the lignocellulosic substrates was determined by a COSTEC elemental analyzer (Giresun, Turkey). A Hitachi SU-1510 (Hitachi, Ltd. Tokyo, Japan) scanning electron microscope (SEM) was used to scan the surfaces of the organic waste. Prior to SEM analysis, the organic sample was coated with gold nanoparticles for better conductivity. Liquid samples were centrifuged at 10,000 rpm and then, samples were pretreated using a 20-μm membrane filter to analyze the soluble matter. sCOD analyses were performed according to closed reflux method (cod closed reflux titrimetric method) [19]. The content of the amount of gas produced as a result of all experiments was determined as % volumetric. This measurement was made by "IRCD4 Multi-Gas Detecting Instruction" (biogas analyzer with infrared sensor). Thus, CH_4, CO_2, and H_2S (ppm) values were obtained.

2.3 Anaerobic digestion setup and biogas potential test

AD processes were carried out in 500-mL batch reactors. Heating temperature was determined as 35 ± 2 °C. Heating was done with the help of a flat plate. Dry matter rate was 10% in all reactors. AD was maintained with 0.5–0.3-L gas collection bags (Fig. 1). The experiments were carried out with 3 replications. The biogas volume and sCOD removal were measured every 5 days.

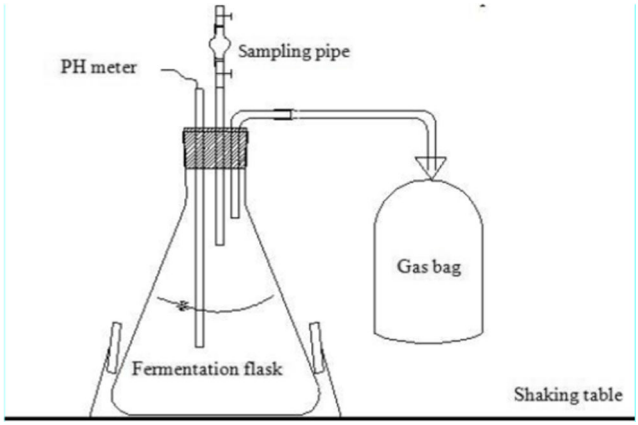


Fig. 1 Anaerobic digestion setup [20]

Biogas potential test was carried out on the sugar beet pulp samples so as to determine the biogas yield from the substrate under standard condition. The equipment for biogas potential test was 500-mL batch reactors connected to a 300–500-mL gas bag at 35 °C for 35–40 days [21]. Biogas volume measurements were performed every 5 days. Production was discontinued when the cumulative biogas productions (CBPs) were equal.

2.4 Acid thermal and alkali thermal pretreatments

Acid thermal and alkaline thermal pretreatments are called thermochemical pretreatments [22]. The acid thermal pretreatments [23] were applied to the aqueous mixture by first adding 5% (v/v) H_2SO_4 and HNO_3 solutions. The solution amounts were added at 5%, 10%, 15%, 20%, and 30% (v/w) of the solids in the reactor. The aqueous mixture was exposed in an autoclave bottle to a temperature of 100 °C and 1 atm for 1 h. Alkaline thermal pretreatments [22] were applied to the aqueous mixture with addition of 3 N NaOH and 3 N KOH solutions. The solution was added in an amount equal to 5%, 10%, 15%, 20%, and 30% of the solids in the reactor. The mixture was exposed in an autoclave bottle to a temperature of 100 °C for 1 h. After pretreatment, the pH of the aqueous mixture was adjusted to 7.1 with buffer solutions. After pretreatment was applied to organic sample, it was determined gravimetrically in % water solubility with the help of glass cottons which were brought to constant weight. As a result of the pretreatments, the amount of water-soluble solids was determined by filtration of the slurry with glass cotton.

Figure 2 shows the organic matter as a result of the application of alkali thermal and acid thermal pretreatments. Accordingly, the organic sample was light color due to the application of acid thermal pretreatment (3 and 4). Application of alkaline thermal pretreatment as a result of the organic sample was dark color (1 and 2).

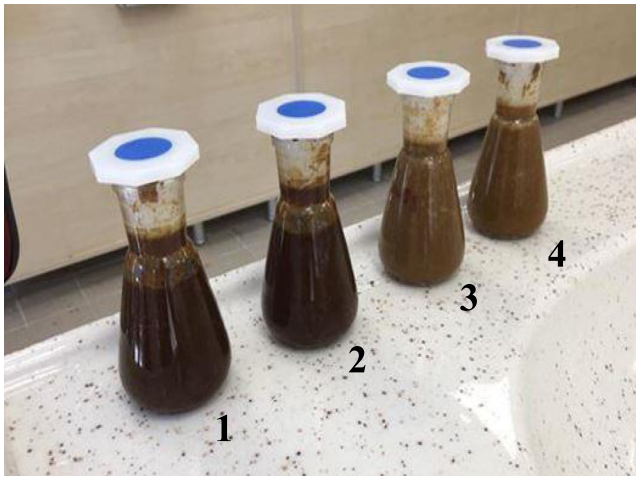


Fig. 2 Image of organic matter as a result of alkali and acid thermal treatments: NaOH thermal (1), KOH thermal (2), HNO_3 thermal (3), H_2SO_4 thermal (4)

2.5 Statistical analysis

All statistical analysis was carried out using SPSS 21.0. Biogas production yields were analyzed for 20 reactors with acid thermal and alkali thermal pretreatments in 1–40-day time interval. Biogas yields obtained from the reactors were found to be normal distribution since the Shapiro-Wilk test was $p > 0.05$. Therefore, Pearson's correlation coefficients were calculated between the same pretreated reactors.

2.6 Model definitions for CBP

The CBP, measured every 5 days, was written in the program (SPSS 21.0) and the estimated values were obtained for the MR model and MG model. In this study, the modified form of the Richards sigmoidal function by Zwietering et al. [16] (Eq. (1)) was applied to the experimental data to determine the maximum biogas production quantity (A), maximum methane production rate (μ_m), and the lag time (λ). The MR model also incorporates a fourth parameter (v) that permits flexibility in the shape of the curve. The Gompertz equation is similarly used in sigmoidal growth curves [16]. The modified Gompertz model (Eq. (2)) is widely used for biogas [24].

$$\text{modified Richards model} \quad y = A\left[1 + ve^{(1+v)} \cdot e^{\left[\frac{\mu_m (1+v)^{\left(1+\frac{1}{v}\right)} (\lambda - t)}{A}\right]}\right]^{\frac{-1}{v}} \tag{1}$$

$$\text{modified Gompertz model} \quad y = Ae^{\left(\left(-e^{\left[\frac{\mu_m e(\lambda - t)}{A} + 1\right]}\right)\right)} \tag{2}$$

where A is the maximum biogas production quantity (mL/g TS), λ is the lag time (days), μ_m the is specific biogas

Table 2 Untreated, acid thermal pretreatment, and alkali thermal pretreatment results

Pretreatment conditions	Pretreatment amount (% v/w)	Incremental dissolution (%)	Reactor	Biogas production (mL/g TS)	Incremental production (%)	sCOD removed (%)
Untreated	-	0	R_1	168.7 ± 2.1	-	45.5 ± 2.9
5% (v/v) H_2SO_4 (24 h) and 100 °C thermal (1 h)	5	12.5 ± 2.2	R_2	229.5 ± 3.2	36.04	61.1 ± 2.8
	10	*55.8 ± 1.9*	*R_3*	*355.6 ± 3.4*	*110.78*	*75.4 ± 5.5*
	15	56.9 ± 3.5	R_4	346.5 ± 4.2	105.39	80.9 ± 3.8
	20	36.8 ± 4.1	R_5	306.4 ± 3.6	81.62	71.2 ± 3.5
	30	26.8 ± 3.2	R_6	272.5 ± 5.5	61.52	65.6 ± 3.7
5% (v/v) HNO_3 (24 h) and 100 °C thermal (1 h)	5	12.5 ± 2.9	R_7	223.5 ± 6.7	32.48	60.4 ± 3.8
	10	*40.9 ± 3.1*	*R_8*	*323.4 ± 5.2*	*91.70*	*72.1 ± 4.5*
	15	40.5 ± 3.5	R_9	301.5 ± 6.6	78.71	69.2 ± 2.7
	20	50.4 ± 4.1	R_{10}	322.4 ± 5.4	91.10	72.2 ± 2.9
	30	35.1 ± 5.1	R_{11}	288.9 ± 3.9	71.25	67.0 ± 3.9
3 N NaOH (24 h) and 100 °C thermal (1 h)	5	15.9 ± 4.2	R_{12}	240.4 ± 2.8	42.50	63.5 ± 3.6
	10	60.5 ± 3.5	R_{13}	381.5 ± 5.7	126.14	82.0 ± 4.3
	15	*70.9 ± 4.2*	*R_{14}*	*398.5 ± 6.2*	*136. 12*	*85.9 ± 4.5*
	20	55.9 ± 5.0	R_{15}	355.4 ± 6.0	110.66	82.1 ± 3.1
	30	25.6 ± 3.1	R_{16}	255.4 ± 5.6	51.39	62.0 ± 2.7
3 N KOH (24 h) and 100 °C thermal (1 h)	5	22.2 ± 2.1	R_{17}	248.5 ± 5.2	47.30	64.5 ± 3.4
	10	*90.5 ± 2.3*	*R_{18}*	*458.4 ± 6.8*	*171.72*	*87.1 ± 3.8*
	15	80.8 ± 3.4	R_{19}	399.4 ± 7.5	136.75	84.7 ± 4.2
	20	35.6 ± 4.1	R_{20}	291.5 ± 3.8	72.79	68.1 ± 1.9
	30	39.2 ± 3.2	R_{21}	304.6 ± 4.7	80.55	70.1 ± 3.5

The italic values are the conditions in which the highest biogas production is achieved

production rate (mL/g TS.d), t is time (days), and e is 2.71828. In this study, Statistical Package for the Social Sciences (SPSS 21.0) program was used to calculate growth curve parameters (λ, μ_m, A, v) from growth curves. The model with the highest coefficient of determination (R^2) was chosen as the most suitable model.

3 Results and discussion

3.1 Untreated, acid thermal pretreatment, and alkali thermal pretreatment results

Untreated, thermal acid pretreatment, and thermal alkaline pretreatment results are given in Table 2.

In this table, acid thermal pretreatments are defined as R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, and R_{11} according to acid amounts and solution types. Similarly, alkaline thermal pretreatments are defined as R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, and R_{21} according to acid amounts and solution types. While the biogas yield in the untreated reactor was 168.7 mL/g TS, it was 355.6 ml/g TS in H_2SO_4 thermal pretreatment (R_3). The highest biogas yield at HNO_3 thermal pretreatment was 323.4 mL/g TS (R_8). As a result of NaOH thermal pretreatment, the highest biogas yield was 398.5 mL/g TS (R_{14}). As a result of KOH thermal pretreatment, the highest biogas yield was 458.4 mL/g TS (R_{18}). The highest biogas yield after the pretreatment occurred in reactor R_{18} (KOH thermal pretreatment). After the thermochemical pretreatment, the water solubility of the samples changed according to the amount and type of the chemical substance. In the literature, there are no optimization studies of acid thermal and alkali thermal pretreatments for SBP. In one study, methane yield was increased by 51.65% as a result of anaerobic digestion of SBP under 120 °C hydrothermal pretreatment temperature and the sCOD removal in this reactor was 71% [14]. In this study, the highest yield as a result of KOH thermal pretreatment was 136.75%. The maximum sCOD removals for H_2SO_4 thermal, HNO_3 thermal, NaOH thermal, and KOH thermal pretreatments were 80.9%, 72.2%, 85.9%, and 87.1%, respectively. Biogas yields in these reactors were 110.78%, 91.70%, 136.12%, and 136.75% respectively. As the amount of acid and alkali increased, the solubility in water increased. The water solubility was at least 12.5% (w/w) (R_2), while it was the highest of 90.5% (R_{18}). Biogas yield in all reactors was directly proportional to the amount of water-soluble organic matter.

In Table 2, it is shown that the yield decreased for all reactors when pretreatment amounts increased from 20 to 30%. The possible causes of this are the toxic effect of anaerobic microorganisms due to the excess amount of acid or alkali used. In a study, different NaOH loadings (1%, 2.5%, 5.0%,

Table 3 Comparing the increase in biogas production with literature values as a result of acid thermal and alkali thermal pretreatments

Pretreatment conditions	Pretreatment effect (incremental yields)	Type of organic substance	References
Addition of 3 N NaOH amount to 15% (v/w) of solid mass to reactor and 100 °C, 1 h	136.12%	SBP	(This study) R_{14}
Addition of NaOH amount to 15% (w/w) of solid mass to reactor and 100 °C, 10 min	181.2%	Softwood pine	[26]
Addition of NaOH amount to 15% (w/w) of solid mass to reactor and 100 °C, 1 h	54.5%	Wheat straw	[27]
Addition of NaOH amount to 1% (w/w) of solid mass to reactor and 180 °C, 1 h	244 mL/g VS biogas yield	Pine wood	[28]

and 7.5% (w/w)) were tested for organic matter and study suggested 5% (w/w) ratio as the optimal ratio but a 7.5% caused inhibition of methanogenesis due to rapid hydrolysis and acidogenesis.

As a result of NaOH thermal pretreatments, maximum biogas production was achieved when the alkali content was equal to 15% of the solids content. However, in other pretreatments, maximum biogas production was achieved when the amount of alkali or acid was equal to 10% of the solids content. This can be explained by the fact that anaerobic microorganisms are more resistant to Na^+ ions. In one study, NaOH concentrations were applied as 0.1–0.9 N and the optimum NaOH concentration was 0.46 N [25]. In this study, the optimum concentration of NaOH was determined as = 0.45 N (3 N × 0.15) for the 10% solids reactor (R_{14}).

Table 3 shows the comparison of the increases in biogas production and methane production with the literature value as a result of alkali thermal pretreatment. In the literature, according to Salehian et al. [26], the highest incremental biogas yield was 181.2%. In this study, the incremental biogas yield was 136.12% as a result of NaOH thermal pretreatment. As it was understood from the result, the amount of alkali was used in the pretreatment greatly affected the production of biogas.

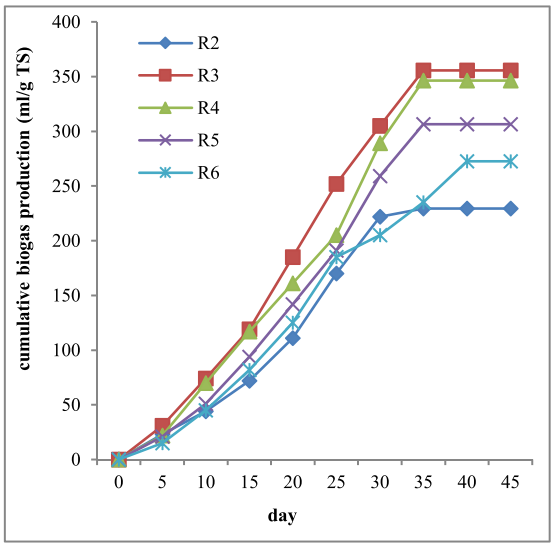
The biogas contents of the pretreated and untreated reactors are given in Table 4. The highest CH_4 content was 63.5% in R_{14}. The lowest methane content was 57.5% in R_{17}. The CO_2 content varied among 36.1–42.0%. H_2S values varied among 885–1553 ppm. While the H_2S value of the untreated reactor was 774 ppm, it increased as the pretreatment was applied. The possible reasons for this are that the lignocellulosic components, which were dissolved by the pretreatments, reacted more with the S^{2-} ion.

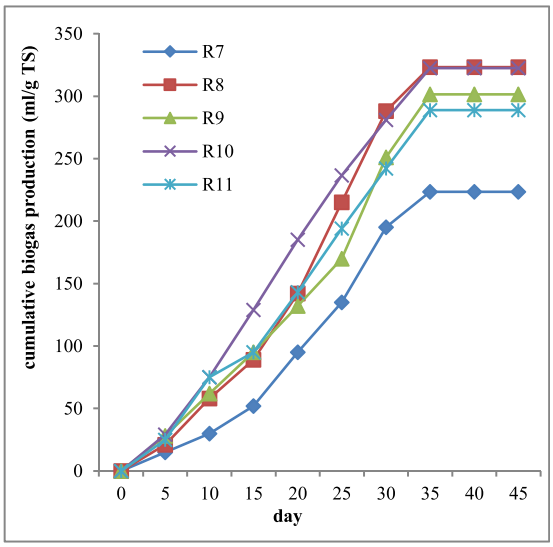
Figure 3 shows the anaerobic process of all reactors applied alkali thermal pretreatment, acid thermal pretreatment, and untreated. The AD time was 45–50 days in the untreated reactor, while that of the alkali thermal and acid thermal pretreatments was 35–40 days. Thus, the hydrolysis step was shortened by about 10 days. R_3, R_8, R_{14}, and R_{18} were determined as the most efficient reactors.

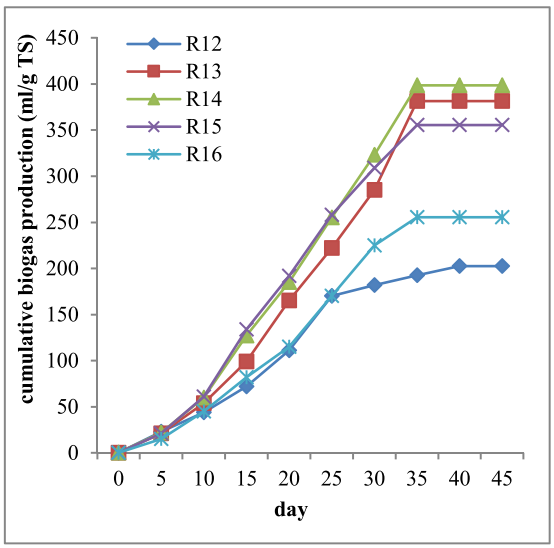
In Fig. 3, biogas production for the first 10 days for the untreated reactor (R_1) was 23.98 ml/g TS. However, at the same time, in reactors R_3, R_8, R_{14}, and R_{18}, these values were 74, 58, 60, and 69 ml/g TS, respectively. The implementation of the pretreatment began to increase biogas production significantly from day 10 onwards. A similar situation occurred in the reactor mixed with SBP and vinasse equal masses, and the increase in biogas production was 29.88% on the 8th day of enzymatic pretreatment [15]. In this study, the increase in biogas production on the 10th day varied between 141.86 and 187.77% according to the alkali and acid amounts. The higher increases in this study were due to higher alkali or acid concentrations. Thus, the cumulative biogas production of all reactors was consistent with the literature.

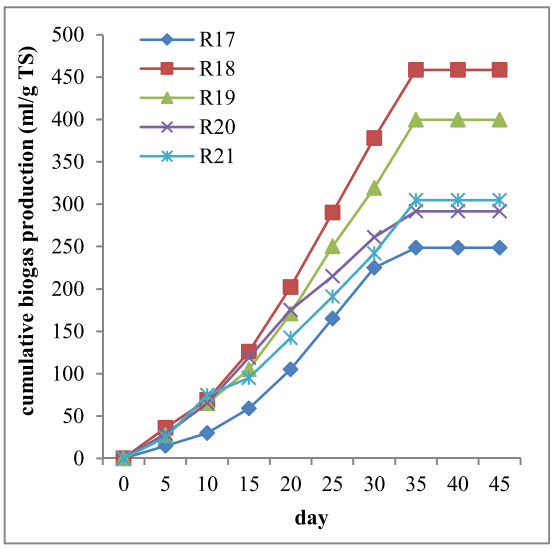
Table 4 Biogas content as a result of pretreatment, acid pretreatment, and alkali pretreatment

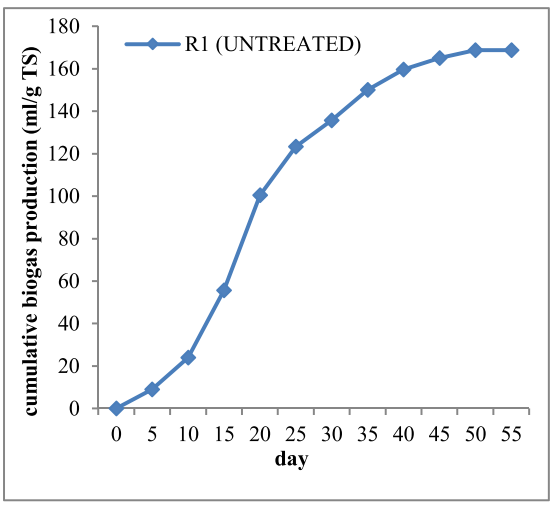
Reactor	CH_4 % (v/v)	CO_2 % (v/v)	H_2S (ppm)
R_1	60.2 ± 1.5	39.1 ± 1.6	774 ± 24
R_2	62.4 ± 1.9	37.4 ± 2.0	885 ± 25
R_3	58.5 ± 2.1	41.1 ± 1.9	1152 ± 38
R_4	56.9 ± 2.2	36.9 ± 2.0	1258 ± 21
R_5	60.0 ± 3.4	39.6 ± 3.2	1325 ± 27
R_6	62.5 ± 3.3	37.1 ± 3.5	1525 ± 35
R_7	63.4 ± 4.2	36.1 ± 3.5	952 ± 21
R_8	62.5 ± 4.1	37.2 ± 3.4	998 ± 35
R_9	59.8 ± 3.2	40.0 ± 3.2	1098 ± 24
R_{10}	58.9 ± 2.1	40.9 ± 2.5	1352 ± 32
R_{11}	59.9 ± 1.9	39.8 ± 2.1	1412 ± 25
R_{12}	60.5 ± 2.8	39.2 ± 2.6	925 ± 22
R_{13}	61.2 ± 2.5	38.5 ± 2.3	992 ± 21
R_{14}	63.5 ± 2.4	36.1 ± 2.2	1065 ± 31
R_{15}	63.2 ± 2.7	36.5 ± 2.4	1032 ± 25
R_{16}	58.5 ± 3.0	41.2 ± 2.8	1285 ± 22
R_{17}	57.5 ± 2.5	42.0 ± 2.3	1009 ± 19
R_{18}	58.6 ± 2.1	41.0 ± 2.3	1235 ± 24
R_{19}	60.5 ± 2.6	39.0 ± 2.8	1365 ± 29
R_{20}	62.5 ± 3.4	37.2 ± 3.2	1495 ± 35
R_{21}	59.8 ± 2.0	40.0 ± 2.1	1553 ± 33


a
cumulative biogas production (ml/g TS)
day
R2
R3
R4
R5
R6


b
cumulative biogas production (ml/g TS)
day
R7
R8
R9
R10
R11


c
cumulative biogas production (ml/g TS)
day
R12
R13
R14
R15
R16


d
cumulative biogas production (ml/g TS)
day
R17
R18
R19
R20
R21


e
cumulative biogas production (ml/g TS)
day
R1 (UNTREATED)

◀ **Fig. 3** CBP rates of all reactors during thermochemical pretreatment. **a** H_2SO_4 thermal pretreatment. **b** HNO_3 thermal pretreatment. **c** NaOH thermal pretreatment. **d** KOH thermal pretreatment. **e** Untreated

Figure 4 shows the relationship between the amounts of TS, VS, and sCOD according to the pretreatment amounts which were optimized as a result of acid and alkali pretreatments applied to organic matter. Initially, sCOD value of organic matter was determined as 6850 mg/L. sCOD removal result of the H_2SO_4 thermal, HNO_3 thermal, NaOH thermal, and KOH thermal pretreatments was 83.21%, 93.57%, 71.53%, and 105.54%, respectively. After the pretreatments were applied, the amounts of VS and TS were decreased. The increase in sCOD amounts of organic substances up to about twice as a result of thermochemical pretreatment was supported in a study by Kavitha et al. [29].

As a result of the pretreatment applied in different ratios, cellulose, hemicellulose, and lignin removals are shown in Table 5. In H_2SO_4 thermal pretreatments, cellulose, hemicellulose, and lignin removals increased as the amount of acid increased. The highest cellulose, hemicellulose, and lignin removals were 27.7%, 30.5%, and 37.6% in R_7, respectively. As a result of HNO_3 thermal pretreatment, the highest cellulose, hemicellulose, and lignin removals were 26.8%, 31.9%, and 39.8% in R_{11} respectively. As a result of acid thermal pretreatment, lignin removal showed a significant increase in acid amounts for 15% of the solids in the reactor. Cellulose and hemicellulose removals increased as the amount of acid increased, but reached the point of saturation after R_5 and R_{10}. In NaOH thermal pretreatment, lignin removal increased as the amount of alkali increased. Cellulose and hemicellulose removals did not increase significantly as lignin. As a result of the NaOH thermal pretreatment, the highest cellulose removal was 38.9% in R_{16} and the highest hemicellulose and lignin

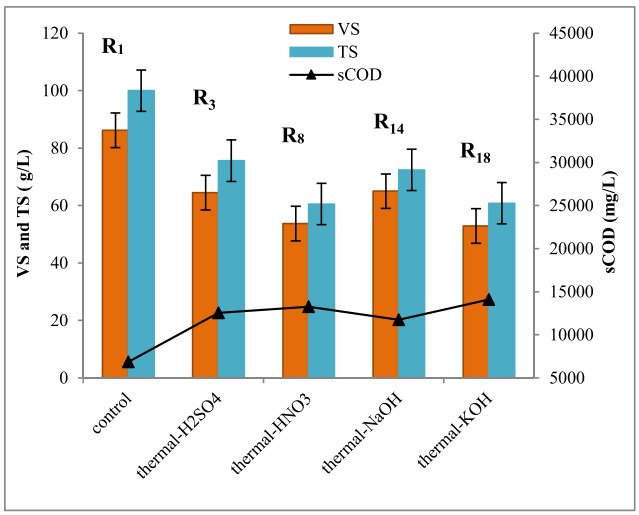


Fig. 4 Change of TS, VS, and sCOD quantities of organic matter as a result of acid-alkali thermal pretreatment

removal rates were 35.9% and 45.9% in R_{16}, respectively. In KOH thermal pretreatments, cellulose, hemicellulose, and lignin removals increased as the amount of acid increased. The highest cellulose, hemicellulose, and lignin removals were 34.5%, 35.5%, and 46.8%, in R_{21} respectively. In one study, rice straw was applied to 0.01% (v/v) H_2SO_4 solution at 120 °C for 60 min. After this pretreatment, cellulose, hemicellulose, and lignin removals were 31.6%, 32.9%, and 66.5%, respectively. As a result, high-temperature acid pretreatment resulted in the removal of most lignin [30]. In this study, alkaline thermal pretreatment was more efficient than acid thermal pretreatment in lignin removal. In one study, the alkaline thermal pretreatment was prepared to be applied to the corn stalk for 10 h at 90 °C (with a ratio of 2:1 (w/w) with the banana peel ash and lime). After this pretreatment, cellulose, hemicellulose, and lignin removals were 16.3%, 32.9%, and 45.3% respectively. However, when the same pretreatment was applied to rice straw, the removals of cellulose, hemicellulose, and lignin were 16.6%, 29.7%, and 38.7% ,respectively [31]. In this study, the removal of cellulose was higher. Possible reasons for this were the excessive use of acid or alkali quantities. In another study, pretreatment was performed with the addition of NaOH solids to the reactor at a rate of 7% (w/w) and was exposed to for 60 h at 60 °C. As a result of this pretreatment applied to rice straw, the removals of cellulose, hemicellulose, and lignin were realized as 19.1%, 77.5%, and 61.0% respectively [32]. Thus, acid pretreatments were more effective in hemicellulose removal. However, in this study, the difference of acid or alkali pretreatments in hemicellulose removal was not significant.

Figure 5 shows SEM images of the surface of the organic sample untreated and pretreated. According to the untreated, it was observed that the surface sample of the organic sample had a surface crystal and a hard layer. As a result of H_2SO_4 thermal pretreatment, the surface hardness of the organic sample was reduced. The thinner and softer surface formed. As a result of HNO_3 thermal pretreatment, the surface hardness of the organic sample decreased and cracks of about 1–5 μm were formed. Possible causes of these cracks include HNO_3 thermal pretreatment. As a result of the NaOH thermal pretreatment, the surface sample of the organic sample was reduced and surface cracks were about 1–5 μm in size. The possible causes of these cracks include NaOH thermal pretreatment. A 1000-fold enlarged surface shows a small size (1–5 μm) of pores opening on the surface of a lignocellulosic part. As a result of the KOH thermal pretreatment, it was observed that the surface crystal of the organic sample decreased and large pores with a circular appearance about 5–30 μm were observed. It was observed that these pore sizes were different from those of other pretreatments and were larger in size. KOH thermal pretreatment is among the possible causes of the pores formed in this large structure. In the previous study, SEM images were given as a result of

Table 5 Removal of lignocellulosic components as a result of acid thermal and alkali thermal pretreatments

Reactor	Cellulose removal (% w/w)	Hemicellulose removal (% w/w)	Lignin removal (% w/w)
R_2	18.4 ± 3.2	10.5 ± 2.2	10.2 ± 3.1
R_3	19.5 ± 2.1	19.7 ± 1.5	22.4 ± 5.1
R_4	22.3 ± 1.8	25.2 ± 1.9	32.5 ± 2.9
R_5	27.4 ± 2.8	30.2 ± 2.5	37.4 ± 2.5
R_6	27.7 ± 3.5	30.5 ± 2.2	37.6 ± 4.2
R_7	7.8 ± 2.1	11.6 ± 3.5	12.5 ± 3.8
R_8	15.6 ± 2.2	20.5 ± 3.3	22.2 ± 5.4
R_9	21.2 ± 3.5	25.4 ± 4.2	37.6 ± 3.5
R_{10}	26.5 ± 5.1	31.4 ± 4.4	39.5 ± 5.5
R_{11}	26.8 ± 5.3	31.9 ± 3.2	39.8 ± 6.1
R_{12}	32.4 ± 4.2	27.6 ± 2.1	30.4 ± 2.8
R_{13}	35.6 ± 3.2	28.5 ± 2.2	32.5 ± 4.1
R_{14}	37.8 ± 2.9	34.6 ± 3.4	35.6 ± 3.8
R_{15}	38.8 ± 5.5	35.9 ± 4.5	45.9 ± 3.9
R_{16}	38.9 ± 6.1	35.7 ± 3.8	45.7 ± 4.5
R_{17}	30.4 ± 3.5	25.6 ± 4.1	32.6 ± 3.9
R_{18}	32.4 ± 3.2	28.6 ± 2.1	33.5 ± 4.4
R_{19}	31.8 ± 3.5	33.5 ± 1.9	35.6 ± 6.7
R_{20}	32.9 ± 4.2	34.4 ± 3.4	46.7 ± 5.5
R_{21}	34.5 ± 5.0	35.5 ± 1.8	46.8 ± 5.4

ultrasound wave pretreatment of organic matter. According to these images, 10-μm-tall cavities were observed [33].

3.2 Statistical analysis results

Pearson correlation coefficients of the same pretreated reactors were examined between each other. The closer the value of correlation coefficient is to 1, the stronger the correlation among the variables is [34]. The lowest correlation coefficient was 0.986 as a result of H_2SO_4 thermal pretreated reactors (R_2–R_6). The lowest correlation coefficient between HNO_3 thermal pretreated reactors (R_7–R_{10}) was 0.986. The lowest correlation coefficient between NaOH thermal pretreated reactors (R_{12}–R_{13}) was 0.974. The lowest correlation coefficient between KOH thermal pretreated reactors (R_{17}–R_{20}) was 0.986.

3.3 Data analysis results

Kinetic models are often used in AD processes to estimate experimental results and to control anaerobic process performance [35]. MR and MG models were implemented to the reactors which give optimum results for each pretreatment. These reactors were designated as R_1 for untreated, R_{14} for NaOH pretreatment, R_{18} for KOH pretreatment, R_3 for H_2SO_4 pretreatment, and R_8 for HNO_3 pretreatment. Determined constants of the optimum reactors for the MR and MG model are given in Table 6.

Specific biogas productions were found to be proportional to actual biogas production in all reactors. Kinetic constant of λ showed the lag time needed by bacteria to adapt in the substrates [36]. After the pretreatments were applied, the delay times decreased in all reactors. It was reported that as a result of the MG model, λ was found to be 4.083 days in untreated reactor, while the values of − 2.725 and − 2.169 days were lower in the pretreated condition [37]. In this study, the λ values in the untreated reactor for the MG model were 6.739 days and the lowest after the pretreatment was 5.494 days. In the modeling study of SBP for the MG model, it was reported that λ values decreased and μ_m and A values increased as a result of enzymatic pretreatment [15]. This study supported this situation.

AD of slaughterhouse wastes was carried out by Ware and Power [38] and as a result of MR model application, R^2 values varied among 0.991–0.999. In this study, R^2 values varied between 0.996 and 0.998 for the MR model and between 0.997 and 0.999 for the MG model. The best fitting reactor for the MR model was the R_{14}, while the best fitting reactor for the MG model was R_3. In the MG modeling study, the deviation between the estimated and actual values varied between 0 and 17.5% [39]. In this study, the maximum deviation was 26.2% for the MG model (in R_{14}) and was 21.15% for the MR model (in R_{14}).

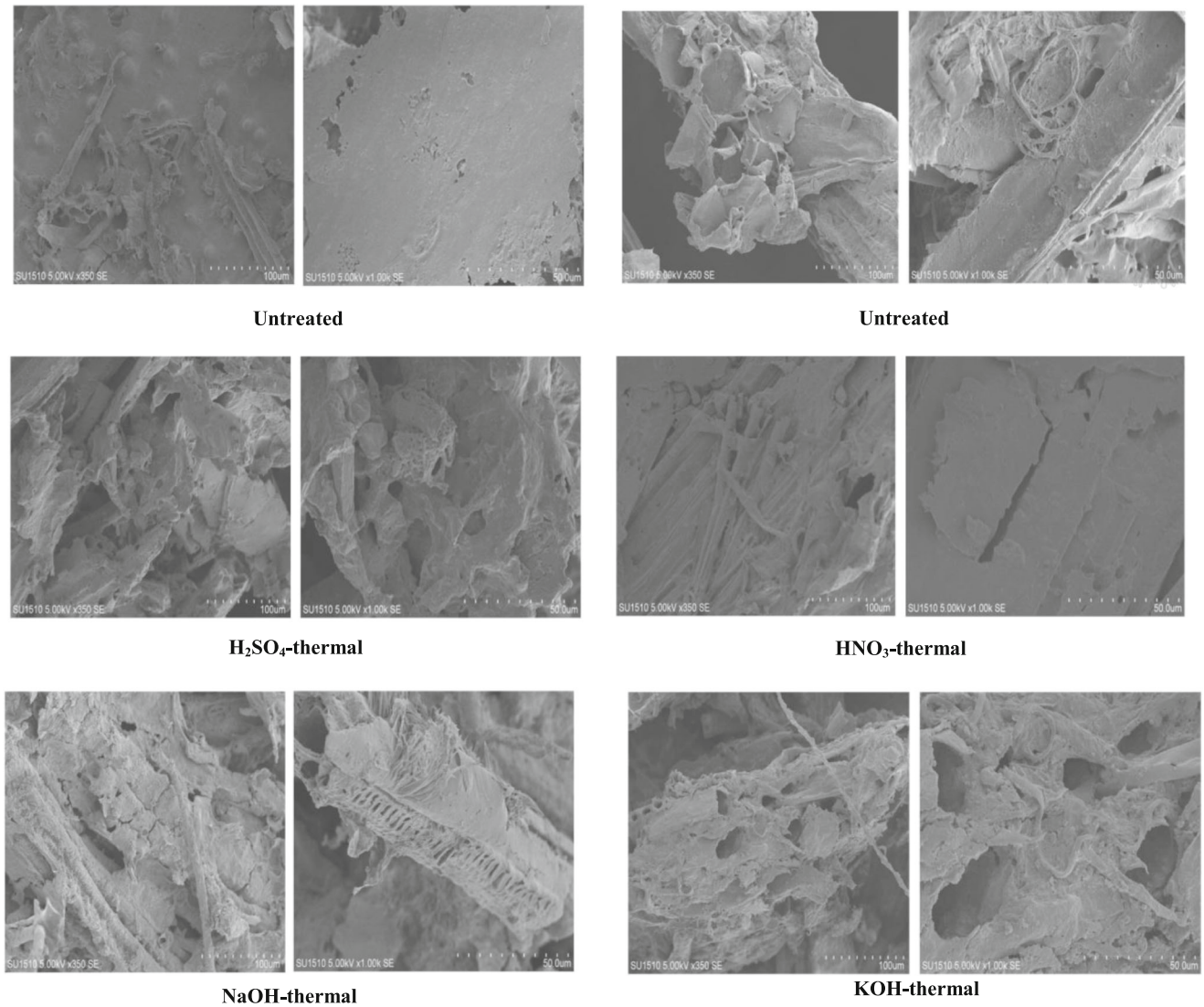


Fig. 5 SEM images of the surface as a result of thermal acid pretreatment, thermal alkali pretreatment, and untreated

4 Conclusion

In this study, biogas production was successfully increased by the alkaline thermal and acid thermal pretreatments. The highest biogas yield was achieved by KOH thermal pretreatment in R_{18}. In this reactor, incremental biogas yield was 171.72%. The effects of acid thermal and alkali thermal pretreatments for sugar beet pulp were compared and KOH thermal pretreatments were more effective than acid thermal pretreatments. The reason for this may be the further dissolution of lignocellulose. Alkaline thermal pretreatments were more effective than acid thermal pretreatments for the removal of

Table 6 Determined constants of modified Richards and modified Gompertz models with experimental data

Reactors	Modified Richards model					Modified Gompertz model			
	λ (day)	μ_m (mL/g TS.d)	A (mL/g TS)	v	R^2	λ (day)	μ_m (mL/g TS.d)	A (mL/g TS)	R^2
R_1	6.726	6.713	170.354	0.058	0.996	6.739	7.184	169.816	0.998
R_3	6.398	20.736	395.973	0.931	0.996	5.494	13.103	429.124	0.999
R_8	6.249	53.591	332.195	2.692	0.997	6.553	12.632	403.965	0.998
R_{14}	6.382	17.645	482.785	0.748	0.998	6.410	14.617	502.962	0.998
R_{18}	6.467	43.267	496.323	1.775	0.996	6.512	17.098	595.875	0.997

cellulose, hemicellulose, and lignin components from lignocellulosic components. Optimization of acid and alkali thermal pretreatments was performed and no higher yields were obtained from higher acid or alkali pretreated solutions. The cumulative biogas yields were successfully adapted to the modified Richards model and modified Gompertz model.

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