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Optimization of temperature and pretreatments for methane yield of hazelnut shells using the response surface methodology

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ABSTRACT

In this study, NaOH pretreatment, H_2SO_4 pretreatment, thermal pretreatment and production temperature were optimized to ensure maximum methane yield from hazelnut shells (HS) using the response surface methodology (RSM). A Box-Behnken design was achieved with four different independent variables and one dependent variable (methane yield). A total of 29 tests were performed after pretreatment according to the RSM design and to different production temperatures, suggesting optimum values for NaOH pretreatment, H_2SO_4 pretreatment, thermal pretreatment and production temperature were 3.5% w/v, 2.56% v/v, 145.66 °C and 34.65 °C, respectively. Under these conditions, the RSM-predicted methane yield was 215.896 mL/g volatile solid (VS). The high R^2 value (0.9904) showed that the model could be applied effectively in the digestion of HS for the predicted methane yield according to the production temperature and pretreatments. In addition, lignocellulosic solubilisation was tested after pretreatment of the reactors according to the RSM operating conditions, which showed that the highest cellulose, hemicellulose and lignin solubilisation that could be achieved was 38.7% w/w (R_{10}), 36.9% w/w (R_{22}) and 50.5% w/w (R_{10}), respectively. The modified Gompertz model supported the experimental cumulative methane yields (CMYs).

1. Introduction

One of the biggest problems facing the world in recent years is managing waste and energy needs. Rapid population growth has caused serious problems in terms of energy needs and disposal of waste [1]. Anaerobic digestion (AD) of agricultural wastes is the most effective method of address these issues because it allows for stabilization of wastes and recovery of biomass energy [2].

Hazelnut shells (HS) are among the main forms of agricultural waste in Turkey [3]. The actual amount of hazelnut shells in 2008 was reported to be 566,437 tonnes [4]; indeed, Turkey alone was responsible for 56% of world hazelnut production in 2016 [5]. HSs are responsible for 48.25% of the mass of hazelnuts produced [6] and, therefore, are the main waste associated with hazelnut production. HS are not yet used in the industrial area in Turkey [7]. Due to the high organic matter content of the hazelnut shell, it is added to soils to improve physical properties such as stability, aggregation, hydraulic conductivity and ventilation [8]. One of the alternative uses for HS, however, is biogas production, which could be very important for Turkey given the country's predominance in world hazelnut production [6].

Due to the fibrous carbohydrates such as cellulose, hemicellulose and lignin found in HSs, it is not suitable for direct AD. Several pretreatment (acid, alkaline and thermal) technologies have been developed to provide for AD of lignocellulosic components such as HSs [9]. Lignin is the most resistant to biodegradation as it forms a barrier to the microorganisms that access cellulose [10]. Acid pretreatments allow for the greatest amount of hydrolysis of hemicellulose from lignocellulosic components [11]. This pretreatment is useful in terms of converting energy plants into energy. As a result of the acid pretreatment of *Salvinia molesta*, biogas production was increased from 13.28 mL/g volatile solid (VS) to 24.14 mL/g VS [12]. Alkaline pretreatments allow for the greatest amount of lignin hydrolysis [13]. In addition, they increase the internal surface area of the lignocellulosic material. As a result of the alkaline pretreatment of sugarcane bassage, biogas production was increased by 330% [14]. Thermal pretreatment is a physical pretreatment based on the application of organic matter in the temperature range 50–240 °C) [15]. Prior to the AD of wheat, barley, rice and corn stalk, thermal pretreatment performed at 120 °C for 30 min has resulted in an increase in methane yields by 64.2, 40.8, 32.4, and 7.1%, respectively, compared to untreated controls [16]. Other studies have showed a 27%

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increase in methane yield from thermal pretreatment at 200 °C for 5 min [17]. In the current literature, acid, alkali and thermal pretreatment studies of organic wastes containing mostly lignocellulosic components are available, but to date there are no studies that have examined the various pretreatment effects on HS. Also, as each pretreatment method affects different parts of the lignocellulosic material, differences will be observed in the results obtained by different pretreatments of the same substrate [9]. Therefore, the examination of various pretreatment methods and combinations of pretreatments will further a better understanding of the specific effects of different pretreatments on certain substrate types. AD studies of HSs are very limited in the literature. In one study, the biogas potential of HSs was determined as 3,176,636 m^3/year for the city of Giresun [6].

Response surface methodology (RSM) effectively optimizes multiple parameters at the same time to eliminate the shortcomings of optimization techniques that require a large number of experiments and thus considerable time. RSM considerably decreases the number of trials required to predict the conditions for optimal performance, studies the interactive effects between multiple factors, improves the interpretation of complex phenomena and provides a basis for process scaling and maximising process efficiency [18]. One such RSM experimental design, the Box-Behnken design, is the most widely used statistical method to predict the relationship between the independent variable and results [19]. In the literature, RSM has been used to optimize various factors in AD such as the C/N ratio, substrate mixing ratio, substrate pretreatment and feed rate [20–22]. Previous studies have focussed on optimization of micronutrient concentrations [23], working temperature, pH, solid ratio, and retention time [24] through the use of RSM applications; they have also focussed on optimization of substrate weight, ultrasonic duration time, alkaline (NaOH) pretreatment time [25] and inoculum, total solid, mixing ratio, and temperature [26]. However, the RSM optimization of acid pretreatment, alkali pretreatment, thermal pretreatment and temperature parameters is not, to the best of our knowledge, currently available in the literature.

The aim of this study was to provide the RSM optimization of acid pretreatment, alkali pretreatment, thermal pretreatment optimization and digestion temperature (production temperature) for the AD of HSs. Although acid, alkali and thermal pretreatment considerably increased methane yields, it is clear that there are associated costs [9]. Therefore, RSM optimization was achieved in order to obtain higher yields with less volumes or extent of pretreatment (optimum amount).

2. Materials and methods

2.1. Organic raw materials

HS was collected from Giresun, Turkey. Foreign materials such as leaf and soil were removed from the sample. The HS were thoroughly cleaned and then ground to a particle size range of 0.1–0.5 mm by means of a grinder, with the resultant powder then maintained at 4 °C for subsequent anaerobic experiments and pretreatments. Freshly used cattle manure has an important effect in accelerating enzymatic hydrolysis due to its mesophilic methanogens [27], and thus fresh cattle manure was used as inoculum. All batch reactors were set to an substrate/inoculum ratio of 5 on a VS basis.

2.2. Batch anaerobic digestion study

AD processes were carried out in 500 mL batch reactors. Heating was provided by the water bath and adjusted to lie within the temperature range (either 23 °C, 39 °C or 55 °C) provided by the RSM. The reactor temperature kept even throughout the mix using a magnetic stirrer heater. Solid content has ranged from 4% to 15% in previous studies [28], whereas here the total solid (TS) in all reactors was 10% w/w. For AD, the apparatus consisted of a silicone hose, syringe, 0.5 L serum bottle, pH meter and 0.5–0.3 L gas storage bag. At the beginning of each AD experiment, batch reactors were flushed with N_2 gas for 5 min to obtain anaerobic conditions and remove oxygen from the reaction medium. The optimum pH for AD is neutral [29], so the pH of the batch reactors was adjusted to 7.0 using only sodium hydroxide or sulphuric acid solution at the beginning of the experiments. The biogas content was measured with a 0.3–0.5 L gas collection bag every day and maintained to determine the content via gas chromatography [30]. The reactors were continuously stirred using a magnetic stirrer at a speed of 100 rpm to ensure homogeneity of slurry [31]. AD was terminated when the last measured value was < 2% of the previous measured value. All AD experiments were performed in triplicate. For each experimental group, a control reactor and a pretreated reactor were used. To determine whether the temperature distribution of the reactors was homogeneous, the temperature of the upper slurry was measured at regular intervals using a thermometer.

2.3. Pretreatments

Chemical pretreatments were categorized as being either alkaline or acid pretreatments. Alkali pretreatments [32] were carried out using a 0–5% w/v NaOH reagent. Acid pretreatments [33] were performed using a 0–5% v/v H_2SO_4 reagent. In a 500 mL erlenmeyer, 50 g of biomass were soaked in 500 mL of 1–5% (w/v) NaOH solution. This erlenmeyer was allowed to stand at room temperature (about 25 °C) for 24 h. Acid pretreatments were applied using the same concentration of H_2SO_4 and biomass at the same rate. After the acid and alkaline pretreatment, the biomass was filtered off and then dried in air until use. The thermal pretreatments [15] were applied to each reactor at temperatures determined by RSM. Thermal pretreatments were performed in an incubator at 50, 100 and 150 °C. Thermal pretreatment times were fixed at 2 h. The amounts of cellulose, hemicellulose, lignin, and the soluble chemical oxygen demand (SCOD) were analysed before and after pretreatment.

2.4. Analytical methods

In Table 1, TS, volatile solid (VS), ash, C, N, SCOD, cellulose, hemicellulose and lignin analyses were performed before starting AD on the organic waste. The pH value was determined using a pH meter (FE28-S, METTLER-TOLEDO Co., Shanghai, China). TS and VS were analysed according to Standard Method 2540G [34]. The carbon to nitrogen ratio (C:N) of the lignocellulosic substrates was determined via an elemental analyser (Elemental Analyzer NA 2500). The lignocellulosic contents (cellulose, hemicellulose and lignin) were measured using a fibre analyser (ANKOM A2000i, US) [35]. Liquid samples were centrifuged at 10,000 rpm using a 0.25 μm membrane filter. Soluble chemical oxygen demand (SCOD) analyses were performed according to Standard Method 5220C [34]. The percentage (v/v) methane content was determined via gas chromatography (GC), Shimadzu GC-8A, Japan, SUS Packed Column Porapak Q, 3 mm × 5 m I.D., 170 kPa inlet pressure and FID detector with 50 °C column over temperature.

Table 1
Characteristics of inoculum and hazelnut shells.

Parameters	Inoculum	Hazelnut shells
TS (% w/w)	19.95 ± 1.00	92.12 ± 1.00
VS (% TS)	79.90 ± 0.50	91.62 ± 0.50
Ash (% w/w)	3.39 ± 0.10	11.32 ± 0.10
sCOD (g O_2/L)	104.5 ± 1.12	10.22 ± 1.28
pH	7.79 ± 0.03	–
Cellulose (% w/w)	21.30 ± 0.5	27.55 ± 0.52
Hemicellulose (% w/w)	18.92 ± 1.0	28.92 ± 1.09
Lignin % w/w)	10.85 ± 0.5	39.91 ± 0.93
% C (% w/w)	30.15 ± 0.50	49.25 ± 0.50
% N (% w/w)	1.92 ± 0.15	1.01 ± 0.15
C/N	15.70 ± 0.37	48.76 ± 1.09

The concentration of hydrogen sulphide in the biogas was directly analysed via an electrochemical detector (GFM series, GASDTA, UK). SCOD analyses were performed according to the closed reflux titrimetric method [36].

2.5. Kinetic study

The kinetics of the methane yield in a batch reactor were assumed to be suitable for the growth rate of the methanogens in these same reactors. Averaged data for the methane yield derived from AD experiments was used in kinetic modelling. In this study, estimated values for the modified Gompertz (MG) model were obtained using CMYs measured every 5 days. This model is given in Eq. (1).

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

where y is the estimated methane yield (mL/g VS) with respect to time t (day); A is ultimate methane yield at $t = \infty$ (mL/g VS); λ is the lag phase (day) and e is a Euler's function equal to 2.71828. In this study, the Statistical Package for the Social Sciences (SPSS 23.0) program was used to calculate growth curve parameters (λ, μ_m, A) by fitting to experimental growth curves. The model compatibility for the reactors was determined according to the R^2 values so determined.

2.6. Statistical experimental design

RSM is a mathematical technique that interprets the relationship between multiple independent variables and dependent variables and determines the best experimental conditions [37]. The Box-Behnken design is advantageous in that it allows for fewer experimental runs to gain a reasonable optimization [38]. A Box-Behnken design was performed to examine three different pretreatment (thermal, alkali and acid) and production temperature effects. Methane yield (mL/g VS) was used as the response variable. NaOH concentration (0–5% w/v), H_2SO_4 concentration (0–5% v/v), thermal pretreatment temperature (50–150 °C) and production temperature (23, 39 and 55 °C) were chosen as the independent variables. The NaOH pretreatment (A), H_2SO_4 pretreatment (B), thermal pretreatment (C) and production temperature (D) were chosen as shown in Table 2. Concentrations reported in the literature were used to determine the concentration ranges of H_2SO_4 [12], NaOH [39] and thermal [9] pretreatments. Then, a statistical approach, the RSM with a Box–Behnken design, was applied.

A quadratic polynomial regression model was assumed for predicting the independent variable (response). This model was:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (3)$$

where Y is dependent upon x_i, the ith independent variable; β_0 is a constant term or the offset; β_i is the ith linear coefficient; β_i is a quadratic coefficient and $\beta_{ij}$are the interaction coefficients. The Design Expert 7.0.0 (trial version, Stat Ease Inc., Minneapolis, USA) computer program was used to determine the coefficients via regression analysis of the experimental data.

Table 2
Levels of factors and variables chosen for Box–Behnken experimental design.

Variable	Parameters	Level		
		−1 (Low)	0 (Medium)	+1 (High)
A	NaOH pretreatment	0	2.5	5
B	H_2SO_4 pretreatment	0	2.5	5
C	Thermal pretreatment	50	100	150
D	Production temperature	23	39	55

3. Results and discussion

3.1. Optimization and anaerobic digestion results

The matrix of the Box-Behnken design for methane yield was used as the response variable, with RSM-predicted methane yields, H_2S and CH_4 concentrations reported in Table 3. The values obtained were subject to response analysis to evaluate the relationship between NaOH pretreatment (A), H_2SO_4 pretreatment (B), thermal pretreatment (C) and production temperature (D). 29 reactors (Run) proposed by the RSM design were prepared with different combinations of NaOH pretreatment, H_2SO_4 pretreatment, thermal pretreatment and production temperature. The reactors of 29 different experimental designs were termed R_1 to R_{29}.

Experimental methane yields varied according to the severity of the pretreatment and the digestion temperature. Methane yields were examined at two different NaOH (2.5 and 5%, w/v), and H_2SO_4 pretreatment concentrations (2.5 and 5%, v/v), three different thermal pretreatment temperatures (50, 100 and 150 °C) and three different digestion temperatures (23, 39 and 55 °C). The highest methane yield so obtained was 238.67 ± 4.1 mL/g VS in reactor R_{15}. In the previous study, biogas production was 113 mL/g TS when the HS was thermally pretreated at 100 °C and the digestion temperature was 39 °C [6]. In this study, the methane yield was 150.06 mL/g VS from reactor R_{27}. Although the pretreatment temperature and digestion temperature were the same, the reason for the different production yields can be attributed to the different thermal pretreatment temperature times. In the previous study, the thermal pretreatment temperature was applied for 1 h [6]. In one study, pistachio hulls, which have similar organic components to HSs, were subjected to thermal and chemical pretreatment prior to AD, and for which methane yields varied between 78.5 and 213.4 mL/g VS [40]. Therefore, the relationship between pretreatment and methane yields in this study was supported, at least to some extent, by the literature.

The methane and hydrogen sulphide contents of each reactor were analysed. The methane content of the reactors varied between 61.01% v/v and 55.85% v/v. Hydrogen sulphide content varied between 635 ± 402 and 1302 ± 319 ppm. Standard deviations for hydrogen sulphide content ranged from 185 to 512 ppm. Wang et al. [41] reported the standard deviation range in hydrogen sulphide concentrations after AD of lignocellulosic material, where the deviations in this study were of a similar range.

By applying multiple regression analyses the results could be expressed by a quadratic polynomial equation [42]. The equation so obtained as a function of real values is as follows:

Table 3
Box-Behnken design, optimization test and methane yield results.

Reactor (Run)	Independent variables				Experimental methane yield (mL/g VS)	Methane concentration (% v/v)	H_2S concentration (ppm)	RSM predicted methane yield (mL/g VS)
	A (NaOH pretreatment,w/v)	B (H_2SO_4 pretreatment, v/v)	C (thermal pretreatment, °C)	D (production temperature, °C)				
R_1	5	0	100	39	204.27 ± 3.8	62.52 ± 1.12	958 ± 355	194.95
R_2	2.5	2.5	150	23	68.92 ± 6.7	62.85 ± 1.52	1125 ± 412	69.93
R_3	2.5	2.5	100	39	225.8 ± 4.6	65.01 ± 0.95	1052 ± 326	215.84
R_4	2.5	2.5	100	39	221.42 ± 5.5	61.55 ± 2.05	1258 ± 452	215.84
R_5	0	2.5	100	23	60.4 ± 6.6	56.95 ± 2.08	1352 ± 352	60.01
R_6	5	2.5	50	39	184.61 ± 7.1	58.75 ± 1.52	1158 ± 255	189.80
R_7	2.5	0	150	39	202.52 ± 6.4	59.91 ± 0.99	1302 ± 319	199.86
R_8	0	2.5	50	39	144.61 ± 5.7	62.45 ± 1.52	1285 ± 199	138.54
R_9	2.5	0	100	55	201.91 ± 7.5	56.98 ± 2.55	966 ± 295	199.62
R_{10}	5	5	100	39	230.72 ± 7.2	55.85 ± 2.51	1085 ± 278	222.03
R_{11}	2.5	5	100	55	228.42 ± 6.9	58.45 ± 2.01	1232 ± 345	219.91
R_{12}	2.5	5	50	39	196.77 ± 5.9	62.25 ± 1.15	1145 ± 296	191.09
R_{13}	2.5	5	150	39	225.97 ± 7.0	63.15 ± 1.86	685 ± 319	221.90
R_{14}	2.5	2.5	100	39	210.14 ± 7.2	61.98 ± 1.75	789 ± 305	215.84
R_{15}	5	2.5	100	55	238.67 ± 4.1	60.85 ± 1.65	952 ± 421	230.72
R_{16}	2.5	0	50	39	170.02 ± 5.9	57.45 ± 1.55	1123 ± 295	165.75
R_{17}	5	2.5	100	23	78.6 ± 6.7	59.52 ± 0.85	635 ± 402	69.56
R_{18}	2.5	5	100	23	91.6 ± 5.8	58.84 ± 1.85	1185 ± 255	92.58
R_{19}	2.5	2.5	100	39	212.14 ± 7.2	59.81 ± 2.42	1095 ± 185	215.84
R_{20}	2.5	0	100	23	65.28 ± 6.2	58.95 ± 2.85	908 ± 259	65.48
R_{21}	0	2.5	100	55	159.61 ± 5.1	58.86 ± 2.65	888 ± 339	160.30
R_{22}	5	2.5	150	39	201.22 ± 4.1	59.85 ± 3.12	1257 ± 245	210.99
R_{23}	2.5	2.5	50	55	165.61 ± 7.2	59.35 ± 2.25	1168 ± 352	168.20
R_{24}	0	2.5	150	39	188.76 ± 7.7	64.75 ± 2.35	950 ± 308	182.26
R_{25}	2.5	2.5	100	39	209.96 ± 7.2	62.83 ± 2.09	809 ± 248	215.84
R_{26}	0	5	100	39	169.72 ± 6.7	57.76 ± 2.39	918 ± 365	178.65
R_{27}	0	0	100	39	150.06 ± 5.8	56.93 ± 1.38	955 ± 512	158.35
R_{28}	2.5	2.5	50	23	64.72 ± 4.5	58.62 ± 1.85	1155 ± 289	71.93
R_{29}	2.5	2.5	150	55	232.72 ± 3.8	60.59 ± 1.65	1291 ± 385	235.12

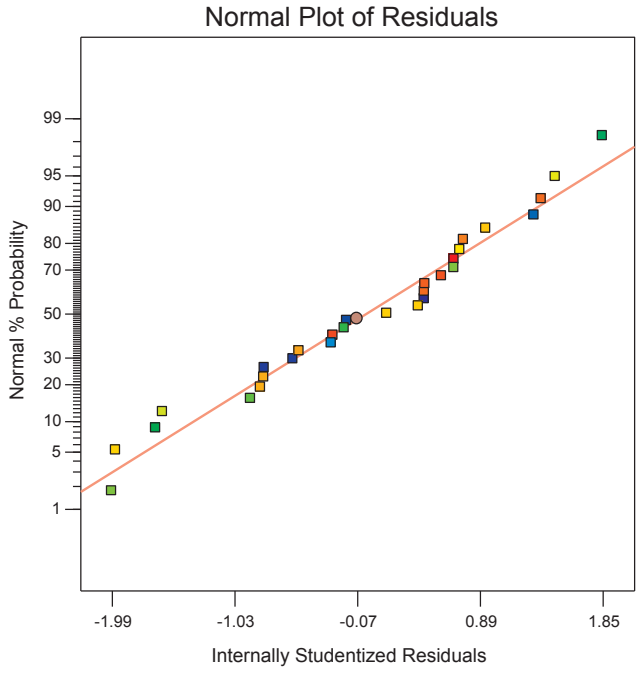
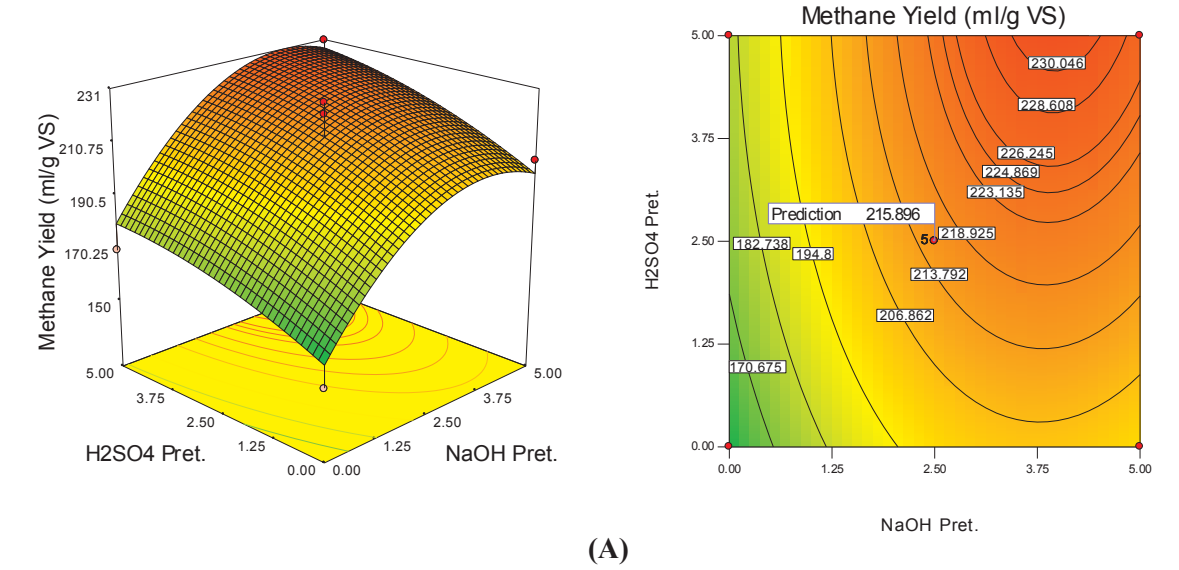


Fig. 1. Normal probability plots for methane yields.

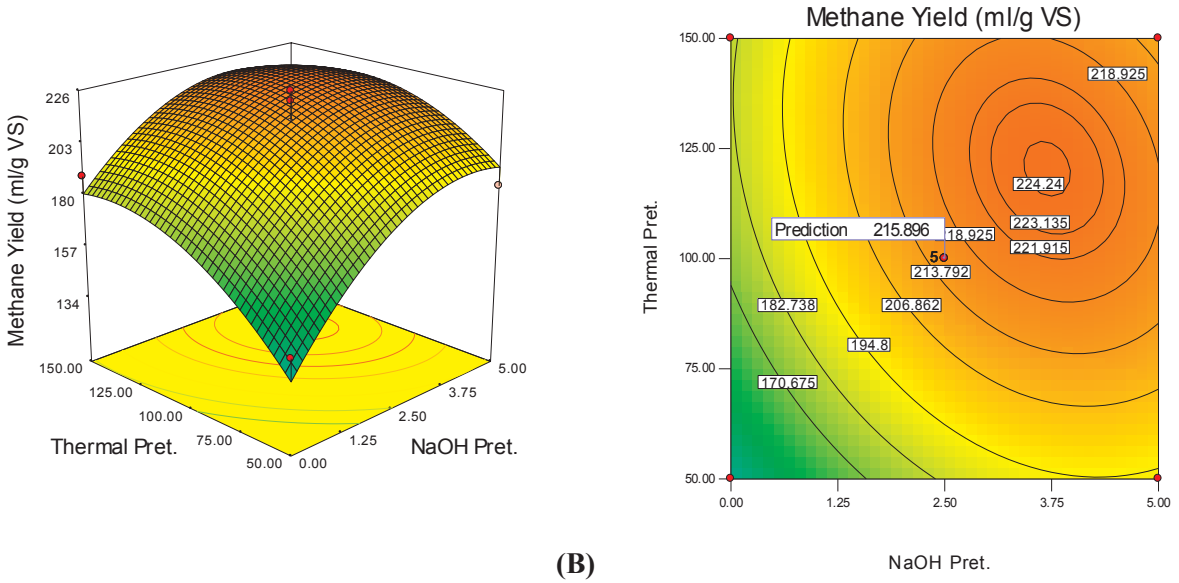
Table 4
ANOVA of the model.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	93972.92	14	6712.35	102.80[a]	< 0.0001
A-NaOH Pretreatment	5848.99	1	5848.99	89.58	< 0.0001
B-H_2SO_4 Pretreatment	1853.56	1	1853.56	28.39	< 0.0001
C-Thermal Pretreatment	3128.90	1	3128.90	47.92	< 0.0001
D-Production Temperature	52989.89	1	52989.898	11.53	< 0.0001
AB	11.53	1	11.53	0.18	0.6808
AC	189.61	1	189.61	2.90	0.1104
AD	925.98	1	925.98	14.18	0.0021
BC	2.72	1	2.72	0.042	0.8411
BD	9.025E-003	1	9.025E-003	1.382E-004	0.9908
CD	989.42	1	989.42	15.15	0.0016
A^2	2624.00	1	2624.00	40.19	< 0.0001
B^2	123.40	1	123.40	1.89	0.1908
C^2	1601.50	1	1601.50	24.53	0.0002
D^2	26953.41	1	26953.41	412.79	< 0.0001
Residual	914.15	14	65.30		
Lack of Fit	702.67	10	70.27	1.33[b]	0.4213
Pure Error	211.48	4	52.87		
Core Total	94887.07	28			

Std. Dev. = 8.08, C.V = 2.06, Mean = 172.59, PRESS = 4377.81, R^2 = 0.9904.
$Precision_{adeq}$ = 30.467, R^2_{adj} = 0.9807, R^2_{pred} = 0.9539.
[a] Significant in 5% level.
[b] No significant.

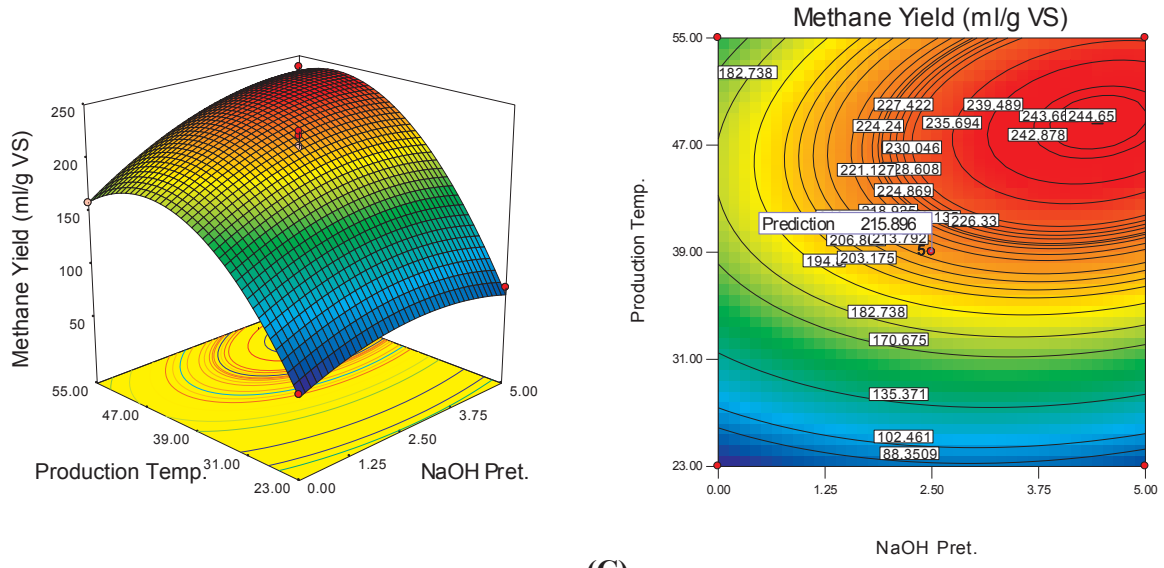


(A)

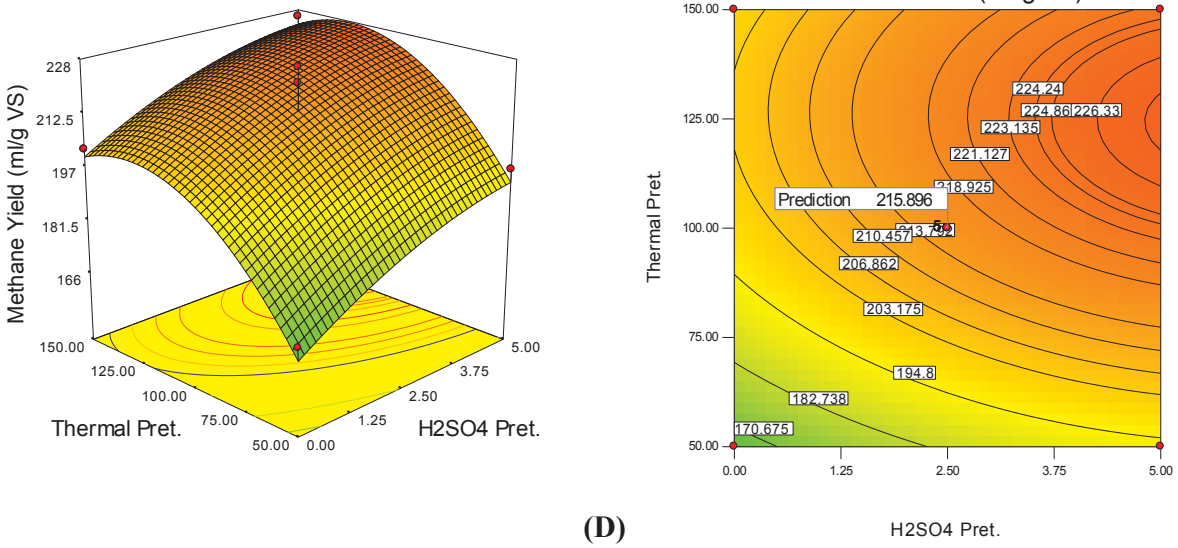


(B)

Fig. 2. 3D response surface and contour plots for methane yield at (A) H_2SO_4-NaOH pretreatments and (B) thermal-NaOH pretreatments.



(C)



(D)

Fig. 3. 3D response surface and contour plots for methane yield at (C) production temperature-NaOH pretreatment and (D) thermal-H_2SO_4 pretreatment.

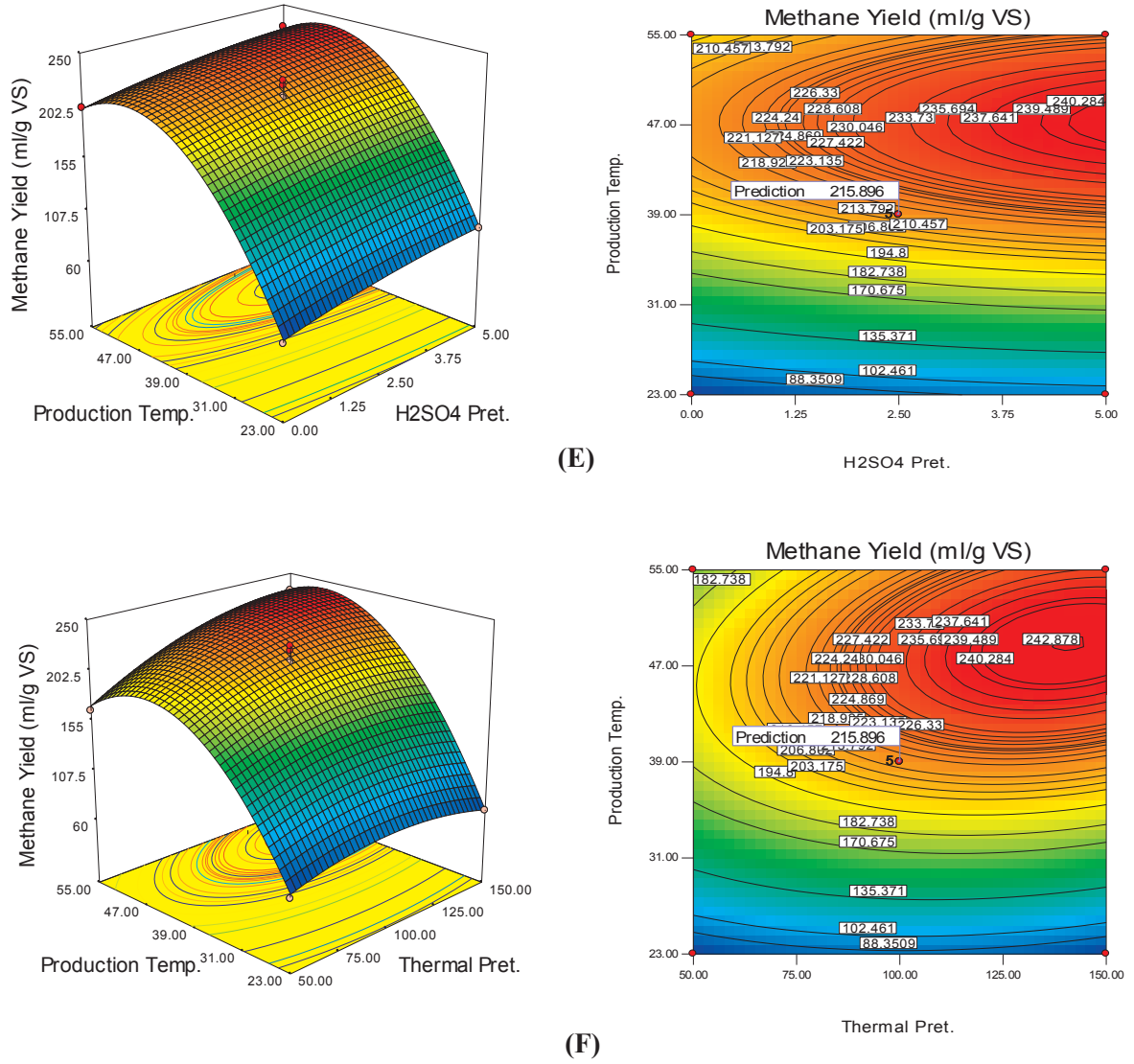


Fig. 4. 3D response surface and contour plots for methane yield at (E) production temperature and H_2SO_4 pretreatment, and (F) production temperature and thermal pretreatment.

$$\begin{aligned}(\text{Methane yield}) &= -383.04956 + 14.91578 * (\text{NaOH Pretretament}) + 8.39542 \\ &* (H_2SO_4\text{Pretreatment}) + 0.96747 * (\text{Thermal Pretreatment}) \\ &+ 20.87407 * (\text{Production Temperature}) + 0.27160 \\ &* (\text{NaOH Pretreatment}) * (H_2SO_4 \text{ Pretreatment}) + 0.27160 \\ &* (\text{NaOH Pretreatment}) * (H_2SO_4 \text{ Pretreatment}) - 0.055080 \\ &* (\text{NaOH Pretreatment}) * (\text{Thermal Pretreatment}) - 0.055080 \\ &* (\text{NaOH Pretreatment}) * (\text{Thermal Pretreatment}) + 0.38037 \\ &* (\text{NaOH Pretreatment}) * (\text{Production Temperature}) \\ &- 6.60000E - 003 * (H_2SO_4 \text{ Pretreatment}) * (\text{Thermal Pretreatme nt}) + 1.18750E - 003*(H_2SO_4 \text{ Pretreatment}) * (\text{Production Temperature}) + 0.019659 * (\text{Thermal Pretreatment}) \\ &* (\text{Production Temperature}) - 3.21808 \\ &* (\text{NaOH Pretreatment})^2 - 0.69788 * (H_2SO_4 \text{ Pretreatment})^2 - 6.28520E - 003 \\ &* (\text{Thermal Pretreatment})^2 - 0.25180 * (\text{Production Temperature})^2 \end{aligned} \quad (2)$$

Fig. 1 shows the normal probability and residual plots for the methane yield. These plots were examined to verify the adequacy and validity of the model. The data points appear to lie on a straight line showing the normal distribution of errors.

The mathematical regression model generated by RSM is given in Eq. (2). According to this model, NaOH pretreatment, H_2SO_4 pretreatment, thermal pretreatment and production temperatures each have a direct effect on methane yield. The production temperature's primary effect was on methane yield. When NaOH and H_2SO_4 pretreatments were applied together, it was observed that this could directly increase methane yield. However, the simultaneous thermal and alkali pretreatment was not as effective as simultaneous NaOH and H_2SO_4 pretreatment. In addition, NaOH, H_2SO_4 and thermal pretreatment had a second-order effect on methane production.

Analysis of variance (ANOVA) was used to assess the adequacy of the model. The statistical significance of Eq. (3) was verified by an F–test, with all associated data reported in Table 4. The F-value of 102.5 indicates the model was highly significant. A P-value less than 0.05 showed that the model terms were significant. The quadratic regression model indicated that the model was significant ($p < 0.05$). The P-value serves as a means to check the significance of coefficients, including the interaction power of each parameter. The higher the

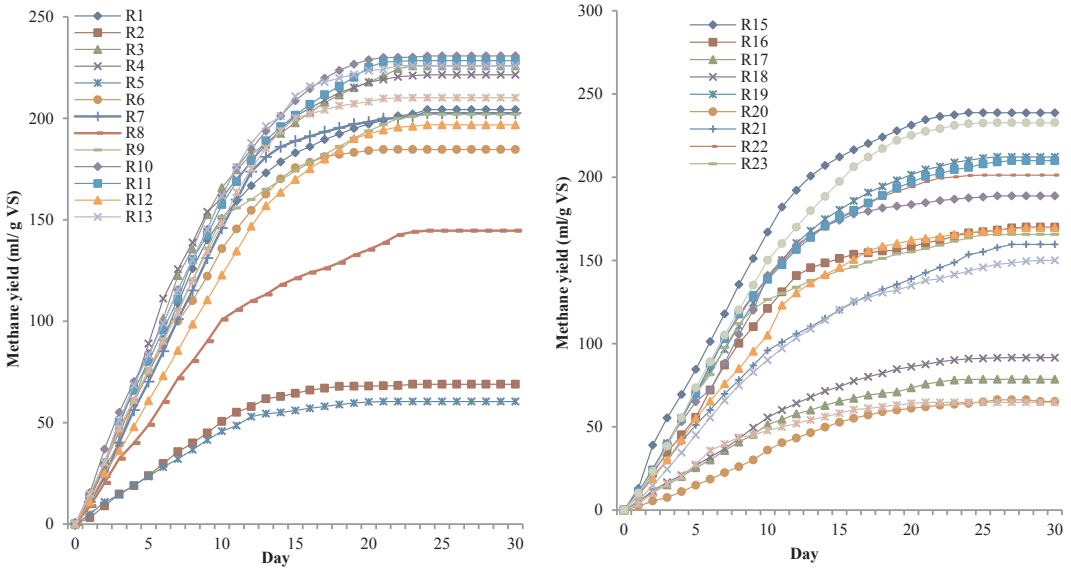


Fig. 5. Effect of pretreatments on lignocellulose content of hazelnut shell (R: reactor).

significance of the variables, the smaller the P-value [43]. The values of the experimental design seem to be very significant, at P = 0.6808, P = 0.1104, P = 0.8411, and P = 0.9908, respectively, except for AB, AC, BC and BD. The quadratic model terms seem to be highly significant except for B^2 (P = 0.1908). The closer the R^2 values are to 1, the better the correlation between the predicted and experimental values [42]. The R^2 value of 0.9904 for methane yield demonstrates the accuracy of the model. The R^2 value of the polynomial equation was found to be 0.9904. This indicated that the variation of 99.04% of the methane yield could be explained by the model and only about 0.96% was out of its scope. Therefore, the quadratic model was chosen in this study. The adjusted R^2 (R^2_{Adj}) of 0.9807 indicated the high significance of the model. The predicted R^2 (R^2_{Pred}) of 0.9539 indicated good agreement between the predicted and experimental values for methane yield. The R^2_{Pred} of 0.9539 also indicated the reasonable agreement with the R^2_{Adj} of 0.9807. The object of RSM is to detect which experimental parameters generate signals, that is, which are large in comparison to any noise. '$Precision_{adeq}$' measures the signal-to-noise ratio and it is desirable for this to be greater than 4 [26]. This ratio was found to be 30.467, which showed an adequate signal. The coefficient of variation (CV %) is a measure of the residual variation of data relative to the average; the higher the CV, the lower the reliability of the experiment [44]. In this study, the CV value of 2.06% indicated a greater reliability of the experiment. The smaller the PRESS value, the higher the fit to the model [45]. In this study, the PRESS value was found as 4377.81. Additionally, the "Lack of Fit F-value" of 1.33 indicated that this is insignificant. There was only a 0.4213% chance that a "Lack of Fit F-value" could take place due to noise. The model found a standard deviation and mean of 8.08 and 172.59, respectively.

3.2. Interactions among independent variables

The three-dimensional response surfaces plots and corresponding contour plots in Fig. 2 were generated using Eq. (2). The main purpose of the experimental design was to maximize methane yield while keeping the pretreatment concentration and temperature as low as possible. The plots show the interaction between parameters and their effects on response. Fig. 2A shows the effect of NaOH and H_2SO_4 pretreatment on methane yield, namely that methane yield increases as NaOH and H_2SO_4 pretreatment concentration increases when the production temperature and thermal pretreatment temperature are otherwise constant. In previous studies, the optimum concentration for NaOH pretreatment [39] was 5% v/v, while for H_2SO_4 [12] it was 4% v/v. Fig. 2B shows the effect of NaOH and thermal pretreatment on methane yield. Here, the concentration of NaOH and methane yield increased as the temperature increased, when the H_2SO_4 concentration and production temperature were otherwise kept constant. However, when the Fig. 2A and 2B H_2SO_4 pretreatments are examined, it appears to be more effective than thermal pretreatment at identical NaOH concentrations. In one study, biogas production was maximized when thermal pretreatment was applied at a temperature between 130 and 150 °C [46]. Also, the alkali and thermal pretreatment results in this study were consistent with the outcomes of Ref. [47]. Fig. 3C shows the effect of NaOH pretreatment and production temperature on methane yield. When other independent variables were kept constant, methane yield increased with increasing NaOH concentration and temperature. It can also be seen that higher methane yield is observed at lower NaOH concentrations when the production temperature is between 39 and 55 °C. However, when the Fig. 2A and B and Fig. 3C are examined, it seems that the production temperature is more effective at increasing methane yield than the thermal and H_2SO_4 pretreatments when the NaOH concentration is constant. Ref. [48] examined the relationship between NaOH (0–12% w/w) and thermal pretreatment (30–50 °C), finding the associated optimal conditions of 7.8% w/w NaOH and a temperature of 48 °C for three days. In this study, a lower concentration of NaOH and a higher thermal pretreatment temperature were applied. The effects of H_2SO_4 and thermal pretreatment on methane yield are shown in Fig. 3D. Here, methane yield increased as H_2SO_4 concentration and thermal pretreatment increased, but it appears that a higher methane yield could be achieved at relatively low H_2SO_4 concentrations. The thermal and H_2SO_4 pretreatment results in this study were consistent with the outcomes reported in Ref. [49]. Fig. 4E shows the effects of H_2SO_4 pretreatment and production temperature on methane yield. The graph shows that higher methane yield can be achieved at lower H_2SO_4 concentrations. Figs. 3D and 4E show that when H_2SO_4 concentration is constant, the production temperature's effect on methane production is relatively more effective than the thermal pretreatment temperature. In AD, temperature is important because it is known that the various bacterial sequences inducing the biological transformations work best at particular temperatures [50]. Failure to determine these temperature ranges can result in a permanent failure of the AD system [51]. The most effective production temperature among the independent variables for methane yield can be attributed to exactly this situation. The effect of production temperature and thermal

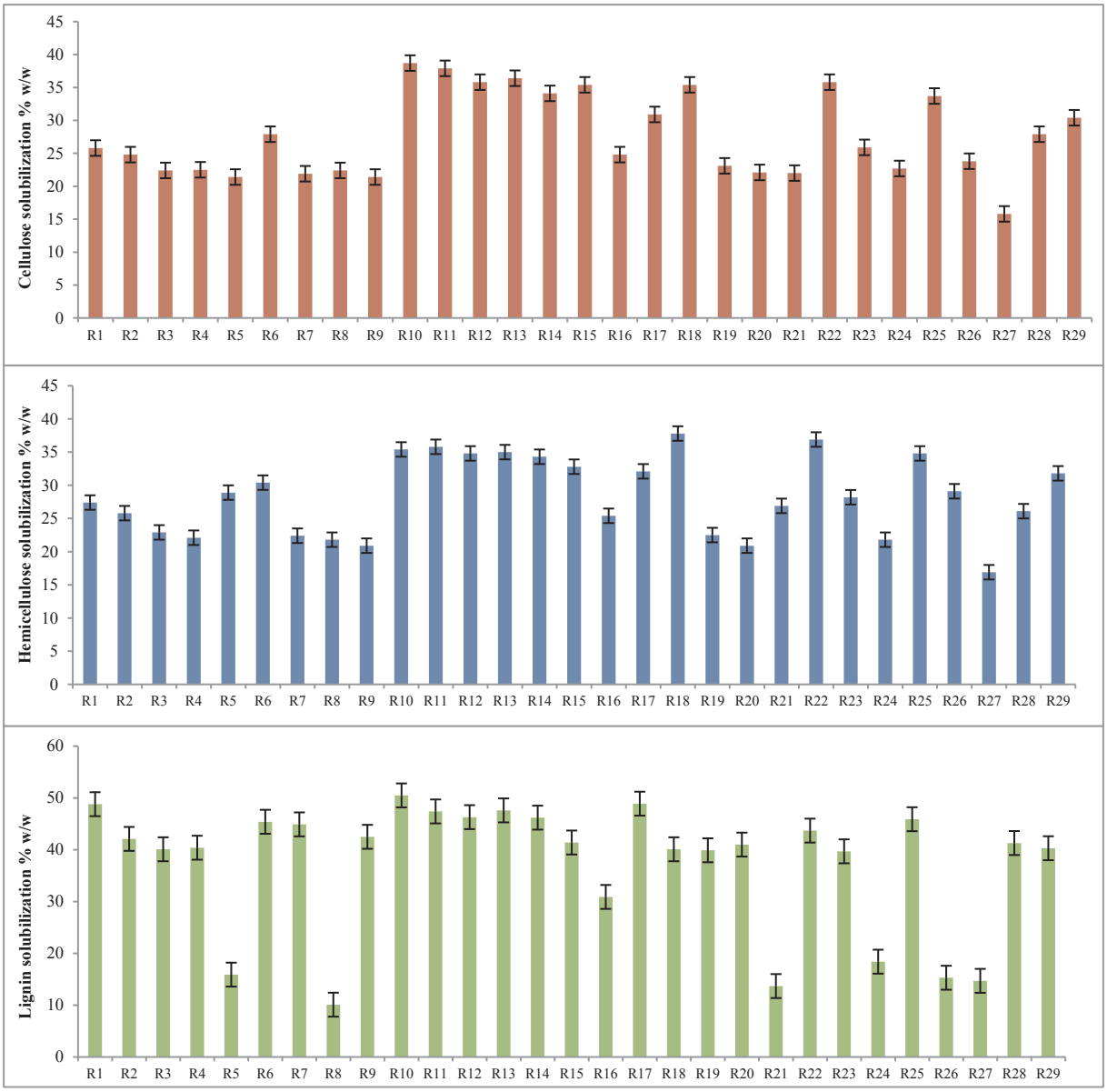


Fig. 6. Effect of pretreatments on lignocellulose content of hazelnut shell (R: reactor)

pretreatment on methane yield is shown in Fig. 4F. When other variables are kept constant, it appears that methane production increases with increasing production temperature and thermal pretreatment temperature. However, in comparison with Fig. 4E and F, the thermal pretreatment is more effective than the acid pretreatment when the production temperature is constant. Zheng et al. [52] emphasized the fact that the use of acid pretreatments at greater than optimum values is toxic to bacteria. The more ineffective H_2SO_4 pretreatment in the reactor can thus be attributed to the fact of this toxicity.

3.3. Optimum conditions

In this study, a second-order polynomial equation was used to determine optimum methane yield conditions, which were calculated by setting the partial derivatives of Eq. (1) to zero with respect to their corresponding variables. The optimum conditions were an NaOH concentration of 3.05% w/v, an H_2SO_4 concentration of 2.56% v/v, a thermal pretreatment temperature of 145.66 °C and a production temperature of 34.69 °C. Under optimal conditions, the predicted methane yield was 215.896 mL/g VS. The graphs in Fig. 5 show that methane production decreases as it moves away from the optimum point. Thus, the model was obtained in such a way that it could reasonably predict the methane yield.

3.4. Effects of pretreatments on lignocellulosic composition solubilization

The influence of pretreatments on the lignocellulosic composition of HS was also investigated. As a result of the pretreatments, the percentage w/w removal efficiencies of cellulose, hemicellulose and lignin are given in Fig. 6. The total lignocellulosic fraction of raw HS used in the study was 96.38% w/w, as shown in Table 1. This rate was 98.39% w/w in a previous study [6]. In the previous studies, after pretreatment of lignocellulosic components, cellulose, hemicellulose and lignin contents were compared in terms of percentage increases or decreases [15,53,54]. However, in this study, the percentage difference between the initial value and the final value of the lignocellulosic content was instead calculated.

The cellulose content of the crude HS was initially 27.55% by weight. After pretreatments, it degraded to between 15% w/w and 35% w/w. In the literature, the relationship between the removal of

Table 5
Experimental methane yields, modified Gompertz predicted methane yields and kinetic constants.

Reactor	Experimental methane yields (mL/g VS)	Modified Gompertz fit results				
		Predicted methane yields (mL/g VS)	λ (day)	μ (mL/g VS.d)	*A* (mL/g VS)	R^2
R_1	204.27 ± 3.8	203.80	0.6069	17.2245	204.459	0.999
R_2	68.92 ± 6.7	69.70	1.1399	6.2461	69.871	0.998
R_3	225.82 ± 4.6	224.99	0.8398	19.1816	225.719	0.998
R_4	221.42 ± 5.5	221.62	0.573	19.1307	222.234	0.997
R_5	60.4 ± 6.6	61.07	0.5991	5.3382	61.227	0.997
R_6	184.61 ± 7.1	187.31	0.5345	16.0341	187.868	0.997
R_7	202.52 ± 6.4	204.09	1.2222	18.2900	204.599	0.998
R_8	144.61 ± 5.7	144.25	0.2783	10.3825	145.478	0.996
R_9	201.91 ± 7.5	201.06	0.3255	15.9768	201.998	0.996
R_{10}	230.72 ± 7.2	234.08	0.5094	18.3524	235.316	0.997
R_{11}	228.42 ± 6.9	230.88	0.6267	17.8568	232.248	0.998
R_{12}	196.77 ± 5.9	200.32	0.9742	14.4365	202.282	0.998
R_{13}	225.97 ± 7.0	228.90	0.7807	19.2670	229.707	0.998
R_{14}	210.14 ± 7.2	213.67	0.8956	18.1406	214.397	0.996
R_{15}	238.67 ± 4.1	240.15	0.5424	18.8274	241.407	0.998
R_{16}	170.02 ± 5.9	167.15	0.9273	14.4328	167.66	0.998
R_{17}	78.6 ± 6.7	79.02	0.4481	5.3843	79.979	0.998
R_{18}	91.6 ± 5.8	92.71	0.7942	6.0662	94.228	0.999
R_{19}	212.14 ± 7.2	212.82	0.7462	15.5563	214.652	0.999
R_{20}	65.28 ± 6.2	66.55	1.9667	4.5063	67.677	0.999
R_{21}	159.61 ± 5.1	157.81	−0.2450	9.0158	162.302	0.993
R_{22}	201.22 ± 4.1	201.59	0.7162	16.0257	202.616	0.998
R_{23}	165.61 ± 7.2	161.51	0.3195	14.3493	161.849	0.993
R_{24}	188.76 ± 7.7	189.97	1.1891	16.6807	190.516	0.997
R_{25}	209.96 ± 7.2	208.40	0.5431	15.2265	210.101	0.997
R_{26}	169.72 ± 6.7	170.16	0.9950	12.7422	171.47	0.998
R_{27}	150.06 ± 5.8	147.81	0.6404	9.8229	150.009	0.997
R_{28}	64.72 ± 4.5	64.60	0.2966	5.6223	64.759	0.994
R_{29}	232.72 ± 3.8	235.22	1.0050	17.2007	237.342	0.999

lignocellulosic components as a result of pretreatment of HS has not to date been explained. In one study, thermal pretreatment was applied to sugarcane bagasse at a temperature of 160–190 °C, for which cellulose removal varied between 20 and 30% w/w. It has previously been reported that the solubilization of cellulose, hemicellulose and lignin in lignocellulosic biomass varies depending on the thermal pretreatment temperature and the concentration of acid or alkali [9]. Previous studies showed 5% w/w to be the optimal NaOH concentration [39]. However, in this study, the maximum lignocellulosic content solubilization was reached at lower chemical reagent concentrations and a lower thermal pretreatment temperature. Hemicellulose solubilization was between 16.9 and 36.9%, where an increase in such due to thermal pretreatment of lignocellulosic biomass at higher temperature has also been demonstrated in other studies [55]. In this study, when the pretreatments applied to 29 reactors were examined, acid pretreatment affected hemicellulose removal whilst alkaline pretreatment affected lignin removal. Previous studies corroborate this observation [9]. Lignin degradation was between 10.1 and 50.5% w/w. There was no noticeable difference in lignin degradation as a result of thermal pretreatment of wheat straw up to 180 °C [15]. However, in this study, lignin degradation significantly increased after low temperature (50 °C) thermal pretreatment and alkali pretreatment. In conclusion, the combination of low concentrations of alkali, acid pretreatment and low temperature thermal pretreatments was more effective in the solubilisation of the lignocellulosic composition than the effect of any single pretreatment.

3.5. Modified Gompertz model estimation

As a result of our consideration of the 29 different production conditions proposed by RSM, actual cumulative methane yields, modified Gompertz predicted methane yields, lag phases, specific methane yields and maximum methane yields are reported in Table 5. The R^2 values of the reactors for the modified Gompertz model ranged from 0.993 to 0.999. The R^2 values of the modified Gompertz model after the AD of the pretreated wheat straw ranged from 0.863 to 0.952 [56]. A better fit was observed in this study. The kinetic constant for the lag phase shows the lag time needed by the bacteria to adapt to the substrates [57]. The λ value of ≤ 0 days indicates that anaerobic bacteria does not need time to adapt, that is, the lag time is 0 days [12]. The delay times ranged from −0.2450 to 1.9667 days. In the literature, the lag phases of chemical pretreated lignocellulosic matter was reported to vary from between 0.4 and 0.8 days according to the modified Gompertz model [57]. In this study, most of the delay stages were found within this range. Specific methane production ranged from 4.5063 to 19.2670 mL/g VS.d. For the modified Gompertz model, the deviation from the actual values varied between 0.09 and 2.47%. In one study, cumulative biogas production of chemical pretreated water hyacinth was fitted using a modified Gompertz model, in which a resultant fitting error of 0.271–9.789% was found [33]. A better fit was achieved in this study. This can be attributed to the more organic substances' solubilization through the simultaneous use of different alkali, thermal and acid pretreatments.

4. Conclusion

A RSM with a Box–Behnken design was used to evaluate the effects of NaOH pretreatment, H_2SO_4 pretreatment, thermal pretreatment and production temperature on methane yield. RSM optimization of pretreatment and production temperature was successfully achieved. The results showed that NaOH pretreatment, H_2SO_4 pretreatment, thermal pretreatment and production temperatures have a direct effect on methane yield. Production temperature was effective on first-order methane yield. Pretreatments were effective in cellulose, hemicellulose and lignin solubilisation. Pretreatment results showed that alkali and thermal pretreatments were more effective at lignin solubilisation, while acid and thermal pretreatments were more effective at cellulose and hemicellulose solubilisation. It is advocated that HS be used for

energy production, especially in the locations of its abundance. In addition, the AD of the HS is promising, and it is recommended that this should be examined using different pretreatment techniques. Thus, an economically important energy source will be obtained.

CRediT authorship contribution statement

Halil Şenol: Conceptualization, Methodology, Software, Visualization, Writing - review & editing. **Mehtap Erşan:** Data curation, Writing - original draft. **Emre Görgün:** Investigation, Supervision, Software, Validation.

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.

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