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Research Article

The Effect of Alkaline Pretreatment of Spent Malting Grains for Biogas Production, Mathematical Modeling and Process Optimization

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Abstract: Spent grains from brewing industries are considered a suitable source for biogas production due to their high accessibility and affordability. However, lignocellulosic materials, due to their fiber content (cellulose, hemicellulose, and lignin), encounter implementation issues in the anaerobic digestion process. To enhance the efficiency of anaerobic digestion of brewery spent grain, an alkaline treatment was performed using sodium hydroxide (NaOH). The parameters of alkaline treatment were temperature (T) and soda-to-spent grain ratio (S/D). The characterization of the raw spent grains indicates that the organic matter (OM), total organic carbon (TOC), nitrogen (N), protein (P), N/C ratio, and pH were 99%, 57.39%, 3%, 18.75%, 19.13%, and 5.6%, respectively. The respective contents of hemicellulose, cellulose, and lignin were 33.3%, 30.4%, and 6.5%. The pre-treatment process yielded a 5% reduction in hemicellulose and a 43% reduction in cellulose while increasing the volume of biogas produced from 0 to 577 mL. After pre-treatment, two biodigesters produced volumes of 23.03 mL per day (100 °C with a soda/spent grain ratio of 0.01%) and 22 mL per day (28 °C with a soda/spent grain ratio of 0.05%). The mathematical model showed an interaction between temperature and the S/D ratio. The predictive modeling analysis indicated that the maximum volume of biogas can be obtained at 23.3 mL per day after pre-treatment of spent grains at 100 °C with a NaOH/spent grain ratio of 0.01.

***Keywords*:** biogas from malting drain, NaOH treatment, taguchi optimization, predictive mathematical modeling

Nomenclature

N	Nitrogen (%)
OM	Organic matter (%)
CH_4	Methane
H_2S	Hydrogen sulphide
CO_2	Carbon dioxide
NaOH	Sodium hydroxide

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DM	Dry matter
MO	Organic Matter (%)
TOC	Total Organic Carbon (%)
C/N	Carbon-to-nitrogen ratio
H	Humidity (%)
pH	Hydrogen potential
E	Extractable (%)
He	Hemicellulose (%)
Ce	Cellulose (%)
L	Lignin (%)
S/*D*	Soda-to-spent malting grains ratio
BD	Bio-digester
T	Temperature (°C)
V	Volume (mL)
FTIR	Fourrier transform infrared
DTGS	Deuterated triglycine sulfate

1. Introduction

More than 80% of the energy used globally comes from fossil fuels.[1,2] This type of energy is non-renewable and releases polluting residues into the atmosphere, notably, NO_x and SO_x compounds, including greenhouse gases that are partly responsible for global warming, air pollution, ocean acidification, and loss of biodiversity.[3] Some research is based on removing S and N atoms from these fuels to reduce pollution problems.[4,5] The production of biogas is now attracting attention concerning the sustainable nature of the energies resulting from the transformation of biomass or the recovery of industrial organic waste.[6,7] In the context of industrial development, the valorization of local raw materials is encouraged. The popularization of the principle of circular economy encourages the recovery of industrial waste. This recovery concerns waste treatment and its transformation into a raw material that can be reused in an industrial production chain. Brewing grains are raw materials considered to be industrial residues from the production of beer in the brewing industries. It is a lignocellulosic conglomerate of lignin, hemicellulose, and cellulose. Cellulose is a polysaccharide with formula $(C_6H_{10}O_5)_n$ consisting of an assembly of glucose molecules provided by carbohydrate bonds, in particular β-glucosidic bonds.[8,9] Hemicellulose is also a polysaccharide, it has a more complex structure and bonds than cellulose. It is made up of different types of monosaccharides (hexose, pentose). Hemicellulose is naturally bound to cellulose by non-covalent bonds and is more sensitive to thermochemical degradation than cellulose.[8,9]

Global spent grain production is estimated at around 43 million tonnes per year worldwide.[10,11] Not all spent grains are the same. The composition of spent grain varies according to the variety of barley, the timing of harvest and brewing conditions.[10,12,13] However, their energy value is still high.[14,15] It consists of a large amount of protein and lipid, but also cellulose (15-30%), hemicellulose (15-25%) and lignin.[16,17] These fibers are biopolymers resistant to enzymatic and bacterial biodegradation. Under specific conditions, the fermentable material contained in the spent grain is transformed into biogas: this is called anaerobic digestion.

Anaerobic digestion is the anaerobic process of transforming organic matter into biogas under the methanogenic action of certain specific microorganisms. Biogas, a product of the degradation of materials contained in organic residues in general and lignocellulosic residues in particular, is a natural process that can be optimized.[6,16,18] Under special conditions, part of the carbon contained in organic matter is oxidized to CO_2 (30-40%), while the other is reduced to CH_4 (60-70%), a useful component of biogas.[1,16] The intrinsic molecules of the matter must be in a form reducible by methanogenic microorganisms under anaerobic conditions.[19,20] Organic materials such as animal manure and common organic residues are recommended as raw materials in the anaerobic digestion process because of the quantity and quality of the metrizable molecules they contain.[6,7] However, lignocellulosic matter, due to its fiber content (cellulose, hemicellulose, and lignin) encounters problems of implementation in the anaerobic digestion process, which is relatively abundant in the brewing industry.[6,21] Spent grain is a by-product of breweries, considered an industrial residue. At the exit of the factory, the spent grain is used in the livestock industry as livestock feed with varying degrees of success.

Indeed, the conversion of lignocellulosic materials into biogas is time-consuming and the production yield does not exceed 20%.[6,18] Given the availability of this material and its structural potential, it is important to find concerted solutions to take advantage of it. Among the potentially interesting raw materials for the production of biogas, malting grains occupy an important place. It is a potential energy reservoir because the components it has can be used to produce the raw material for the production of thermal energy by combustion. However, the high fiber content is a contributing factor to the declining energy potential of malting grain. The fibers that make it up are difficult to destructure in an anaerobic fermentation situation in the presence of microorganisms. For this reason, the pre-treatment stage remains essential.[20]

The purpose of pretreatment is to break the long chains of polymers into their constituent monomers by breaking β-1,6-glucosidic and β-1,3-glucosidic bonds. This process of chemical destructuring results in compounds that are more easily degradable by microorganisms under the conditions mentioned.[20] Pre-treatment techniques such as hydrolysis in an acidic or alkaline medium are mentioned by the researchers.[22,23] The use of enzymes is an alternative process that leads to the same result,[21] and pretreatment by sonication is also an alternative process used.[24,25]

Sunday et al.[26] used the design of experiments method, in particular, the response surface methodology (RSM) to optimize biogas production by co-digestion of a digestate of maize, straw, and cow dung. A study by Jiya et al., on the modeling and optimization of biogas production used parametric elements: pH, holding time, and substrate/water ratio.[27] Edwin et al. did an optimization by co-digestion by modeling the effects of the substrate-water ratio with a fixed amount of water. These studies have shown that the main parameters used to describe biogas production are most of the time interacting. There is a multi-criteria correlation between the different parameters governing the anaerobic digestion process and the biogas yield. This methodological logic justifies the need to use mathematical models to better describe the evolution of a system according to the variables involved.[1,17,23,28] This feedback provides a quantitative assessment of the determinants associated with the thermochemical pretreatment of spent grains. These parameterized determinants are as follows: the concentration of the base or acid; solid load; temperature and pre-treatment time. While the identification of these parameters is a significant advantage, the interdependence between the various parameters remains an enigma. It turns out that each type of raw material reveals its realities in the face of the anaerobic digestion process. The parametric optimization of the pretreatment process has the advantage of saving energy during the process. On the other hand, the combined effects of the different parameters on the performance of the anaerobic digestion process must be taken into account. The main objective of this study is to determine the methanogenic potential improvement by NaOH pretreatment of malting grain.

The novelty of this study is the use of predictive modeling by regression analysis techniques using soda/spend grain ratio and temperature as predictive parameters. The use of the response surface method combined with that of multiple linear regression allows the parametric optimization of the malting grain pretreatment process. The characterization of the rendering allows an assessment of the deviations and the proposal of technical orientations related to the choice and definition of optimal variables to enhance the cleavage of β-1,6-glucosidic and β-1,3-glucosidic bonds in cellulosic molecules.

2. Experimental

2.1 *Materials*

All the following chemicals are analytical grade and are purchased from Sigma Aldrich, United Kingdom. Sodium hydroxide (NaOH) (99.99%) was used for the pretreatment of the spent grain. NaOH solutions (0.17 % w/v, 0.83% w/v, and 0.20% w/v) were prepared in a solution containing 600 mL of water and were used to pre-treat this feedstock. Sulphuric acid (H_2SO_4, 95 wt.%), salicylic acid ($HOC_6H_4CO_2H$) (99%), ammonium chloride (NH_4Cl, 99.5 wt.%), and ammonia (NH_3, 99.98%), were used for the determination of total percentage of nitrogen (TN) and total percentage of protein (TP). For the determination of lignocellulosic content, HCl (75%) and $BaCl_2$ (99.99%) were used. The spent grain was collected from the brewing industries of the city of Bafoussam in Cameroon.

Some properties of the spent grain were characterized in our previous study and the results are as follows: The physicochemical characterization of the spent grains revealed a pH of 5.6, a moisture content of 8%, and an ash content of 9.8% at 450 °C for 2 h using a muffle furnace with an increasing rate temperature of 10 °C/min.[29] The organic composition included a high iron content of 194.2 mg/100 g, an organic matter content of 99%, a total organic carbon (TOC) content of 57.39%, a total nitrogen content of 3%, and a nitrogen-carbon ratio of 19.13%. Furthermore, the spent grains displayed notable concentrations of total protein (18.75%), crude fiber (3.6%), lipids (8.7%), and carbohydrates (51.15%), with an energy value of 14.97 MJ/kg. Furthermore, the chemical oxygen demand (COD) was established at 3,880 mg/kg, while the lower calorific value (LCV) was determined to be 19.76 MJ/kg, resulting in a COD/TOC ratio of 86.03.

2.2 *NaOH treatment process optimization by taguchi method*

The search for the optimal characteristic parameters that influence the basic hydrolysis constitutes the optimization phase of the pretreatment. Two main parameters were used, namely: the combined ratio between the mass of soda, that of the spent grain, and the pre-treatment temperature. The experiments were conducted according to the method proposed by Taguchi[30-32] using the software minitab 19. This is a two-factor design of experiments of three levels each, executed according to the L9 design incorporating 3 replicates per experiment as summarized in Table 1. Three characteristic temperature ranges are selected (28, 50, and 100 °C) according to the optimal proposals of the experimental design during a pre-treatment time of 1 h. The requirement not to exceed 100 °C stems from the need to take into account the principle of energy saving on the one hand. On the other hand, it is a question of respecting the optimal limits of the response surface resulting from the predictions underlying this study. The characteristic ratio of soda mass to spent grain mass is also varied according to three optimized reference values (0.01, 0.05, and 0.1%), in the specific case of processing a mass of spent grain equivalent to 100 g. The mass of water incorporated in each experiment is equivalent to 600 mL. The selection of reference values for soda mass to spent grain mass ranged from 0.01 to 0.05 and 0.1, yielding dilute (S/D of 0.01) and concentrated solutions (S/D of 0.05 and 0.1), respectively. The range from 0.05 to 0.1 was based on the variation of hydroxide ion activity in concentrated solutions from 0.18 (S/D of 0.05) to 0.31 (S/D of 0.1). The hydroxide ion activities were calculated using Güntelberg approximation.

The dependent variables associated with the evaluation of the effects of basic treatment are the % of lignocellulosic materials (lignin, hemicelluloses, and cellulose), water absorption rate, and the total volume of biogas produced.

Some studies examine the effect of pH in biogas production,[5,33] but this is not necessary in the case of pretreatment using concentrated solutions. The solutions prepared by adding[1,5] 10 g of sodium hydroxide to 600 mL of water have pH values of 12.62, 13.25, and 13.49, respectively. Therefore, the pH values of these solutions are similar and do not need to be tested.

Table 1. Design of experiments by taguchi method

Biodigester	Experiments No.	Soda / spent grain	Temperature
BD1	1	0.01	28
BD2	2	0.01	50
BD3	3	0.01	100
BD4	4	0.05	28
BD5	5	0.05	50
BD6	6	0.05	100
BD7	7	0.1	28
BD8	8	0.1	50
BD9	9	0.1	100

In the absence of sodium hydroxide, no biogas production was observed for more than 40 days in the biodigester.

Then, the 9 digesters (BD1 to BD9) following the experimental design presented in Table 1 were performed. Each digester contains pre-treated and pre-dried spent grain at 11.11 % w/v. The various reactors are empirically agitated daily throughout the anaerobic digestion process.[34,35]

2.3 *Experimental laboratory-scale biodigester set-up*

Biogas production tests were carried out in batch or batch biodigesters, the physical model of which is shown in Figure 1.[36] There are 9 digesters (BD1~BD9), represent laboratory models. They are made of polyvinyl chloride (PVC) plastic material, which is easy to make with the advantage of being hermetically sealed to meet the anaerobic requirements of the reaction medium. The various biodigesters used are equipped with an orifice allowing the gas produced to be conveyed to a quantifier operating on the principle of the displaced liquid. The usable volume of the biodigester is approximately 1.5 L and the primary storage has a capacity of 0.5 L.

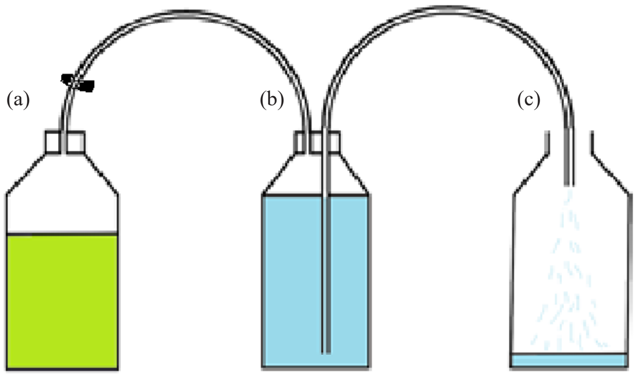

Figure 1. Experimental setup (a) substrate; (b) gas collector; (c) water collector

2.4 *Characterizations*

The raw spent grain undergoes complementary characterization by the percentages of lignocellulosic materials (cellulose, lignin, and hemicellulose). The effect of the pretreatments was evaluated by Fourier Transform Infrared Spectroscopy (FTIR).

2.4.1 *Determination of lignocellulosic content*

The following protocol was used for the determination of the lignocellulosic content of the studied spent grain samples. 60 mL of acetone is incorporated into 1 g (M_1) of spent grain. The solution is then heated at a reflux temperature of 90 °C for 2 h. The residues resulting from the process were also then dried at a temperature of 105 °C in an oven according to the required protocol. The mass (M_2) represents the mass obtained at the end of the experiment.[37-39] The extractable (E) material content was approximated by Eq.1.

$$E = \frac{M_1 - M_2}{M_1} \times 100 \tag{1}$$

1 g (M_3) of extractable-free spent grain was introduced into 150 mL of a NaOH solution of 0.5 N and heated for 3.5 h at 80 °C. The residues were rinsed with distilled water until the potential residual sodium ions were eliminated, confirmed by obtaining a pH of 7, characteristic of acid-base neutrality. The residues obtained were also dried at 105 °C in an oven until a constant mass product (M_4) was obtained.[40] The % of hemicellulose (He) was deducted by Eq.2.

$$He = \frac{M_3 - M_4}{M_1} \times 100 \tag{2}$$

30 mL of hydrochloric acid (HCl, 14.8 M) was incorporated into 1 g (M_3) of extractable free spent grain. The whole thing was left to sit for 24 hours at room temperature. The resulting residues were rinsed in distilled water, until the sulfate ions completely disappeared, confirmed by a pH of 7. The sulfate ion test is performed using a solution of barium chloride ($BaCl_2$). The resulting residues are dried at 105 °C to obtain a completely dehydrated mass product (M_5). The percentage of lignin (L) is approximated by Eq.3.

$$L = \frac{M_3 - M_5}{M_1} \times 100 \tag{3}$$

The percentage of cellulose (Ce) is determined by Eq.4.

$$Ce = 100 - (E + He + L) \tag{4}$$

2.4.2 *Structural analysis by fourier transform infrared spectroscopy (FTIR)*

The polarized chemical bonds of the molecular structure of the studied malting grains were determined by FTIR. The infrared analysis was performed by using an alpha spectrometer from Bruker equipped with a DTGS detector, in Germany. It was performed between 400 and 4,000 cm^{-1} of wavenumber in absorbance mode with a resolution of 4 cm^{-1} and a precision of 0.001 cm^{-1} with KBr.

2.5 *Kinetic study of biogas production*

Several kinetic models can be used to predict the anaerobic digestion process under particular operating conditions. These include hyperbolic, modified Gompertz, cone, logistic growth model, first-order kinetics, and transfer function models. Details of these can be found in the literature[41-46]. The present study employs the modified Gompertz model for kinetic analysis of the experimental data. The modified Gompertz model is an appropriate choice for our study, as it has demonstrated effectiveness in describing the kinetics of biogas production from organic waste mono-digestion[47].

Moreover, the modified Gompertz model demonstrates a low RMSE (Root Mean Squared Error) and a high value of the correlation coefficient (R^2) between the maximum biogas yield and the concentration of VS of the digester input (substrate)[47,48]. The modified Gompertz equation is also suitable for optimizing kinetic parameters for methane production in batch digesters. It has been widely used by researchers to predict cumulative biogas production based on biogas production potential, maximum biogas production rate, and waiting time before biogas production. The Levenberg-Marquardt Algorithm (LMA) is used with Origin Pro software to perform the fitting:

$$P = A \cdot \exp\left[-\exp\left(\mu \cdot \frac{e}{A}(\gamma - t) + 1\right)\right] \tag{5}$$

Where P is the cumulative volume of biogas per gram of total solid (mL/g TS), e is Euler constant equal to 2.71828, A is the biogas production potential (mL/g TS), μ is the production rate (mL/day) and γ is the waiting time (in the day) before the onset of the biogas production.

2.6 *Predictive modelling of quantitative biogas production*

Modeling was used in the context of the parametric optimization of the main determinants of the raw material pre-treatment. This effect can be observed through the volume of biogas obtained. Minitab software version 19, Scikit-learn library, and Python 3 language were used to determine the optimal pre-processing parameters. The descriptive model of phenomenology was generated and refined by the numerical method of multiple linear regression, which in turn was coupled with the least squares method. The selection of variables allowed the most important factors and interactions between factors to be deduced for pretreatment. The degree 3 model including interactions between factors up to order 2 facilitated the different choices and the neglect of higher-order interactions by Eq.5.

$$\hat{Y}_{CI}(w) = b_0 + \sum_{i=1}^{k} \beta_i w_i + \sum_{i=1}^{k} \beta_{ii} w_i^2 + \sum_{i=1}^{k} \beta_{iii} w_i^3 + \sum \sum_{1 \le i < j}^{k} \beta_{ij} w_i w_j \tag{6}$$

Where b_0 is the intercession, β_i represents the respective coefficients of the repressorsand w_i and the products $w_i w_j$ represent the interactions between the factors.

β_i are the coefficients estimated by minimizing the residuals using Eq.7.

$$\hat{\beta} = \left({}^{t}X \cdot X \right)^{-1}, \ {}^{t}XY \tag{7}$$

3. Results and discussion

3.1 *Lignocellulosic characterization*

The values of the dependent parameters are presented along with the quantitative estimate resulting from the design of experiments. Table 2 presents the physical and chemical characteristics and percentage of lignocellulosic material in the spent grain.

The lignocellulosic composition of the raw material studied shows the following values: hemicellulose 33.3%, cellulose 30.4%, and lignin 6.5%. Lignin and hemicellulose are complex polysaccharides whose bonds are difficult to break without proper pre-treatment. However, cellulose is easier to process than its counterparts under the same experimental conditions[49,50]. Previous studies suggest that a percentage of cellulose greater than 40% is minimal for cost-effective biogas production[51,52]. The cellulose content of 30.4% obtained in this study is below the tolerance values. Studies have shown that the predominance of lignin in materials hurts the yield of biogas production. This is because lignin traps cellulose and hemicellulose and prevents the closers from reaching them under anaerobic digestion conditions[37,51,52]. The reported lignin content of 33% of the spent grain studied shows that it will have a mixed biogas yield if no pre-treatment process is considered. A lignin content of more than 20% is considered detrimental to the performance of a direct digestion operation. The lignin content estimated at 6% in this study demonstrates that pre-treatment could increase the overall yield if biogas production is considered using this spent grain. As this spent grain is rich in lignin, hemicellulose, and cellulose (about 70%), pre-treatment should make fermentable molecules more available and improve production yield.

Table 2. Results of lignocellulosic characterization of spent grain

Parameters	*E*	*He*	*Ce*	*L*
Spent grain	29.8	33.3	30.4	6.5

3.2 *Influence of pretreatment on lignocellulosic content*

The levels of lignocellulosic matter, as well as the quantities of extractable contained in the BD3 and BD4 biodigesters that give the best biogas production, are shown in Figure 2.

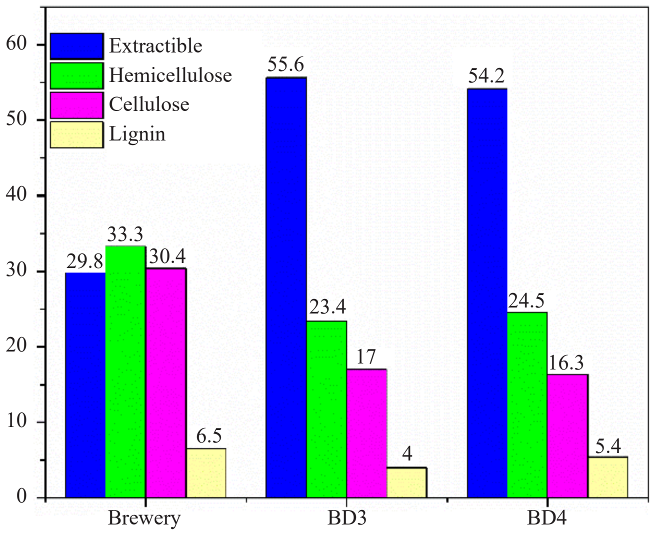

Figure 2. Effect of alkaline (NaOH) pretreatment on the percentage of lignocellulosic material

A progressive decrease in lignocellulose materials and an increase in extractable are observed. This observation demonstrates a characteristic activity in the conversion of lignocellulosic materials into sugar, by the breaking of the glucosidic bonds between the monomers constituting these chains. This decay is visible on the infrared spectra confined in Figure 3.

FTIR analysis shows that both temperature and soda content have an impact on the length of the bonds, with an impact on the lignocellulosic material content. The intensities provide information on the predominance of the chemical bonds at the origin of the vibrations detected by the equipment. Their amplitudes provide information on the evolution of the variation in the number of characteristic links.

In the area between 1,200 and 800 cm^{-1}, infrared spectra indicate the presence of a faint peak at 855.75 cm^{-1} representing an asymmetric vibration characteristic of β-1,6-glucosidic bonds and saccharides. On the other hand, at 1,100 cm^{-1} a characteristic frequency of β-1,3-glucosidic vibrations of hemicellulose is identified[53]. The preliminary soda/spent grain ratio used leads to a progressive decrease in the maximum absorption intensities of the β-1,6-glucoside bonds of the saccharides and β-1,3-glucosidic bonds of the hemicellulose, reflecting the progressive hydrolysis of these bonds and the release of glucose monomers (from hemicellulose) and the monosaccharides constituting cellulose. The change in bond strength is a function of the value of the soda-to-spent grain ratio.

Indeed, for soda-to-spent grain ratios of 0.01 and 0.05, the maximum intensities are identical (between 15,000 and 20,000 counts). From a soda/spent grain ratio of 0.1, the intensity is significantly reduced (less than 12,000 Counts). This observation suggests that from a soda/spent grain ratio of 0.1, the breakage of the leaves is more accentuated and the conversion of lignocellulosic materials (into glucose and monosaccharides) is greater. The effect of temperature on the basic hydrolysis of monomer bonds is correlated. Figure 3 shows that the characteristic absorption intensities of the bonds decrease with increasing temperature. This would prove that an increase in temperature promotes basic bond hydrolysis as also observed by Ottah et al. Indeed, the breaking of the different bonds under these experimental conditions would be favored by an increase in molecular agitation under the influence of a temperature gradient that weakens the β-1,3-glucosidic and β-1,6-glucosidic bonds. The number of bonds between monomers decreases as the temperature increases, this is observable from the decrease in the intensities of the characteristic vibrations. The effects of temperature are more pronounced for a ratio of 0.1, as the difference between the intensities at 28 °C (19,500 Counts) and 50 °C (12,500 Counts) is large. A decrease in intensity of 7,000 units is also observed. The comparative intensities of the characteristic vibrations of the different β-1,3-glucosidic bonds observed at 50 and 100 °C show that these intensities decrease from 16,000 Counts (at 50 °C) to 15,000 Counts (at 100 °C). The decrease in intensity shows only a regression of 1,000 units. This observation leads to two interpretations: the effect of temperature depends on the mass ratio of soda to spent grain in the process of bond hydrolysis. On the other hand, above 50 °C, the effects of temperature on glucosidic bond breaks are relatively negligible. It then seems that the increase in temperature above 50 °C would not contribute to a significant change in the bonds because when the ratio is high, the hydrolytic activity of the soda is very marked and the increase in temperature would then represent a waste of energy.

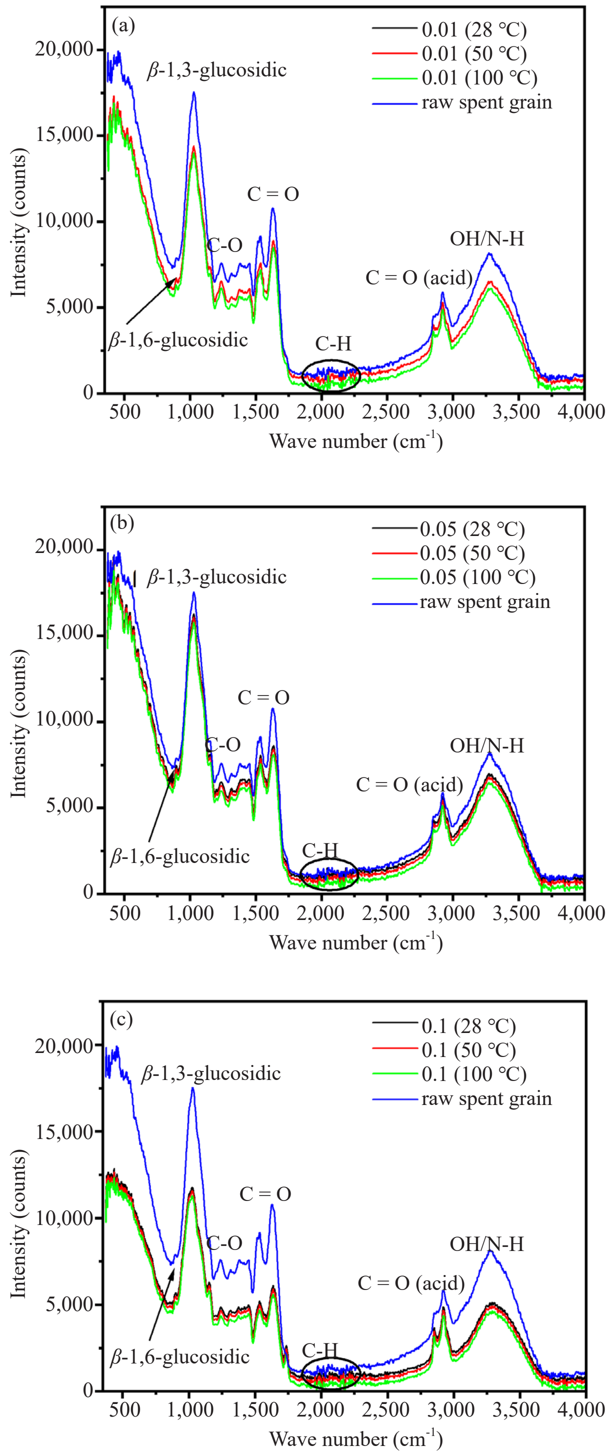

Figure 3. FTIR analysis of pretreated spent grains soda/spent grain ratio: 0.01 (a); 0.05 (b) and 0.1 (c)

3.3 *Influence of pretreatment on biogas production*

Figures 4 and 5 respectively show the influence of pretreatment on daily production and the total volume of biogas produced per month.

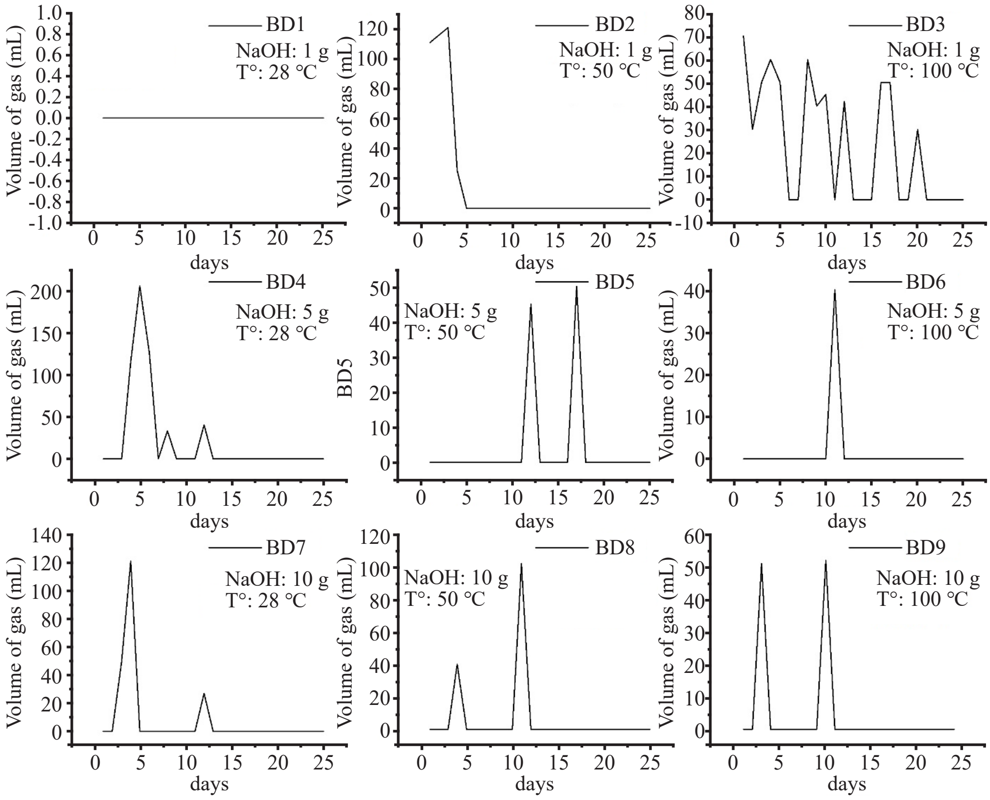

Figure 4. Influence of pre-treatment on daily biogas production

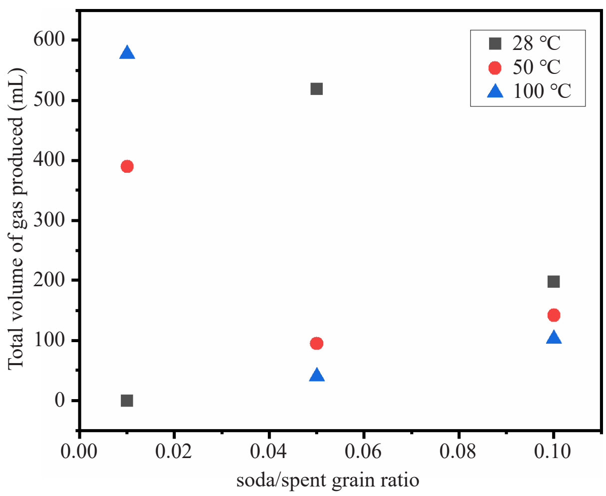

Figure 5. Influence of pre-treatment on the total volume of biogas produced in one month

Figures 4 and 5 show that the latency and volume of biogas produced are influenced by temperature and the S/D ratio. Indeed, at 28 °C, the minimum S/D ratio that leads to the production of the gas is 0.05. The BD1 biodigester did not produce any gases in measurable proportions under the conditions of this study. Latency times were 3 and 2 days, followed by the production of 200 and 120 mL, respectively for pretreatments using the S/D ratios of 0.05 (BD4) and 0.1 (BD7) at 28 °C. These two biodigesters yielded biogas volumes of 550 and 200 mL, respectively, the characteristic values of which are confined to Figure 5. Three (3) and two (2) production peaks were observed with respectively an intense production peak for each of the bioreactors considered. At 50 °C, the observed latency times were: 0 (S/D 0.01), 11 (S/D 0.05), and 3 (S/D 0.1) days, respectively, while the volumes produced directly after latency were 110, 45, and 40 mL, respectively, as shown in Figure 4. The two bioreactors, BD5 and BD8, had two relatively low production peaks for biogas volumes of 100 and 125 mL, shown in Figure 5. The BD2 bioreactor had the most intense production estimated at 400 mL as shown in Figure 5 and without any lag time in Figure 4. The S/D ratio of 0.01 would have favored a significant release of sugar, which was rapidly digested without observing the characteristic latency time. At a temperature of 100 °C, the BD6 and BD9 biodigesters show respectively 1 and 2 production peaks for gas volumes of 40 and 50 mL after latency times of 10 and 3 days, observable in Figure 4. The final production volumes observed are 70 and 100 mL of biogas, values contained in Figure 5.

The BD3 biodigester, on the other hand, has a regularity of production, identifiable in Figure 4, by producing successive small volumes, with no latency after pre-treatment and whose values remain between 70 and 30 mL. The total volume of biogas produced by the BD3 bioreactor is 577 mL. For the same S/D ratio (0.01, 0.05, or 0.1), the variation of the pretreatment temperature would affect the digestion characteristics of the reactor under consideration.

As illustrated in Figure 5, the initial optimization conditions for each temperature are as follows: the volume of biogas is optimal for an S/D ratio of 0.01 at 100 °C, with a volume of 370 mL, and at 50 °C, with a volume of 519 mL. If the temperature is reduced further, the S/D ratio must be increased to 0.05 to achieve a volume of 519 mL. The graph also shows that an S/D ratio greater than 0.05 is detrimental to production.

3.4 *Kinetic study results*

Modeling using the modified Gompertz equation was conducted exclusively on the BD3 due to its consistent production throughout the study period. The other biodigesters exhibited only a few instances of elevated production. This is not conducive to modeling purposes. Figure 6 illustrates the regression analysis conducted on biodigester BD3.

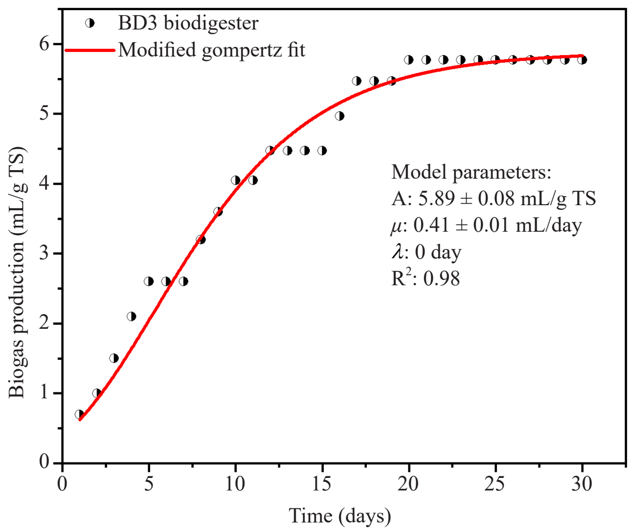

Figure 6. Modified gompertz fit for the biodigester BD3

According to this result, the modified Gompertz equation is as follow:

$$P = 5.89.\exp[-\exp\ (-0.189t + 1)]$$

The results of this model demonstrate that the maximum potential of biogas production for the BD3 biodigester is 5.89 ± 0.08 mL/g of total solid, with a relative error of 1.4%. The rate of biogas production is 0.41 ± 0.01 mL per day, with a relative error of 2%. These relative errors are below 5%, which demonstrates the precision of these predictions. The values of A and μ are in close alignment with those derived from Figure 6, which is consistent with the R^2 of 0.98 obtained for the fitting model. Accordingly, the Modified Gompertz equation is an appropriate means of predicting the anaerobic digestion of brewery spent grains treated at 100 °C with a ratio of 0.01 soda to spent grains.

3.5 *Results of predictive modeling*

3.5.1 *Regression model and ANOVA*

The obtained model is expressed as follows:

$$V(mL) = 2{,}116 - 21{,}726 \cdot \left(\frac{S}{D}\right) - 39 \cdot T + 422 \cdot T\left(\frac{S}{D}\right) + 1{,}653 \cdot T\left(\frac{S}{D}\right)^2 - 4 \cdot T^2\left(\frac{S}{D}\right) + 0.003T^3 \quad (8)$$

Where, *V*, *T*, and *S*/*D* represent the volume of biogas, temperature, and soda-to-spent malting grains ratio, respectively

The regression coefficient of this model is $R^2 = 1$, so this model has significant descriptive potential. Through the different determinants involved, it shows that interactions exist between the different input variables (temperature and *S*/*D* ratio). The existence of a parametric interdependence between the triptych: temperature and *S*/*D* ratio is an underlying reality that emerges from the proposed model. This parametric interdependence influences the entire hydrolysis process, with repercussions on the biogas yield during the digestion process.[27] The most significant interaction is $T(S/D)^2$ with a regression coefficient of 1,653. The temperature would therefore interact with the square of the *S*/*D* ratio to increase the volume of the desired biogas.

The Analysis of Variance (ANOVA) for this model is presented in Table 3. The *F*-ratio is the ratio of the mean square error to residual error and it is used to determine the importance of a parameter. A parameter with a high *F*-ratio indicates its high significance, while a lower *p*-value suggests greater importance and impact.

Table 3. ANOVA for the model of volume of biogas produced

Source	DL	Sum of square	Mean square	*F* value	*P* value	
Régression	6	184,272	30,712	214,900	0.000	
S/*D*	1	24,366	24,366	3,480	0.000	
T	1	16,887	16,887	121,586	0.000	
$T\cdot(S/D)$	1	36,435	36,435	255,010	0.043	
$T\cdot(S/D)^2$	1	42,757	42,757	299,300	0.043	Significant
$T^2\cdot(S/D)$	1	11,885	11,885	71,310	0.0145	
T^3	1	3,689	3,689	22,134	0.015	
Erreur	2	171,305	85,653			
Total	8	355,577				

According to Table 3, the *p* value of the model is less than 0.0001, indicating the high degree of accuracy for this model[54]. All the model's parameters are significant for the description of the evolution of the biogas volume during production process. The most significant parameters are the *S*/*D* ratio and the Temperature.

3.5.2 Interactions effects of temperature and S/D ratio on the biogas total volume produced

Figure 7 shows the effect of temperature and soda-to-spent grain interactions on the total volume of biogas produced.

Figure 7 shows that the different characteristic parameters, i.e., temperature and *S*/*D* ratio, interact in such a way as to influence the total volume of biogas produced. When the *S*/*D* ratio is set at 0.01, the increase in temperature has a positive effect on the volume of biogas produced. Whereas when this ratio is 0.05 or 0.1, an increase in temperature induces an opposite effect on the volume of biogas produced. However, this decrease is more pronounced when the *S*/*D* ratio is 0.05. The maximum values of the different volumes are obtained for a temperature of 28 °C, *S*/*D* ratio of 0.05, and an *S*/*D* ratio of 0.01 under a temperature of 100 °C. Concerning the effects of the *S*/*D* ratio on biogas production efficiency, the following observations are made. For a temperature set at 28 °C, an increase in the *S*/*D* ratio from 0.01 to 0.05, respectively, induces an increase in the volume of biogas produced, whereas when this ratio increases from 0.05 to 0.1, the volume produced decreases. On the other hand, when the temperature is at 50 or 100 °C, the increase in the ratio leads to a decrease in the total volume of biogas produced.

These interactions result in a multitude of (*T*, *S*/*D*) combinations that elicit the same response. This is illustrated by the response surface shown in Figure 8.

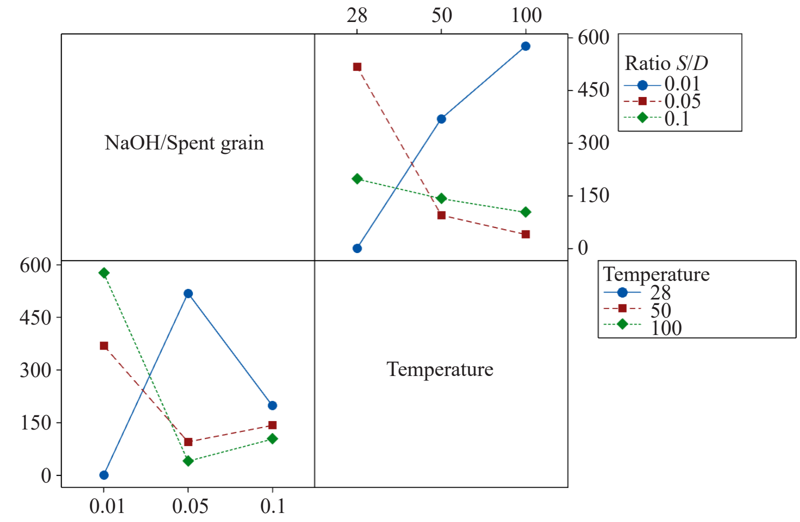

Figure 7. Effects of temperature and soda/spent grain ratio interactions on total volume produced

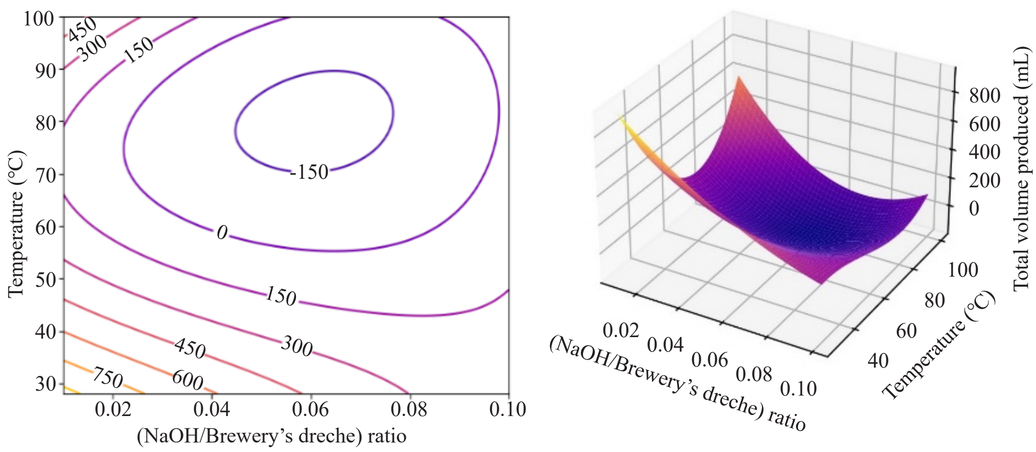

Figure 8. Response surface and isoresponse curve of total volume produced

Figure 8 shows the response surface and isoresponse curve obtained from the regression model. This indicates that there are rows on which the results are identical. This means that it is possible to combine different values of the soda/spent grain ratio as well as the temperature to obtain the same volume of gas. The isoresponse curve shows that the maximum values of the volume of biogas produced are obtained for a ratio of soda to the spent grain of less than 0.04 and temperatures below 45 °C or between 95-100 °C. In practice, the maximum value of the biogas volume obtained is 577 mL, during model validation, for the pre-treatment of spent grains at an operating temperature of 100 °C, using a soda/spent grain ratio of 0.01.

4. Conclusions

This study aimed to contribute to modeling and optimizing biogas production from brewers' grains via thermochemical pretreatment of the latter. The study investigated the influence of the soda/spent grain and the pretreatment temperature on the breakage of β-glucosidic bonds between the monomers making up the lignocellulosic material, and their impact on the volume of biogas produced. The results show that the breakdown of the various bonds under these experimental conditions is favored by an increase in molecular agitation under an increase in temperature, which weakens the β-1,3-glucosidic and β-1,6-glucosidic bonds. On the other hand, above 50 °C, the effects of temperature on glucoside bond breakage are relatively negligible. The mathematical model showed several complex interactions between temperature and S/D ratio. The predictive modeling analysis showed that the maximum biogas volume can be obtained at 23.3 ml/day after pretreatment of spent grain at 100 °C with a soda/spent grain ratio of 0.01. This method shows that thermochemical pretreatment improves spent grain digestibility, increases biogas yield, promotes solubilization of organic compounds, and reduces inhibitor concentration. The best operating temperature was 100 °C, with a soda/waste grain ratio of 0.01.

The optimization method used takes into account only two descriptive parameters (temperature and soda/spent grain ratio), while other parameters such as pretreatment time, pH of the alkaline solution, etc., are not taken into account.

Further studies will be carried out in the future to examine internal variables such as the percentage of spent grains and the pH of the alkaline solution to verify their impact on the pretreatment process.

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Conflict of interest

The authors declare that they have no conflict of interest.

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