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Biogas Production Potential and Kinetics of Microwave and Conventional Thermal Pretreatment of Grass

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Abstract Pretreatment methods play an important role in the improvement of biogas production from the anaerobic digestion of energy grass. In this study, conventional thermal and microwave methods were performed on raw material, namely, *Pennisetum* hybrid, to analyze the effect of pretreatment on anaerobic digestion by the calculation of performance parameters using Logistic function, modified Gompertz equation, and transference function. Results indicated that thermal pretreatment improved the biogas production of *Pennisetum* hybrid, whereas microwave method had an adverse effect on the performance. All the models fit the experimental data with $R^2>0.980$, and the Reaction Curve presented the best agreement in the fitting process. Conventional thermal pretreatment showed an increasing effect on maximum production rate and total methane produced, with an improvement of around 7% and 8%, respectively. With regard to microwave pretreatment, maximum production rate and total methane produced decreased by 18% and 12%, respectively.

Keywords *Pennisetum* hybrid · Anaerobic fermentation · Mathematical model · Pretreatment

Introduction

As an alternative energy, biogas from the anaerobic digestion of lignocelluloses (agricultural crops, forest residue, and aquatic plants) has shown much potential for application [1]. Among these materials, perennial energy grass is promising feedstock for biogas production [2] because of its highly volatile solid content and yield potential, possibility of annual cuts,

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and anticipated positive environmental impact [2–5]. However, the tight structure and inherent stability of lignocellulosic biomass present barriers to its utilization in anaerobic digestion. Therefore, various methods based on the biodegradation and solubilization of lignin and hemicellulose have been developed to enable efficient hydrolysis and facilitate optimal biogas production [6–8].

Methods for raw material pretreatment can be generally categorized into physical [9], chemical (alkali treatment [10] or acid hydrolysis [11, 12]), physicochemical, and biological processes [13]. Microwave is an alternative method to conventional heating. Microwave irradiation can rapidly produce focused direct heat and change the dipole orientation of polar molecules [14]. Microwave has been used as a pretreatment method of sludge [15], kitchen waste [16], and dairy manure [17]. Thermal pretreatment can be effective in the degradation of lignin and hemicellulose by improving hydrolysis with the acids formed from the treatment [3]. The feasible and optimal method varies according to different types of lignocelluloses. Himmelsbach et al. [18] found that pretreated switchgrass with aqueous ammonia soaking produced 65% more methane compared to the untreated ones.

Some researchers conducted mathematical models in their studies to obtain kinetic parameters of the anaerobic digestion of energy crops. The first-order kinetic model used by Massė et al. [19] and Mähnert et al. [20] evaluated the methane production of switchgrass, maize silage, whole-crop rye silage, and fodder beet silage. The model fit the experiment data, and the coefficients of determination were higher than 0.99. A multi-compartmental logistic model was used by Malafaia et al. [21] to present the kinetic interpretations of cumulative gas production from corn silage and the forages *Cynodon dactylon*, *Pennisetum purpureum*, *Brachiaria brizantha*, *Brachiaria decumbens*, and *Melinis minutiflora*.

Based on existing knowledge, the main parameter considered is the final quantity of biogas produced; only a few studies investigated the biogas production rate. In the current paper, anaerobic digestion tests were conducted to determine the biogas production of *Pennisetum* hybrid, mainly focusing on the biogas production by conventional thermal and microwave pretreatment. Three mathematical models were also used to evaluate biogas production rate using experimental data.

Materials and Methods

Grass Material and Original Digested Sludge

Pennisetum hybrid (*Pennisetum americanum* × *P. purpureum*) was used as substrate (Electronic Supplementary Material S1). The grass was cultivated in Zengcheng District, Guangdong Province, China. The grass was sown on May 4, 2010 and harvested on October 8, 2010. No fertilizer was applied during this period. Harvested fresh grass was first cut to a particle size of 1 to 2 cm with scissors and then ground for 30 s in a knife mill. Total solid content (TS), volatile solid content (VS), carbon content, nitrogen content, and ratio of carbon to nitrogen of the ground material were 16.01%, 13.72%, 41.88%, 1.16%, and 35.69, respectively. The smashed raw material was stored at 4 °C in the refrigerator before use.

Inoculums were taken from the mesophilic anaerobic digestion reactor fed with swine manure. Before use, the inoculums were sieved through a 1 mm mesh to remove large particles and grit. The pH, TS content, and VS content, of the sieved inoculums were 7.30, 3.59%, and 2.32%, respectively.

Experimental Setup and Procedure

The anaerobic digestion experiments were performed in 1.5 L glass bottles at 35±1 °C. Inoculums (800 g) were added in each bottle followed by the addition of a substrate with a $VS_{substrate}/VS_{inoculum}$ ratio of 1.48. All bottles were filled with 1,000 mL water, and 5 g/L ammonium bicarbonate (NH_4HCO_3) was added as buffer agent. The digesters were flushed with N_2-gas for 3 min to remove oxygen. The bottles were then sealed with butyl rubber stoppers. Biogas potential tests were performed under mesophilic conditions (37±1 °C) controlled by the water bath. Bottles were mixed manually twice a day. The experiment period was about 33 days. Biogas production was given in milliliters per gram of VS (mL/g VS), that is, the volume of biogas production was based on norm conditions: 273 K and 1,013 mbar. Bottles solely with inoculums were considered control reactors. Biogas produced from these digesters was excluded when calculating the biogas yield of the substrates.

Pretreatment Methods

Microwave-Treated Method

A microwave oven (power, 0 W to 1,180 W; frequency, 2,450 MHz; maximum temperature, 260 °C; P80D23N1L-A9, Galanze) was used to treat grass. A flask of a 200 g thoroughly mixed sample was placed in the microwave and exposed to high irradiation for 3 min.

Thermal-Treated Method

Thermal pretreatments were performed in a 10 L autoclave (LS-B50L, Shanghai, China) in which temperature increase was controlled electrically. A 200 g grass sample was placed in a flask and treated with water vapor for 30 min.

Models for Data Fit

Three models were used to estimate the performance parameters. The Logistic function corresponded to the global shape of the biogas production kinetics: an initial exponential increase and a final stabilization at maximal production level. The Logistic function was based mainly on four assumptions and developed to be as simple as possible to avoid unidentifiable parameters [22]. The modified Gompertz equation could be used initially for methane and hydrogen production, but the three parameters in this model are restricted to specific experimental conditions and cannot be used in a predictive mode [23]. The transference function (Reaction curve-type model) predicted maximum gas production solely based on CH_4 production [24].

In the current study, after obtaining cumulative biogas production curves over time from the anaerobic digestion tests, modified Gompertz equation, Logistic function, and transference function (Table 1) presented by Donoso-Bravo et al. [25] were used to determine biogas production potential (P), maximum rate of biogas production (R_m), and duration of the lag phase (λ). P, R_m, λ represented biogas production (in milliliters per gram VS), maximum biogas production rate (in milliliters per gram VS per day), and lag phase (in days), respectively. These procedures were applied to describe the effect of microwave and thermal methods.

Table 1 Equations used in these models

Model	Equation
Modified Gompertz equation	$M = P \times \exp\left\{-\exp\left[\frac{R_{\mathrm{m}} \times e}{p}(\lambda - t) + 1\right]\right\}$
Logistic function	$M = \frac{P}{1+\exp[4R_{\mathrm{m}}(\lambda - t)/P+2]}$
Transference function	$M = P\left\{1 - \exp\left[-\frac{R_{\mathrm{m}}(t-\lambda)}{P}\right]\right\}$

Results and Discussion

Biogas Production

The cumulative biogas production compared with the time for treated and untreated *Pennisetum* hybrid was presented in Fig. 1 and Table 2. The maximum volumes of biogas and methane produced in 30 days were of significant difference for treated and untreated samples. The specific methane yield increased from 189.7 to 198.3 mL/g VS after thermal pretreatment. However, specific methane yield decreased to 163.6 mL/g VS after microwave pretreatment. Thermal pretreatment improved biogas production of the *Pennisetum* hybrid, whereas microwave use had negative effects. Specific methane yields obtained in the current study are within the range of results from other grass species. Mari et al. [26] observed that the specific methane yields of cocksfoot, tall fescue, reed canary grass, and timothy varied from 253 to 394 mL/g VS. Lehtomaki et al. [27] studied anaerobic digestion of grass silage (75% timothy and 25% meadow fescue) in batch leach bed reactors, and the methane potential of the feedstock was found to vary from 141 to 204 mL/g VS.

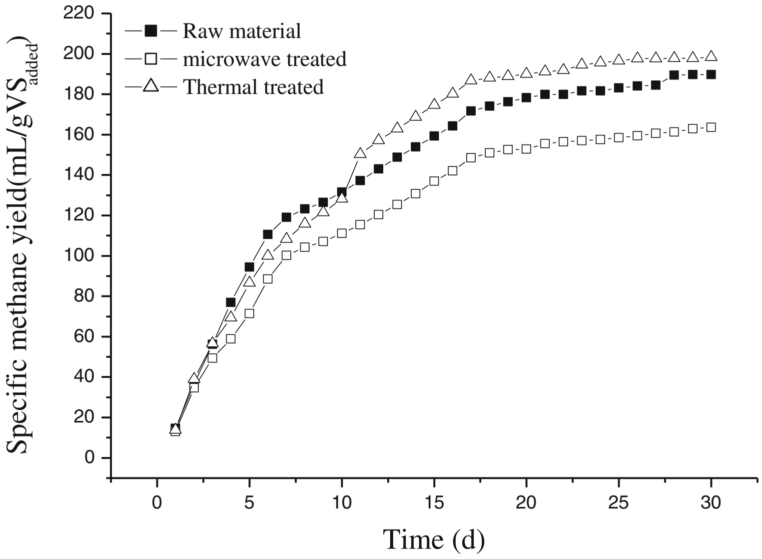

Fig. 1 The specific methane yield of untreated and treated samples

Table 2 Parameters and goodness fit obtained with the evaluated models

		P (mL/g VS)	R_m (mL/g VS days)	Λ (days)	R square
Raw material	Gompertz equation	184.17	14.03	0	0.990
	Logistic function	181.48	12.76	0	0.981
	Transference function	192.54	23.36	0.09	0.997
Microwave	Gompertz equation	160.82	11.39	0	0.992
	Logistic function	158.09	10.47	0	0.985
	Transference function	169.30	19.21	0.05	0.998

The specific methane yield decreased by around 13.8% after microwave pretreatment. Similarly, Jackowiak et al. [28] found that microwave pretreatment has no significant effect on the ultimate volume of methane produced from switchgrass. Specific methane yield increased by about 4.5% after thermal treatment. Similarly, Wang et al. [29] studied the effect of thermal pretreatment on activated sludge at temperatures below 100 °C and achieved a significant increase (30% to 52%) in methane yield. Laser et al. [30] obtained conflicting results: thermal pretreatment produced less methane due to the condensation and precipitation of lignin in the lignocellulosic substrate.

Models for Biogas Production

Figures 2 and 3 show the three models fit the experimental data from the anaerobic digestion of both untreated raw material and microwave-treated samples. The estimated values of the

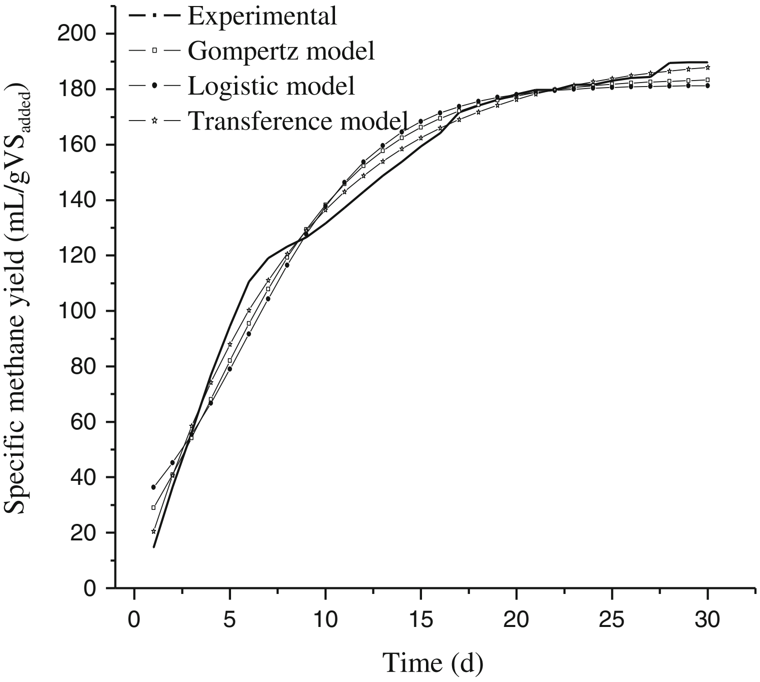

Fig. 2 Model fit with methane yield using non-pretreatment *Pennisetum* hybrid

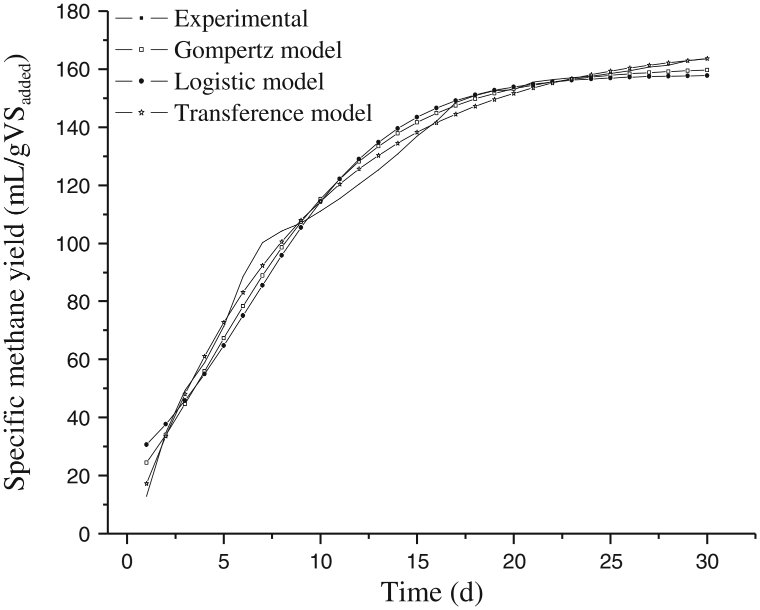

Fig. 3 Model fit with methane yield using the microwave pretreatment *Pennisetum* hybrid

parameters obtained in the optimization process are summarized in Table 2. In general, there was an overall agreement between the models and the experimental data. Comparing the performance models, the best fit was obtained using the Reaction Curve model, which achieved the highest regression of coefficients in all cases (above 0.99). For untreated samples, biogas production potential (*P*, in milliliters per gram VS) was ranked as follows: Transference function (192.5)>Modified Gompertz equation (184.2)>Logistic function (181.5). Maximum specific biogas production rate (R_m, in milliliters per gram VS per day) was ranked as follows: Transference function (23.36)>Modified Gompertz equation (14.03)>Logistic function (12.76) for R_m. For microwave-treated samples, biogas production potential and maximum specific biogas production rate were the same as those of the untreated samples. With regard to the parameter determination, the R_m value was of significant difference among the models, where the Transference function presented values up to 87.9% and 70.8% greater than those obtained with the Logistic function and Modified Gompertz equation, respectively. The lag time (λ) was negligible in the cases of the Logistic function and Modified Gompertz equation, and the lag time obtained from the Transference function model varied from 0.05 to 0.09 days. Maximum values of *P* (192.5 mL/g VS for raw material and 169.3 mL/g VS for microwave pretreatment) were obtained in the Transference function, which were 1.87% and 3.87% greater than the experimental data, respectively.

The three models used to evaluate the effects of thermal pretreatment on biogas production potential are shown in Fig. 4, and the estimated values of the parameters are summarized in Table 3. Although all the correlation coefficients of nonlinear analysis were above 0.990, the best consistency was obtained with the Transference function. Biogas production potential (*P*, milliliters per gram of VS) and maximum specific biogas production rate (R_m, in milliliters per gram of VS per day) of thermal-treated samples were respectively ranked as follows: (a) Transference function (211.4)>Modified Gompertz equation (199.6)> Logistic function (196.0) for *P*; and (b) Transference function (23.97)>Modified Gompertz

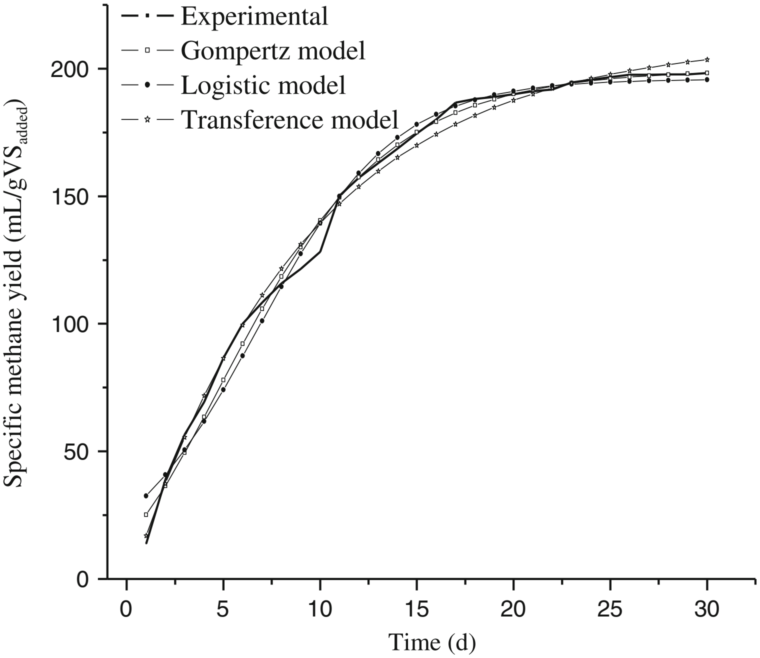

Fig. 4 Model fit with methane yield of thermal pretreatment *Pennisetum* hybrid

equation (14.47)>Logistic function (13.69) for R_m. In the thermal pretreatment case, the R_m value among the models was of significant difference, where the Transference function presented values up to 70.6% and 61.4% greater than those obtained with the Logistic function and Modified Gompertz equation, respectively. Calculated lag time was found to be less than 1 day, ranging between 0 and 0.24 days, because the ready biodegradation component in the material was quickly consumed in anaerobic digestion [31]. Maximum values of P (211.4 mL/g VS) were obtained in the Transference function, which were 6.62% greater than the experimental data.

Similar results were obtained by Donoso-Bravo et al. [25] who studied the effect of thermal and sonication pretreatment on the anaerobic degradation of sewage sludge through the calculation of performance parameters using these three models. All the models consisted of the experimental data with the regression of coefficients above 0.97, and the Reaction curve model presented the best agreement in the fitting process. A comparison between the modified Gompertz, Logistic, and Richards equations was done by Altas [32], who fit these models on biogas production of granular sludge to describe the inactivation of anaerobic culture by heavy metals.

Table 3 Parameters and goodness fit obtained with the evaluated models

Thermal pretreatment	P (mL/g VS)	R_m (mL/g VS days)	Λ (days)	R square
Gompertz equation	199.60	14.47	0	0.996
Logistic function	195.95	13.69	0	0.992
Transference function	211.42	23.97	0.24	0.997

Conclusions

The effects of microwave and thermal pretreatment on biogas production of the *Pennisetum* hybrid were of considerable difference. Thermal pretreatment improved the biogas production of the *Pennisetum* hybrid, whereas microwave use had a negative effect. The three simple models were demonstrated to be proper tools for evaluating performance parameters of anaerobic digestion. A significant difference between the models was observed for the value of maximum biogas production rate, and the Reaction curve model showed better consistency with the experimental data than the Modified Gompertz and Logistic model.

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