



# Steam explosion pretreatment of rice straw to improve structural carbohydrates anaerobic digestibility for biomethanation

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Received: 2 August 2018 / Revised: 1 May 2019 / Accepted: 3 May 2019 / Published online: 30 May 2019  
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## Abstract

Effectiveness of steam explosion (SE) pretreatment for deconstructing the complex structural carbohydrates (SC) and lignin recalcitrance properties of rice straw (RS) for conjunctive improvement of biofuel yield and waste valorization was evaluated. This work exhibited successful pretreatment of RS at a different pressure (1.2, 1.5, and 1.8 MPa) and retention (3, 6, 9, and 12 min) for enhancement of SC contribution to biomethane production. Regression analysis demonstrated that SE pretreatment efficiency improved at high-temperature and short-retention time for biodegradation of RS. Maximum cumulative methane yield (EMY) achieved 254.8 mL/gvs at 1.2 MPa (3 min) of SE-treated RS with 62.7% of very significant improvement compared with untreated RS (156.6 mL/gvs). Furthermore, solid fraction of xylose, arabinose, cellobiose, glucose, and acid-soluble lignin in SE-treated RS of 1.2 MPa (3 min) were biodegraded by 27.4%, 46.4%, 100%, 48.8%, and 14.1%, respectively, after anaerobic digestion. Therefore, SE pretreatment was an encouraging approach for enhancing SC conversion to biomethane and waste resource to circular economy.

**Keywords** Rice straw · Anaerobic digestion · Biodegradation · Modeling · Recalcitrance · Steam explosion · Treatment

## Abbreviations

AD	Anaerobic digestion
ASL	Acid-soluble lignin
B <sub>d</sub>	Biodegradability
C/N	Carbon to nitrogen ratio
EMY	Maximum cumulative methane yield obtained by experiment
FA	Free ammonia nitrogen

MMY	Theoretical maximum methane potential
MPa	Megapascal
RS	Rice straw
SC	Structural carbohydrates
SE	Steam explosion
TA	Total alkalinity
TS	Total solid
VFA	Volatile fatty acids
VS	Volatile solid

Responsible editor: Philippe Garrigues

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s11356-019-05382-w>) contains supplementary material, which is available to authorized users.

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## Introduction

Rice is the prime diet of about 50 % of people worldwide as well as a major cultivated crop in many Asian countries. China is the world leading rice grower and produces around 300 million metric tons of rice crop residues each year, after harvesting the rice (Luo et al. 2019). Disposal of such a huge quantity of rice crop residues is a big issue because of high collection and transportation cost and low market value, and farmers are in a hurry to prepare their farm-field for the next crop cultivation. The commonly used effortless method for disposal a considerable proportion of rice crop residues is open field burning, which causes severe kinds of natural resource depletion and environmental

issues (air pollution, haze, and global warming) (Medina et al. 2015). Hence, there is a need to develop an integrated and sustainable approach to mitigate the rice crop residues issues. Biofuel production from rice crop residues is regarded as a better option for value addition and beneficial re-use (Abraham et al. 2016; Marousek 2013).

Anaerobic digestion (AD) is a low-cost, environmentally friendly, and mature tool for efficiently treating solid organic waste of agricultural sectors. AD process transforms organic matter into biogas in an anaerobic environment and the presence of microorganisms (Chu et al. 2015). Two main products are achieved after the completion of AD process; one is a clean energy in terms of methane (CH<sub>4</sub>) and another is a nutrient-rich by-product as a fertilizer for crops (Ma et al. 2017). However, digestion efficiency of feedstock is significantly reduced by the recalcitrant properties of lignocellulose. Disruption of the recalcitrant lignin bonds with the SC components could improve the hydrolysis of biomass and AD efficiency. Barriers of lignocellulosic biomass can be removed by efficient pretreatment (Koyama et al. 2017b).

The variety of pretreatment mechanisms have been established to deconstruct recalcitrance properties of lignocellulosic biomass for improving anaerobic digestibility for biomethanation. Among the developed pretreatment methods, acid and alkaline pretreatment technologies were most commonly studied and widely used (Digman et al. 2010; Kumar and Sharma 2017). However, acid and alkaline pretreatments could not deploy without a large quantity of water as well as to treat the downstream process to avoid the chemical impacts on the environment. Chemical pretreatment also causes the corrosion of equipment, and chemicals are usually expensive too (Ruiz et al. 2017). SE pretreatment is an environment-friendly technique and could be used to open up complex construction of lignocellulosic biomass. Saturated steam quickly heats lignocellulosic biomass for a short time in SE pretreatment; then the pressure is swiftly released, which cause cleavage of fibers and tearing cross-linkages of cell walls of the biomass (Holtzapfel et al. 1989; Zhang and Chen 2012). Overall, SE pretreatment causes the solubilization of hemicellulose and subsequent conversion into its structural units, while the lignin is relocated and partially transformed into fractional products in SE pretreatment and consequently cellulose undergoes to hydration steps (Aguilar et al. 2018; Ruiz et al. 2013; Siddhu et al. 2016a). However, SE pretreatment conditions greatly influence the open-up complex structure, biodegradation of lignocellulosic biomass, and biomethane yield. Inefficient SE pretreatment might convert the biomass components into inhibitors, which are not only waste of biomass, but also caused the loss of energy in terms of high input (Gikas 2014; Theuretzbacher et al. 2015). The statistical models might be also an effective and reliable approach for evaluating the SE pretreatment performance efficiency to improve anaerobic biodegradability of lignocellulosic feedstock and methane yield (Dandikas et al. 2018). So far, less information elucidated the

efficiency of SE pretreatment for opening up the RS complex bonding of SC and lignin components and subsequent improvement of each component contribution in AD process for biomethanation.

Current study was intended with the following objectives: (1) to examine the SE pretreatment effects on methane production performance of RS; (2) to determine the each SC component contribution in biomethanation of SE-treated and untreated RS during AD; and (3) to compare the biodegradation of SC components of SE-treated and untreated RS after AD.

## Materials and methods

### RS and inoculant

RS was acquired from Jiangsu Province, People's Republic of China. Then, chopped RS was dried at room temperature in laboratory, and large RS particles size was cut-down. After these steps, air-dried RS size in range of 1.5 to 2.0 cm was sieved out and wrapped airtightly and placed at 4 °C. The inoculant utilized in this experiment was effluent of Donghuashan biogas plant, Beijing, People's Republic of China.

### Pretreatment of RS with SE

Pretreatment of RS was carried out in an SE machine (Huada, Jiangsu, China). The highest operating temperature and pressure of SE was 250 °C and 20 MPa, respectively. Machine heating-up rate of temperature was 10° C/min, and maximum water flow rate was 30 mL/min to the steam generator. Each batch of 55 g of RS was soaked in 50 mL tap water to increase the moisture content (MC) to approximately 50% by using Eq. (1) and then fed into 5 L of the high-pressure chamber (Siddhu et al. 2016b). Each pressure (1.2, 1.5, and 1.8 MPa) was used to treat RS at the retention time of 3, 6, 9, and 12 min. All the samples were ejected out (cool down), as suddenly released the operating pressure (less than 1 s) of pretreatment. All the samples were collected (solid and liquid totally) from the collector after SE pretreatment. Then, the sample characteristics were measured for AD test. All SE-treated and untreated RS were put in 4 °C before AD (Li et al. 2015).

$$MC (\%) = [(1 - \text{total solid mass of RS}) / (\text{mass of RS} + \text{water added})] \times 100 \quad (1)$$

### AD of SE-treated RS

The AD test was conducted in 1-L serum bottle to assess digestibility of untreated and SE-treated RS. Feed of each digester on the substrate to inoculant ratio on VS basis was controlled to be 0.50 (Li et al. 2014). After feeding the

substrate and inoculant mixture, distilled water was used to fill up each digester up to 500 mL. Blank digesters were also prepared for correcting biogas yield calculation of RS and had the same amount of inoculant. After this step, nitrogen gas was purged into each digester for 3 min for anoxic condition. After fixing the rubber stopper and screw cap, each digester was set in an incubator for the mesophilic AD. After completion of the AD, effluent characteristics were determined (Zhao et al. 2017).

## Analytical methods

Basic characteristics of RS and inoculant such as total solid (TS) and VS contents were measured by APHA protocol (APHA 2005). Elements, such as C, H, and N, of untreated RS and inoculant, were analyzed by a Vario El cube (Germany) detector, and O was determined as reported previously (Rincón et al. 2012). The daily pressures of biogas in all the digesters were determined as previously reported by our laboratory (Chen et al. 2016; Siddhu et al. 2016b). Biogas volume of each digester was determined by using Eq. (S1) (Shen et al. 2016). The equations form of S1, and details were presented in supplementary material.

Biogas composition was determined via 7890B gas chromatograph (Agilent, Technologies, USA) with thermal conductivity detector, while helium was used as carrier gas. GC's detector and oven temperature during the biogas sample test were 220 and 60 °C, respectively. Volatile fatty acids (VFAs) in effluents after AD were determined via a flame ionization detector fitted in GC-7890A, and nitrogen gas (N<sub>2</sub>) was used as carrier gas. Total ammonia nitrogen (TAN) and total alkalinity (TA) in effluent were measured by HACH protocol, while the free ammonia nitrogen (FA) was calculated via following Eq. (2) (Chen et al. 2016).

$$FA = TAN / \{1 + [(K_b \times 10^{-pH}) / K_w]\} \quad (2)$$

where FA stands for free ammonia nitrogen (mg/L), pH is final pH of effluents, TAN indicates total ammonia nitrogen (mg/L), and  $K_b$  and  $K_w$  stand for dissociation constant for ammonia and water at 37 °C ( $1.855 \times 10^{-5}$  and  $2.355 \times 10^{-14}$  mol/L, respectively).

## RS SC and lignin biodegradation

SC and lignin components were determined in a solid fraction of untreated, SE-treated RS and after AD by using the protocols of the NREL of the US Department of Energy (Sluiter et al. 2008). RS samples of untreated, SE-treated and after AD were treated by 72% sulfuric acid for 1 h at 30 °C. Then 72% sulfuric acid treated samples were diluted up to 4% by adding water and later these samples were autoclaved at 121 °C for 1 h. Then, cooled down and undissolved solid from

the liquid was separated by using a filtering crucible. High-performance liquid chromatography (SHIMADZU) separated with an Agilent Hi-Plex H column (30 × 0.77 cm, column temperature 65 °C), and a refractive index detector was used for determination of SC in liquid part. Five millimolar sulfuric acid was used for carrier solution (flow rate = 0.01 mL/s). Acid-soluble lignin (ASL) was determined at 320 nm wavelength by spectrophotometry method. After the AD, each component of RS (cellobiose, glucose, arabinose, xylose, xylitol, and ASL) biodegradation was calculated by Eq. (3).

$$M_b (\%) = \{(M_{\text{feeded}} - M_{\text{leftover}}) / M_{\text{feeded}}\} \times 100 \quad (3)$$

where  $M_b$  stands for component biodegraded,  $M_{\text{feeded}}$  refers to the component of the fed solid of RS in the digester, and  $M_{\text{leftover}}$  means the component in digested solid of RS.

## Theoretical maximum methane potential yield and biodegradability

Theoretical maximum methane potential yield (MMY) of untreated RS was calculated by using Eqs. (S2) and (S3), and then biodegradability ( $B_d$ ) was calculated by Eq. (S4) as reported previously (Buswell and Mueller 1952; Li et al. 2018). The equations form of S2, S3, and S4, and details were presented in supplementary material.

## Kinetic analysis

A modified Gompertz model was applied for evaluating the kinetics of methane production of SE-treated RS by using Eq. (S5) (Siddhu et al. 2016b): The model equation and description was provided in supplementary material (S5).

## Data analysis

Regression model and one-way analysis of variance were applied to analyse experimental data for determining a meaningful outcome. All statistical analysis was conducted at  $\alpha$  level of 0.01 and 0.05, respectively. Data was analyzed by using software of OriginPro 9.1 (OriginLab, USA).

## Results and discussion

### Basic characteristics of RS and inoculant

Table 1 presents the basic characteristics of untreated RS and inoculant. TS and VS contents were calculated to be 94.6% and 80.5%, respectively, on the basis of the total mass of the sample. According to elemental analysis, the C/N ratio was found to be 34.0, which was slightly higher than the recommendation for an AD in previously reported studies (18 to 30)

**Table 1** Characteristics of rice straw and inoculant

Content	RS	inoculant
TS (%)	94.6	9.4
VS (%)	80.5	4.8
VS/TS (%)	85.1	51.5
pH	ND	7.7
C (%) <sup>b</sup>	40.5	27.5
H (%) <sup>b</sup>	5.5	3.8
O (%) <sup>b</sup>	44.0	ND
N (%) <sup>b</sup>	1.2	2.4
Ratio of C/N	35.0	11.3

ND not determined

<sup>a</sup> As per mass of sample

<sup>b</sup> Based on TS of the sample

(Li et al. 2014). RS could be represented as an organic substrate in the following formula:  $C_{40.8}H_{66.4}O_{33.3}N$ . MMY of RS was determined by Eq. (S2) to be  $407.1 \text{ mL/g}_{\text{vs}}$ .

### AD for SE pretreated RS

Table 1S revealed the daily methane yield (DMY) production of untreated and SE-treated RS. The maximum DMY of 1.2 MPa for 3, 6, 9, and 12 min of SE-treated RS was  $12.0 \pm 0.4$ ,  $13.5 \pm 0.0$ ,  $12.1 \pm 0.0$ , and  $9.9 \pm 0.0 \text{ mL/g}_{\text{vs}}$ , respectively, while that of untreated RS was only  $8.5 \pm 0.3 \text{ mL/g}_{\text{vs}}$ . In addition, the highest peaks of 1.2 MPa SE-treated RS for 3, 6, 9, and 12 min appeared on the fifth day, while the untreated appeared at the eighth day of digestion. The average DMY of SE-treated RS of 1.2 MPa for 3, 6, 9, and 12 min were  $5.5 \pm 0.4$ ,  $5.2 \pm 0.3$ ,  $4.8 \pm 0.4$ , and  $4.2 \pm 0.2 \text{ mL/g}_{\text{vs}}$ , respectively, while the untreated RS was observed to be  $3.5 \pm 0.3 \text{ mL/g}_{\text{vs}}$ . Average DMY of SE-treated RS of 1.2 MPa decreased, as increase of retention time and pressure for pretreatment, while average DMY of each SE-treated RS increased as evaluated with untreated.

Ninety percent of maximum cumulative methane yield (EMY) for all SE-treated RS groups (1.2, 1.5, and 1.8 MPa) was achieved within the first 39 days of digestion. Figure 1a exhibits that the EMYs at 1.2 MPa for 3, 6, 9, and 12 min of SE-treated RS were  $254.8 \pm 16.0$ ,  $246.2 \pm 5.8$ ,  $234.0 \pm 9.3$ , and  $195.1 \pm 5.6 \text{ mL/g}_{\text{vs}}$ , representing a significant improvement of 62.7%, 57.3%, 49.5%, and 24.6%, respectively, compared with the untreated RS ( $156.6 \pm 3.5 \text{ mL/g}_{\text{vs}}$ ). The EMY of SE-treated RS of 1.2 MPa (3 min) was 3.5%, 8.9%, and 30.6% higher, respectively, than retention time of 6, 9, and 12 min for pretreatment. A dwindling in methane yield was noticed per increase in retention time at constant pressure. It was considered that SE treatment at 1.2 MPa for 3 min was effective in altering RS recalcitrant properties compared with the longer retention time.

Figure 1b demonstrates that the EMY of SE-treated RS of 1.5 MPa for 3, 6, 9, and 12 min were  $248.1 \pm 0.2$ ,  $222.9 \pm 4.6$ ,  $214.0 \pm 4.7$ , and  $196.1 \pm 0.1 \text{ mL/g}_{\text{vs}}$ , which were significantly improved by 58.4%, 42.4%, 36.7%, and 25.3%, respectively, compared with untreated RS ( $156.6 \pm 3.5 \text{ mL/g}_{\text{vs}}$ ). EMY of SE-treated RS of 1.5 MPa for 3 min was 11.3%, 15.9%, and 26.5% higher, respectively, than the retention time of 6, 9, and 12 min pretreatment. A pronounced decrease of methane yield was detected with the increase of retention time at 1.5 MPa. It was considered that SE treatment at 1.5 MPa for 3 min was suitable to change the recalcitrant characteristics of RS for AD compared with the longer retention time, which caused increased energy input.

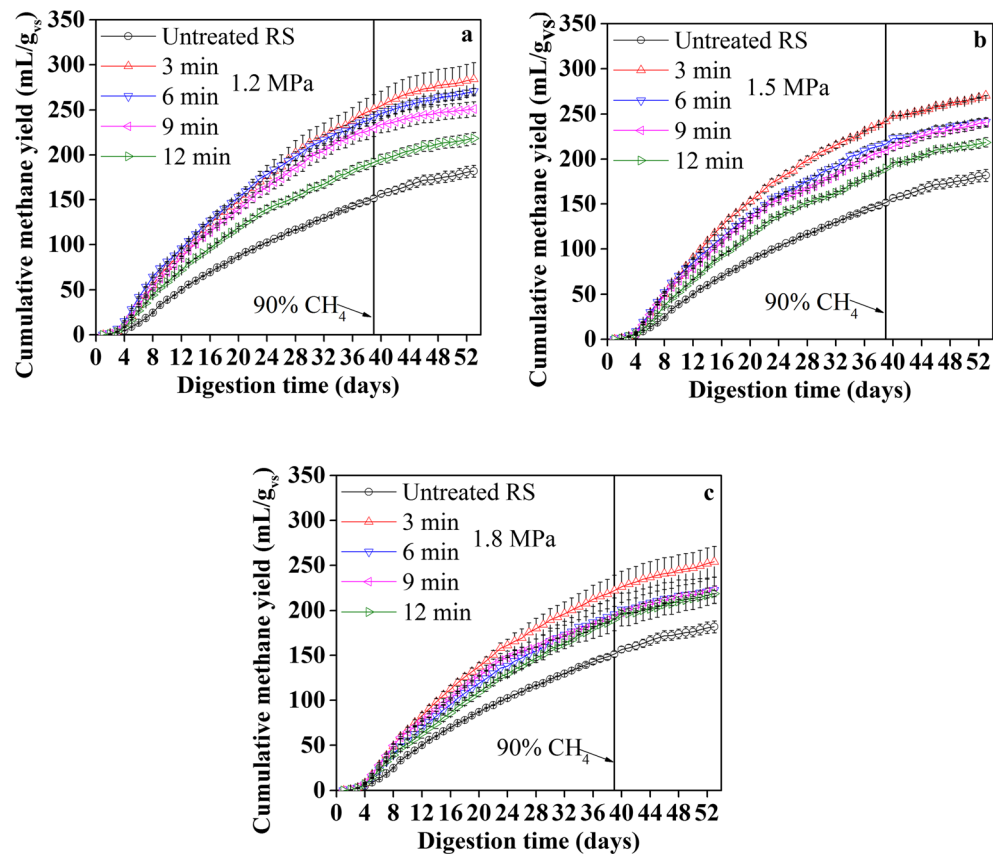
Figure 1c shows that the EMYs of SE-treated RS of 1.8 MPa for 3, 6, 9, and 12 min were  $226.1 \pm 17.3$ ,  $200.9 \pm 18.2$ ,  $197.9 \pm 2.2$ , and  $196.6 \pm 0.6 \text{ mL/g}_{\text{vs}}$ , which were significantly improved by 44.4%, 28.3%, 26.4%, and 25.6%, respectively, compared with the untreated RS ( $156.6 \pm 3.5 \text{ mL/g}_{\text{vs}}$ ). The EMYs of SE-treated RS of 1.8 MPa for 3 min were 12.6%, 14.3%, and 15.0% higher, respectively, than 6, 9, and 12 min of pretreatment. A noticeable decrease in methane yield at long retention for pretreatment at constant (1.8 MPa) pressure and increase input energy for pretreatment. It was considered that SE treatment of RS of 1.8 MPa (3 min) was deconstructed recalcitrant characteristics compared with the longer retention time.

Furthermore, DMY and EMYs of pretreated RS at three different pressures 1.2, 1.5, and 1.8 MPa and constant retention time of 3 min were compared and presented in supplementary material in Fig. 1S. The maximum DMY of 1.2, 1.5, and 1.8 MPa for 3 min of SE-treated RS was  $12.0 \pm 0.4$ ,  $12.1 \pm 0.3$ , and  $10.9 \pm 0.5 \text{ mL/g}_{\text{vs}}$ , respectively, and appeared on the fifth day of digestion. EMY of SE-treated RS of 1.2 MPa was 2.7% and 12.7% higher than 1.5 and 1.8 MPa at 3 min. Therefore, looking at the methane yield, input energy, SE efficiently overcomes the recalcitrant properties; SE pretreatment at 1.2 MPa and 3 min might be the optimal condition for efficient anaerobic digestibility of RS.

### Characteristics of effluent of untreated and SE-treated RS

Effluent parameters of untreated and SE-treated RS are shown in Table 2. The initial pH in AD reactors of untreated and 1.2 to 1.8 MPa SE-treated RS were ranged from  $8.2 \pm 0.0$  to  $8.3 \pm 0.0$ . After the successful AD, the pH inside each reactor was also measured and found to be within a permissible range from  $6.8 \pm 0.0$  to  $8.2 \pm 0.0$  (Koyama et al. 2017a; Theuretzbacher et al. 2015).

**Fig. 1** EMY of SE-treated RS; 1.2 MPa (a), 1.5 MPa (b), and 1.8 MPa (c) and untreated RS



After AD, effluent of untreated and SE-treated RS at 1.2, 1.5, and 1.8 MPa for 3 min was analyzed to assess the anaerobic process stability. Both the TA, VFA, and their relative proportions are important parameters for a successful AD. The TA (carbonate/bicarbonate) is an indicator to evaluate acid neutralization in the AD process. The final TA value for the untreated RS was the highest ( $2750 \pm 50.0$  mg  $\text{CaCO}_3/\text{L}$ ), but TA value decreased at higher pressure (1.2 MPa of  $2600 \pm 50.0$ , 1.5 MPa of  $2275 \pm 125.0$ , 1.8 MPa of  $2250 \pm 50.0$  mg  $\text{CaCO}_3/\text{L}$ ) of SE at constant retention time (3 min). All the final values were found to be within the permissible range (1000 to 3000 mg  $\text{CaCO}_3/\text{L}$ ) (Theuretzbacher et al. 2015). VFAs in the effluent of SE-treated RS reactors were in the range of 18.6 to 57.5 mg/L, while inhibition starts over 350 mg/L concentration (Li et al. 2014).

Nitrogen is an essential nutrient for microbial growth of anaerobic function throughout the AD process. TAN values

of all the digesters were analyzed and found to be within an acceptable range (less than 1700 mg/L) (Theuretzbacher et al. 2015), and no inhibition was occurred in any of the digesters. FA is a pH-dependent portion of the TAN, and FA is most toxic to methanogens. Each calculated value of FA by using an Eq. (3) was below the 50 mg/L and was considered to be sustainable for AD. (Ramos-Suárez et al. 2014). Therefore, no sign of FA-based inhibition was seen in the digesters. All of these results indicated that digesters were stable and conditions were appropriate for the AD after SE pretreatment.

**Modified Gompertz model**

Kinetics of methane production process of untreated and treated RS were investigated by modified Gompertz model, and parameters are presented in Table 3, While  $R^2$  varied from 0.993 to 0.994, which also proved that modified Gompertz model simulated the methane production process very well.

**Table 2** Internal reactor parameters of untreated and SE-treated RS

Samples	Initial pH	Final pH	TA (mg $\text{CaCO}_3/\text{L}$ )	TAN (mg/L)	FA (mg/L)	VFA (mg/L)
Untreated RS	$8.2 \pm 0.0$	$7.0 \pm 0.0$	$2750 \pm 50.0$	$239 \pm 1.0$	$3.3 \pm 0.3$	28.3
1.2SE <sub>3</sub>	$8.2 \pm 0.0$	$7.0 \pm 0.0$	$2600 \pm 50.0$	$281 \pm 3.0$	$3.5 \pm 0.0$	57.5
1.5SE <sub>3</sub>	$8.3 \pm 0.0$	$7.0 \pm 0.0$	$2275 \pm 125.0$	$236 \pm 2.0$	$2.7 \pm 0.0$	18.6
1.8SE <sub>3</sub>	$8.3 \pm 0.0$	$7.0 \pm 0.0$	$2250 \pm 50.0$	$254 \pm 14.0$	$3.2 \pm 0.3$	35.7

**Table 3** Modified Gompertz model parameters of methane production, EMY, and biodegradability of RS

Samples	Parameters of model				EMY (mL/g <sub>vs</sub> )	B <sub>d</sub> (%)
	B <sub>0</sub> (mL/g <sub>vs</sub> )	μ <sub>m</sub> (mL/g <sub>vs</sub> /day)	λ (day)	R <sup>2</sup>		
Untreated RS	165.9 ± 4.1	5.4 ± 0.2	2.7 ± 0.4	0.993	156.6 ± 3.5	38.5
1.2SE <sub>3</sub>	272.0 ± 6.3	9.0 ± 0.3	1.7 ± 0.4	0.993	254.8 ± 16.0	62.6
1.5SE <sub>3</sub>	251.8 ± 4.1	9.5 ± 0.3	2.2 ± 0.3	0.994	248.1 ± 0.2	60.9
1.8SE <sub>3</sub>	233.3 ± 4.4	8.4 ± 0.3	1.9 ± 0.4	0.993	226.1 ± 17.3	55.6

SE stands for steam explosion, and 3 stands for pretreatment retention time

The model estimated simulated maximum cumulative methane yield (B<sub>0</sub>) of untreated RS (165.9 ± 4.1 mL/g<sub>vs</sub>) was slightly higher than the EMY (156.6 ± 3.5 mL/g<sub>vs</sub>). In addition, B<sub>0</sub> of 1.2 MPa SE-treated RS for 3 min (272.0 ± 6.3 mL/g<sub>vs</sub>) was slightly more than the EMY achieved (254.8 ± 16.0 mL/g<sub>vs</sub>). While B<sub>0</sub> and EMY of 1.5 and 1.8 MPa SE-treated RS for 3 min were almost identical. The maximum methane production rate (μ<sub>m</sub>) of untreated and SE-treated RS ranged from 5.4 ± 0.2 to 9.5 ± 0.3 mL/g<sub>vs</sub>/day. The μ<sub>m</sub> of untreated RS was the lowest (5.4 ± 0.2 mL/g<sub>vs</sub>/day) compared to 1.2, 1.5, and 1.8 MPa for 3 min SE-treated RS. On the other hand, the μ<sub>m</sub> value at highest pressure (1.8 MPa) was the lowest among all the SE-treated RS at constant retention time (3 min). λ is the lag phase time and a higher λ value indicates a long start-up time, because of recalcitrant characteristics of RS. RS treated for 3 min at 1.2 MPa had the lowest λ of 1.7 ± 0.4 day, which was because of SE treatment impact for acceleration of hydrolysis, enabling a shorter AD initiating time. Furthermore, B<sub>d</sub> is another indicator to evaluate and compare the performances of untreated and SE-treated RS of AD; “B<sub>d</sub> was calculated from EMY obtained by experiment divided by the theoretical maximum methane potential.” At constant retention time of 3 min, 1.2 MPa pretreated RS achieved the highest B<sub>d</sub> of 62.6%, compared to 1.5 MPa, 1.8 MPa, and untreated RS of 60.9%, 55.6%, and 38.5%, respectively. In general, SE-treated of 1.2 MPa for 3 min resulted in deconstructing complex structure of RS, and B<sub>d</sub> significantly improved 62.6% compared with untreated.

### Regression analysis for retention time and temperature of SE

Variation of retention time and temperature of SE causes influence of methane yield from RS. A regression analysis was developed to explain the consequence of temperature and retention time of SE pretreatment for RS on EMY (at constant pressure of 1.2 MPa of SE) and shown in Eq. (4).

$$EMY_{1.2MPa} = -2382 + 15.2 T - 26.6 t \quad (4)$$

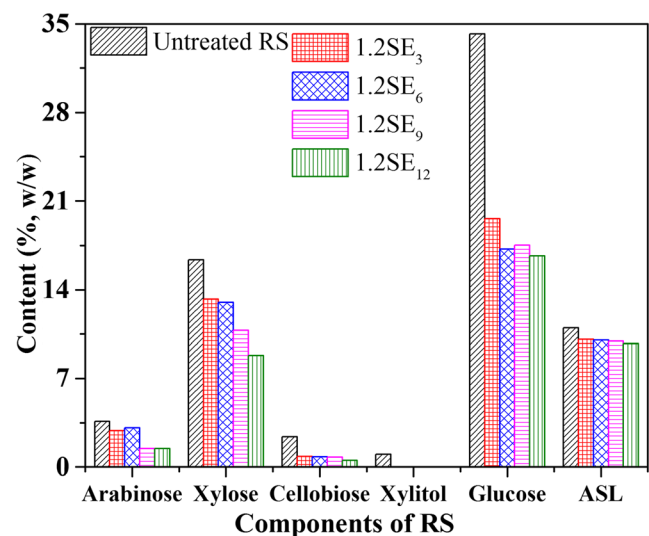
where EMY<sub>1.2MPa</sub> stands for maximum cumulative methane yield at 1.2 MPa of SE-treated RS (mL/g<sub>vs</sub>), *t* represents the

retention time of RS in steam chamber (min), and *T* means the temperature in the steam chamber (°C).

The coefficient of determination (R<sup>2</sup>) of the regression analysis was 0.963, which indicated that model was a reasonable fit. The long retention time for pretreatment of RS was impacted negative to EMY. The long retention time of SE on biomass causes the production of furfural and its derived compounds (Palmqvist and Hahn-Hägerdal 2000). While the temperature of SE treatment was implied as a positive contribution to breakdown the recalcitrance, interlinks of physical and chemical structure of RS and subsequent enhanced the hydrolysis for methane production. The temperature causes “cracking”: Moisture penetrates into the cell wall structure and swells the biomass. This destructive step caused shear stress on the RS tissues and might increase the biomass surface area (Sui and Chen 2014; Zhang et al. 2013).

### SC and lignin components in solid fraction of untreated and SE-treated RS

SC and lignin components of the solid fraction of untreated and SE-treated RS of 1.2 MPa (3, 6, 9, and 12 min) before AD are presented in Fig. 2. Cellobiose and glucose are mainly



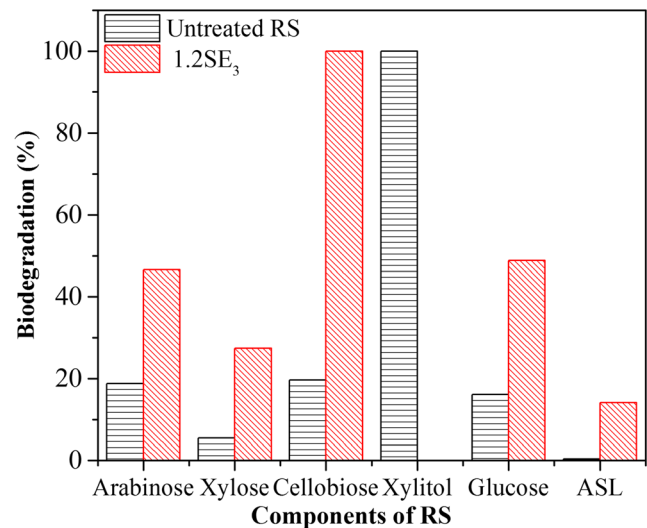
**Fig. 2** Components in untreated RS and SE-treated (1.2 MPa) for 3, 6, 9, and 12 min before AD. Units in percentage (dry basis)

released from cellulose (Philippidis et al. 1992). The cellobiose component of SE-treated (1.2 MPa for 3 min) RS decreased as compared to untreated (0.8% vs 2.4%). The cellobiose component also decreased with the increase in retention time from 3 to 12 min of SE pretreatment of RS (0.8% to 0.5%). The glucose component of SE-treated (1.2 MPa for 3 min) RS was significantly reduced in comparison with the untreated RS (19.6% vs 34.2%). SE pretreatment might cause solubilization of sugar and destruction of microfibrils. Increasing the retention time of SE from 3 to 12 min could also cause solubilization of glucose as measured values indicated (19.6% to 16.7%) of RS (Sasaki et al. 2012).

Arabinose component of SE-treated (1.2 MPa for 3 min) RS decreased in comparison with untreated (2.9% vs 3.6%), and increase in retention time (3 to 12 min) of pretreatment also caused more decrease in arabinose (2.9 to 1.4%). The xylose component of the SE-treated RS for 3 min decreased in comparison to untreated (13.2% vs 16.4%). The xylose component also decreased (13.2% to 8.8%) with the increasing of SE retention time from 3 to 12 min. Xylitol was completely removed after the SE pretreatment, most likely because of its high solubility at high temperature. The ASL was slightly reduced to 10.1% in SE-treated RS as compared to untreated values of 11.0%. Long retention of SE pretreatment caused more hydrolysis of SC, resulting in more destruction of fibrils in RS. However, it not only increased the cost of the pretreatment process but also might lead to conversion of SC into inhibitors, which were toxic for AD process. Therefore, 1.2 MPa for 3 min of SE pretreatment condition for RS was preferred by deconstructing recalcitrance structure for the ultimate improvement in methane production.

### Biodegradation of SC and lignin components in solid after AD

The impact of SE pretreatment on RS for enhancing biodegradation of SC and lignin was analyzed after the successful AD process and is presented in Fig. 3. AD is a very complex process involving consortia of bacteria and archaea. Lignin is highly recalcitrant by nature and is a primary barrier to microbial access of hemicellulose and cellulose during hydrolysis (Ahring et al. 2015). Biodegradation of ASL in untreated and SE-treated RS was 0.4% and 14.1% during the AD. In addition, each SC and lignin component (arabinose, xylose, glucose, cellobiose, and ASL) hydrolyzed differently, and the hydrolysis products formed also varied. It is not surprising that some variations were observed during AD. Hemicellulose plays the link role between cellulose and lignin. Other literatures have found that removal of the covalent bonding in xylose and arabinose with lignin could enhance the hydrolysis and biodegradation of hemicellulose (Barakat et al. 2013). Biodegradation of arabinose and xylose components of SE-treated RS (1.2 MPa, 3 min) was higher (46.4%, 27.4%) as compared to untreated



**Fig. 3** Biodegradation of components in SE-treated (1.2 MPa, 3 min) and untreated RS after AD

(18.8%, 5.5%), respectively, after AD. Glucose and cellobiose components of untreated and SE-treated RS at 1.2 MPa (3 min) were biodegraded 16.1%, 48.8%, and 19.7%, 100%, respectively, after AD.

These collective results indicated that SE treatment of RS at 1.2 MPa for 3 min significantly altered the most recalcitrant lignin shield structure for SC and subsequently caused enhancement of hemicellulose–cellulose components hydrolysis. Glucose, cellobiose, arabinose, and xylose components of SE-treated RS were significantly biodegraded as compared to untreated after the AD process. Therefore, SE pretreatment of RS could deconstruct recalcitrance structure of RS, break fibrils down, enhance the hydrolysis, and was likely a key contributor to the higher biogas production.

### Conclusions

Steam explosion pretreatment (SE) was applied at three different pressures (1.2, 1.5, and 1.8 MPa) for four different retention times to rice straw for improving structural carbohydrate (SC) contribution in methane production during AD. The EMY of SE-treated RS at 1.2, 1.5, and 1.8 MPa for 3 min was increased significantly by 62.7%, 58.4%, and 44.4%, respectively, over untreated.  $B_d$  of SE-treated RS of 1.2 MPa for 3 min achieved 62.6% as compared to 38.5% of untreated. Results confirmed that SE pretreatment significantly enhanced the anaerobic digestibility of SC components of RS for biomethanation and was a promising technique for advanced application.

**Acknowledgments** This work was supported by the National Key Research and Development Program of China (2017YFD0800801) and China Scholarship Council.

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