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In-situ injection of potassium hydroxide into briquetted wheat straw and meadow grass – Effect on biomethane production

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HIGHLIGHTS

- Lignocellulosic biomass was pretreated by in-situ injection of KOH during briquetting process.
- Pretreated capacity ranged from 350 to 800 kg.h^{-1} corresponding to 0.8%–10% (w/w) of KOH injection.
- Improvements in both biomethane yield and hydrolysis rate were observed.

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ABSTRACT

Alkaline pretreatment of lignocellulosic biomass has been intensively investigated but heavy water usage and environmental pollution from wastewater limits its industrial application. This study presents a pretreatment technique by in-situ injection of potassium hydroxide concentrations ranging from 0.8% to 10% (w/w) into the briquetting process of wheat straw and meadow grass. Results show that the biomethane yield and hydrolysis rate was improved significantly with a higher impact on wheat straw compared to meadow grass. The highest biomethane yield from wheat straw briquettes of 353 mL.g^{-1} VS was obtained with 6.27% (w/w) potassium hydroxide injection, which was 14% higher than from untreated wheat straw. The hydrolysis rates of wheat straw and meadow grass increased from 4.27×10^{-2} to 5.32×10^{-2} d^{-1} and 4.19×10^{-2} to 6.00×10^{-2} d^{-1}, respectively. The low water usage and no wastewater production make this a promising technology.

1. Introduction

Lignocellulosic biomass such as agricultural byproducts and grass has been widely utilized for bioenergy/biogas production due to their large fermentable carbohydrate components (cellulose and hemicellulose) and the large quantities that can be harvested from agricultural, forestry, municipal and other activities (Zheng et al., 2014). However, the recalcitrant nature of the lignocellulosic structure and low bulk density of these substrates greatly limit their energetic application (Theerarattananoon et al., 2012). Pretreatment technology prior to anaerobic digestion has been widely investigated (Zheng et al., 2014). The goals of pretreatment are to remove lignin and hemicellulose, reduce the crystallinity of cellulose and increase the porosity of the lignocellulosic materials, which potentially improves the accessibility of microbes and enzymes during biofuel/gas production (Kumar et al., 2009).

Alkaline pretreatments of lignocellulosic biomass using NaOH, $Ca(OH)_2$, KOH, and $NH_3{\cdot}H_2O$ have received most of the research interest (Li et al., 2015). Specifically the pretreatment with KOH is recommended because potassium is a valuable plant nutrient (Liu et al., 2015b). The processes in alkaline pretreatment are believed to be saponification and cleavage of lignin-carbohydrate linkages (Tarkow and Feist, 1969), making the lignocellulosic biomass woollen and increasing its degradability during biogas production. However, industrial application of KOH pretreatment has so far faced difficulties due to the high price of KOH, the large quantities of water needed as a reaction solvent and, as a result, the costs of discharging used black liquid (Liu et al., 2015a). Alkaline pretreatment operated at low or moderate temperatures normally require longer reaction time from several hours to weeks (Kim et al., 2016). In this situation, combining the alkali pretreatment with other pretreatments to reduce the alkaline concentration and shorter the pretreatment time is necessary (Cara et al., 2006; Chandra et al., 2012).

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Briquetting is a mechanical process that condenses the biomass from 0.1 kg.L^{-1} to around 1.2 kg.L^{-1} by screw or piston press (Hood, 2010; Xavier et al., 2015). The use of briquettes in biogas production offers economic advantages by lowering the handling costs (feeding), transportation and storage (Rijal et al., 2012; Theerarattananoon et al., 2012). Furthermore, the use of compacted briquettes as a feedstock for anaerobic digestion can prevent a floating layer and ease the mixing inside the digester (Moset et al., 2015b). Most importantly, excess steam could be produced at moisture content higher than 10% (Baskar et al., 2012), hydrolyzing the hemicellulose and lignin into low-molecular weight carbohydrates, lignin products, sugar polymers, and other derivatives (Grover and Mishra, 1996). In terms of pretreatment, briquetting is not only a mechanical process but also includes thermal pretreatment due to the temperature rise during the process.

In this study, a novel method was investigated involving in-situ injection of KOH into the briquetting process. Aqueous solutions of KOH were injected directly into the compression zone of the briquetting machine by a piston pump connected to a spray nozzle. The aim of this study was to evaluate the effect of in-situ injection of KOH on biomethane production from briquetted wheat straw and meadow grass.

2. Material and methods

2.1. Substrates

Wheat straw was collected from a farm near Viborg (Central Jutland, Denmark), which contained 90.77 ± 0.24% total solids (TS), 87.19 ± 0.06% volatile solids (VS) and 3.59 ± 0.30% ash. The fiber composition of the wheat straw was 44.80 ± 0.78% cellulose, 30.35 ± 0.76% hemi-cellulose and 7.20 ± 0.54% lignin based on dry matter. Meadow grass was harvested from a meadow near Ribe (West Jutland, Denmark). The harvested grass was left in the field and dried naturally for three days before collection. Predominant species in the meadow grass were: *Phalaris arundinacea* (80%), *Holcus lanatus* (10%) and *Glyceria fluitans* (5%). The meadow grass contained 93.42 ± 0.49% TS, 90.15 ± 0.58% VS and 3.27 ± 0.08% ash. The meadow grass fiber was composed of 37.80 ± 0.16% cellulose, 35.87 ± 1.55% hemi-cellulose and 4.02 ± 0.42% lignin based on dry matter. Both wheat straw and meadow grass were hammer-milled with a 20-mm sieve (Cormall HDH770, Denmark) before briquetting.

Mesophilic inoculum was obtained from a mesophilic pilot-scale reactor located at Research Centre Foulum (Aarhus University, Denmark) which had been running for more than one year under mesophilic conditions. The inoculum used in batch assays was pre-incubated for two weeks at mesophilic conditions in order to deplete the residual biodegradable materials (degasification). This inoculum contained 3.18 ± 0.09% TS, 2.30 ± 0.01% VS, 0.93 ± 0.00% ash, 1.40 g.L^{-1} total ammonia (TAN), 166.12 mg.L^{-1} total volatile fatty acids (VFA) and a pH of 7.70.

2.2. Pretreatment

Wheat straw and meadow grass were briquetted with a BP 6500 briquetting unit (CF Nielsen, Denmark). Aqueous solutions of KOH (1000 g KOH.L^{-1}) were injected into wheat straw/meadow grass by a piston pump connected to spray nozzles (two spray nozzles with different ranges of flow rate, as shown in Table 1) directly into the compression zone. The KOH flow rates using spray nozzle A were set to 6.72 L.h^{-1} (wheat straw) and 7.2 L.h^{-1} (meadow grass), which was increased to 31.2 L.h^{-1} (wheat straw) and 38.4 L.h^{-1} (meadow grass) with nozzle B. The injected KOH concentration was calculated based on Eq. (1):

$$\text{KOH concentration}(\%) = \text{Solution flow rate}(\text{L.h}^{-1}) \times 100/\text{Briquetting capacity}(\text{kg.h}^{-1}) \quad (1)$$

The capacity of the briquetting equipment was controlled by changing the frequency of the dosing screw, which ranged from 300 to 900 kg.h^{-1}, producing cylindrical briquettes with a 75 mm diameter. Parameters and corresponding KOH concentrations are shown in Table 1.

2.3. Ultimate biomethane yield

The ultimate biomethane yield (BMP_{90}) was determined following the procedures suggested by Moset et al. (2015a). Each bottle was filled with 200 mL degassed inoculum and substrates to achieve an inoculum-substrate ratio of approximately 1:1, based on VS content. Both the untreated substrates and briquetted substrates without KOH were included in the batch assay as references. A blank control with only inoculum was also included. All bottles were tightly sealed with rubber stoppers and screw caps and then purged with nitrogen gas for two minutes to create anaerobic conditions.

All bottles were incubated at 34 °C for 90 d in triplicates. Biogas yield and composition was periodically measured at day 4, 7, 10, 20, 30, 60 and 90 by inserting a needle attached to a tube with inlet to a column filled with acidified water (pH < 2) through the butyl rubber and was calculated by the water displaced until the two pressures (column and headspace in bottles) were equal. Biogas composition was analyzed using gas chromatography (Agilent technologies 7890A, CA 95051, USA) once a week. Biomethane pro-

Table 1
Parameters and corresponding injected KOH concentrations.

Feedstock	Briquetting capacity (kg.h^{-1})	KOH flow rate (L.h^{-1})[a]	Injected concentration (%, w/w)[a,*]	KOH flow rate (L.h^{-1})[b]	Injected concentration (%, w/w)[b,*]
Wheat straw	428	6.72	1.57	31.2	7.29
	498		1.35		6.27
	678		0.99		4.60
	752		0.89		4.15
Meadow grass	354	7.2	2.03	38.4	10.85
	378		1.90		10.16
	414		1.74		9.28
	564		1.28		6.81
	654		1.10		5.87
	817.5		0.88		4.70

[a] Spray nozzle (HB1/8VV-650017, Spraying system Co., Illinois 60189, USA).
[b] Spray nozzle (TPU650067, Spraying system Co., Illinois 60189, USA).
[*] Calculated concentration.

duction from each sample was calculated by subtracting the volume of methane produced from the inoculum control. The specific methane yield was adjusted to standard conditions (0 °C and 1.013 bar).

2.4. Analyses

Total solids and volatile solids contents were measured according to the standard methods (APHA, 2005). The pH value was measured using a Portamess 911 pH meter (Knick, Germany). Conductivity was measured using an EC300 Conductivity meter (EcoSense®, VMR., OH 45387, USA). All samples for conductivity measurement were kept in an incubator at 25 °C for three hours prior to the measurement.

Samples for fiber analysis and FTIR were well mixed and dried at 60 °C for 48 h prior to analysis. 20 g pretreated samples were taken from a dried briquette (around 240 g) in order to avoid the influence from uneven alkaline distribution. Fiber fractions, neutral detergent fiber (NDF), acid detergent fiber (ADF) and lignin (ADL) were analyzed according to the Van Soest et al. (1991) method, using an ANKOM 2000 Fiber analyzer (ANKOM, Macedon NY 14502, USA). From these fractions, hemicellulose, cellulose and lignin contents were calculated. The hemicellulose content was calculated as the difference between NDF and ADF, the cellulose content as the difference between ADF and ADL, and the lignin content was assumed to be equal to ADL. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 6700 FT-IR spectrophotometer (Thermo Fisher Scientific, 02451 MA, USA) equipped with a DLaTGS detector using a KBR disk containing 1% finely ground samples. The spectra of untreated and treated samples were obtained with a resolution of 4 cm^{-1} taking a total of 30 scans (He et al., 2008).

2.5. Alkaline distribution

In this study, the KOH solution was directly injected into the compression zone during the briquetting process. It is essential to determine the distribution of injected alkali to different parts of a briquette. The pH value of pretreated samples is a common indicator, indirectly reflecting the alkaline consumption as a function of time (Xiao et al., 2013), while electrical conductivity is widely used as an estimate for the total ionic concentration, since it can be readily and accurately measured using portable instruments (Cooper and Charlesworth, 1977). In our study, both the pH value and conductivity were used as indirect indicators of the distribution of alkali in the same sample by the method described below:

(1) A briquette of 12 cm length was picked randomly and divided horizontally into three parts;
(2) The chosen part of the briquette was vertically and evenly divided into three parts (the average weight of each part was around 20 g);
(3) 10 g of homogenized sample was taken from each part and put into flask with 1 L deionized water;
(4) After fully mixing, all flasks were then kept in 25 °C incubator for 3 h;
(5) pH and conductivity were recorded when constant measurements were obtained.

2.6. Calculation and statistical analysis

In this study, a first-order kinetic model was used to fit the measured methane yield (Hashimoto, 1989) (Eq. (2)):

$$B = B_0(1 - exp^{-kt}) \tag{2}$$

where B represents the specific cumulative methane potential (mL $CH_4.g^{-1}$ VS) at time (t) in days, B_0 indicates the ultimate methane potential (BMP_{90}) at 90 days (mL $CH_4.g^{-1}$ VS) and k is the degradation constant (day). k is also considered as the rate of hydrolysis as the value provides information about the required time to acquire a certain proportion of BMP (Moset et al., 2015b).

The significance of the ultimate biomethane yields was obtained using analysis of variance (ANOVA) and Tukey-Kramer test at $\alpha = 0.05$. JMP 13.0 (SAS Institute Inc, 10740 Cary, USA) was used for graphing, modeling and statistical analysis.

3. Results and discussion

3.1. Fiber contents

The fiber composition of the wheat straw and meadow grass before and after pretreatment is shown in Table 2. It was found that the cellulose content from wheat straw briquettes with different KOH injection ranged from 42 to 46% while the hemi-cellulose and lignin contents were 24–30% and 4.5–7.2%, respectively. As shown in Table 2, 22.13% of the lignin and 4.66% of the hemi-cellulose content of wheat straw were hydrolyzed during the briquetting process. During the briquetting process, the steam formed by the moisture could extract hemi-cellulose by breaking the ether bonds in lignin/phenolic-carbohydrate complexes and degrade lignin into free phenolic acids (Buranov and Mazza, 2008; Tumuluru et al., 2011). Compared with untreated wheat straw, the hemi-cellulose and lignin content decreased significantly with increased KOH injection over 4.15%. Hemicellulose removal has proven to be contributing to increase the mean pore size of the substrate and improve digestibility of cellulose (Chang and Holtzapple, 2000). The lowest lignin content was observed from briquetted wheat straw with 4.15% KOH injection. In general, the results indicate that the pretreatment method combining KOH injection and briquetting mainly affect hemi-cellulose and lignin content.

The fiber composition of briquetted meadow grass was determined to be 37.80% cellulose, 29.64% hemi-cellulose and 4.7% lignin. The loss of hemi-cellulose was higher from briquetted meadow grass than from wheat straw. Compared with untreated grass, the hemi-cellulose content were significantly lower from briquetted meadow grass except the briquette with 1.74%, 1.9% and 2.03% KOH injection. However, the removal of hemi-cellulose from meadow grass briquettes was not followed the increased KOH concentrations. The hemi-cellulose content of meadow grass briquettes, for instance, with 10.85% KOH injection (29.12 ± 0.79%), was similar to that of grass briquettes without KOH injection (29.64 ± 0.86%). The lignin content was not significant removed ($p < 0.05$) for all the meadow grass samples. According to Zheng et al. (2014), alkaline pretreatment has the ability to increase the accessible surface, altering the lignin structure and solubilizing lignin, which is more effective with substrates with a high lignin content. The considerable variation in the composition and structure of lignin within and among plants could also explain the different performances (Barrière et al., 2003; Billa et al., 1998).

3.2. Ultimate methane yield

The ultimate methane yields (BMP_{90}) of wheat straw, briquetted wheat straw (with/without KOH injection) are shown in Fig. 1 and Table 3. After 90 day's digestion, the ultimate methane yield of wheat straw was determined to be 309.15 ± 7.37 $mL.g^{-1}$ - VS. Compared with untreated wheat straw, wheat straw briquettes had a 5% higher ultimate methane yield (325.43 ± 5.28 $mL.g^{-1}$ VS). Different KOH injected concentrations (0.99–6.27%) showed significant ($p < 0.05$) improvement (7.39–14.22%) on biomethane yield

Table 2
Fiber compositions and removals in wheat straw, meadow grass and briquettes with KOH injection.

Substrate[1]	Hemi-cellulose ($\%_{DM}$)	Removal[2,3] (%)	Cellulose ($\%_{DM}$)	Removal[2,3] (%)	Lignin ($\%_{DM}$)
WS	30.35 ± 0.76	0	44.80 ± 0.78	0	7.20 ± 0.54
BWS	28.93 ± 0.28	4.66	45.91 ± 0.27	−2.49	5.61 ± 0.59
$BWS_{0.89\%}$	27.65 ± 0.47	8.88	44.25 ± 0.64	1.24	5.11 ± 0.42
$BWS_{0.99\%}$	28.81 ± 0.35	5.07	46.42 ± 0.58	−3.62	5.49 ± 0.29
$BWS_{1.35\%}$	28.22 ± 1.11	7.01	44.56 ± 0.64	0.54	5.29 ± 0.36
$BWS_{1.57\%}$	28.39 ± 1.43	6.45	45.07 ± 0.88	−0.61	6.06 ± 1.45
$BWS_{4.15\%}$	24.03 ± 1.29	20.82	43.53 ± 1.66	2.84	4.56 ± 0.71
$BWS_{4.60\%}$	23.71 ± 0.53	21.87	42.68 ± 0.58	4.73	4.90 ± 0.23
$BWS_{6.27\%}$	25.94 ± 1.21	14.53	42.83 ± 0.87	4.40	5.11 ± 0.97
$BWS_{7.29\%}$	27.18 ± 1.35	10.43	43.41 ± 0.47	3.10	4.87 ± 0.26
MG	35.87 ± 1.55	0.00	37.80 ± 0.16	0.00	4.02 ± 0.42
BMG	29.64 ± 0.86	17.37	37.51 ± 0.71	0.76	4.73 ± 0.33
$BMG_{0.88\%}$	28.53 ± 0.33	20.48	38.88 ± 1.12	−2.87	4.95 ± 0.57
$BMG_{1.1\%}$	28.52 ± 1.13	20.51	38.88 ± 0.91	−2.87	4.09 ± 0.38
$BMG_{1.28\%}$	28.70 ± 1.23	19.99	37.61 ± 0.41	0.49	4.65 ± 0.67
$BMG_{1.74\%}$	32.26 ± 0.21	10.06	37.16 ± 0.91	1.68	4.12 ± 0.41
$BMG_{1.9\%}$	30.41 ± 2.08	15.22	37.58 ± 0.58	0.56	4.36 ± 0.37
$BMG_{2.03\%}$	30.41 ± 0.56	15.23	37.59 ± 1.16	0.54	4.95 ± 0.52
$BMG_{4.7\%}$	28.04 ± 0.95	21.84	37.58 ± 0.68	0.58	4.34 ± 0.63
$BMG_{5.87\%}$	27.20 ± 0.58	24.19	38.68 ± 0.43	−2.34	5.20 ± 0.39
$BMG_{6.81\%}$	21.43 ± 5.86	39.11	35.45 ± 2.36	6.22	4.27 ± 0.76
$BMG_{9.28\%}$	27.58 ± 2.02	23.11	35.99 ± 0.50	4.78	4.63 ± 0.18
$BMG_{10.16\%}$	26.82 ± 0.61	25.24	36.40 ± 0.33	3.69	4.82 ± 0.45
$BMG_{10.85\%}$	29.12 ± 0.79	18.83	36.42 ± 0.45	3.63	3.81 ± 0.48

[1] WS, wheat straw; BWS, briquetted wheat straw; MG, meadow grass; BMG, briquetted meadow grass.
[2] The negative value indicate that there is no removal.
[3] The removal was calculated as [the content (original) − content (pretreated)]/content (original) × 100%.

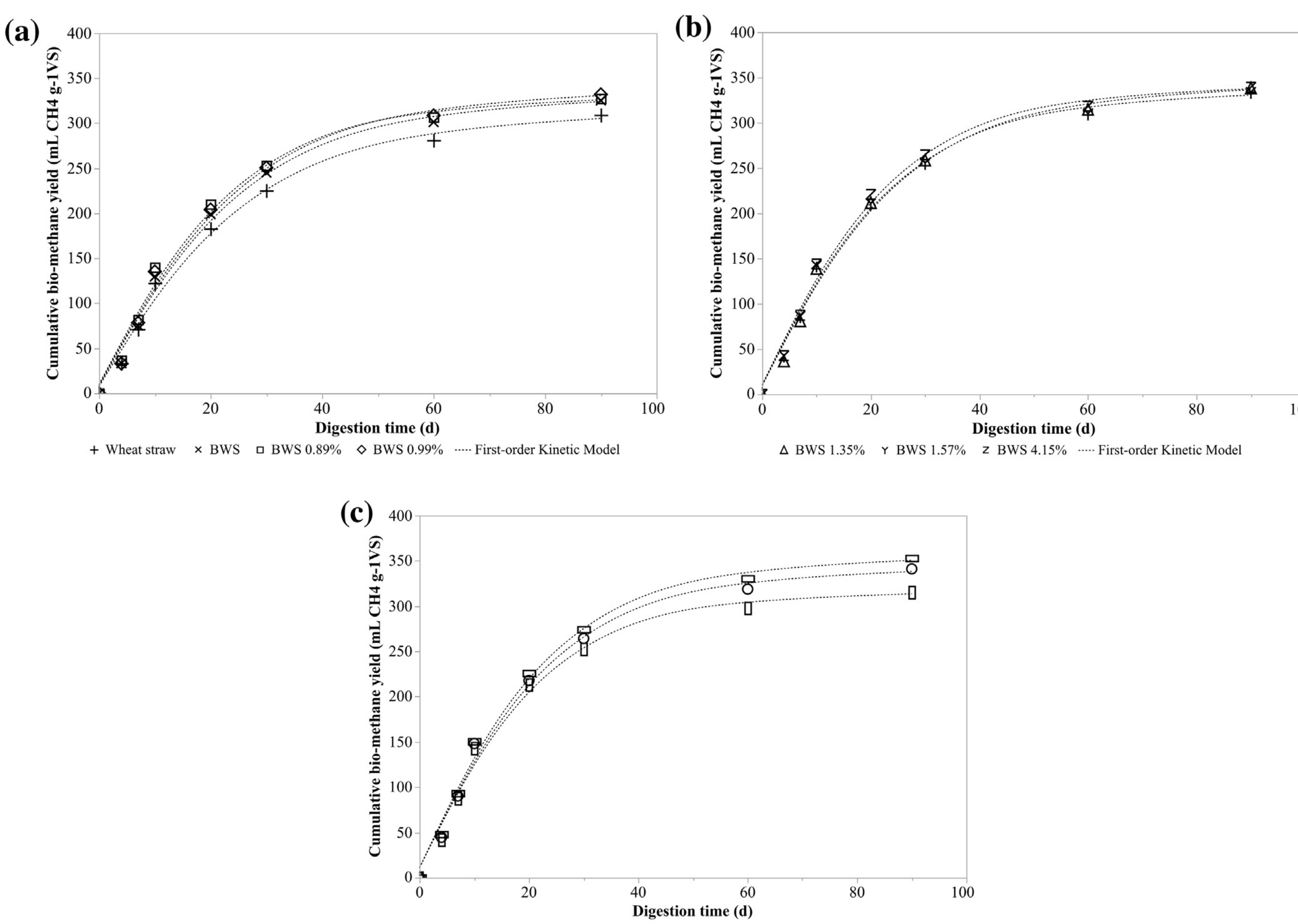

Fig. 1. First-order Kinetic plots of cumulative bio-methane yield of wheat straw and briquetted wheat straw (BWS) with KOH injection.

Table 3
Bio-methane yield at day 30, 60 and 90 of (briquetted) wheat straw with different KOH injection concentrations.

Substrate[1]	BMP_{30} (mL CH_4. g^{-1} VS)	Improved CH_4 yield (%)	BMP_{60} (mL CH_4. g^{-1} VS)	Improved CH_4 yield (%)	BMP_{90} (mL CH_4. g^{-1} VS)	Improved CH_4 yield (%)	B_0 (mL CH_4. g^{-1} VS)	k (d^{-1})
WS	$225.28^{c} \pm 5.54$	0	$281.08^{d} \pm 4.60$	0	$309.15^{d} \pm 7.37$	0	311.84 ± 5.70	0.0427
BWS	$245.25^{b} \pm 7.50$	8.86	$301.33^{bc} \pm 5.98$	7.21	$325.43^{bcd} \pm 5.28$	5.27	330.18 ± 6.22	0.0440
$BWS_{0.89\%}$	$253.11^{b} \pm 8.48$	12.35	$306.70^{bc} \pm 8.45$	9.12	$327.42^{bcd} \pm 8.14$	5.91	330.28 ± 6.71	0.0479
$BWS_{0.99\%}$	$250.59^{b} \pm 9.62$	11.23	$308.67^{bc} \pm 9.90$	9.82	$332.01^{bc} \pm 9.14$	7.39	336.66 ± 7.52	0.0446
$BWS_{1.35\%}$	$258.13^{ab} \pm 6.73$	14.58	$314.28^{abc} \pm 7.85$	11.81	$337.96^{abc} \pm 8.50$	9.32	341.93 ± 6.33	0.0457
$BWS_{1.57\%}$	$255.51^{ab} \pm 5.16$	13.41	$310.33^{bc} \pm 4.77$	10.36	$334.01^{abc} \pm 4.84$	8.04	334.78 ± 4.94	0.0482
$BWS_{4.15\%}$	$264.53^{ab} \pm 6.43$	17.42	$318.27^{ab} \pm 8.07$	13.23	$339.27^{ab} \pm 7.04$	9.74	341.65 ± 5.33	0.0490
$BWS_{4.60\%}$	$264.24^{ab} \pm 5.44$	17.29	$318.82^{ab} \pm 5.08$	13.43	$341.14^{ab} \pm 5.04$	10.35	342.03 ± 5.08	0.0494
$BWS_{6.27\%}$	$274.39^{a} \pm 6.08$	21.80	$330.63^{a} \pm 6.34$	17.62	$353.12^{a} \pm 7.68$	14.22	354.67 ± 4.94	0.0492
$BWS_{7.29\%}$	$252.66^{b} \pm 5.16$	13.42	$297.96^{cd} \pm 4.55$	6.01	$315.33^{cd} \pm 7.27$	2.00	316.10 ± 4.99	0.0532

[abcd]Different letters indicate significant differences at $p < 0.05$.
[1] WS, wheat straw; BWS, briquetted wheat straw.

compared to untreated wheat straw. The highest biomethane yield (353.13 ± 7.68 mL.g^{-1} VS) was obtained with 6.27% (w/w) KOH injection, which was 14.22% higher than from untreated wheat straw and 8.51% higher than from briquetted wheat straw. An adverse effect was observed when the KOH concentration was increased to 7.29%, which resulted in only 2% higher yield compared to untreated wheat straw and lower than from wheat straw briquettes without KOH injection. Low concentrations of KOH were found to enhance the anaerobic digestion at both thermophilic and mesophilic conditions, while a high potassium concentration can be toxic or inhibitory (Chen et al., 2008). Kugelman and McCarty (1965) observed that 0.15 M K^{+} caused 50% inhibition of acetate-utilizing methanogens. Significant differences in ultimate biomethane yield (BMP_{90}) were shown using one-way ANOVA analysis ($F = 7.5742$, $p < 0.0001$). The improvement on biomethane yield was more pronounced during short digestion time. As shown in Table 3, KOH pretreated wheat straw produced 11–22% more methane compared un-treated wheat straw at day 30. At day 60, the biomethane from KOH pretreated straw were 6.0–17.6% higher than untreated straw. The results indicate that the pretreatment increase the accessible surface areas and expose degradable compounds that normally degrade at a later stage in the anaerobic digestion (Hjorth et al., 2011).

The ultimate methane yield (BMP_{90}) of meadow grass, briquetted meadow grass (with/without KOH injection) are shown in Fig. 2 and Table 4. The pretreatment of meadow grass was less effective compared to wheat straw. Meadow grass briquettes (260.79 ± 3.66 mL.g^{-1} VS) produced only 1% more biomethane than untreated grass (257.96 ± 6.57 mL.g^{-1} VS). As shown in Table 4, the combination of briquetting and KOH injection had no significant effect on the ultimate biomethane production from meadow grass at all investigated concentrations (0.88–10.85%) at day 90, but significantly higher ($p < 0.05$) from briquetted meadow grass at day 30 with 1.9%, 6.81% and 10.16% KOH injection (Table 4). Results from the batch test could be explained by the limited effect on lignin removal.

3.3. Hydrolysis rate

Cumulative methane yield was fitted by the first-order kinetic model. The parameters obtained from the model are presented at Tables 3 and 4. The hydrolysis rate (k) of briquetted wheat straw (4.40×10^{-2}) was found to be slightly higher than that of wheat straw (4.27×10^{-2}). As shown in Fig. 3a, hydrolysis rate of briquetted wheat straw with KOH injection was accelerated significantly ($p < 0.05$) as the KOH concentration increased. The highest hydrolysis rate was obtained at a KOH concentration of 7.29%. The promotion of the hydrolysis rate is in line with previously published work on adding alkaline to briquetted wheat straw prior to briquetting (Moset et al., 2015b).

The hydrolysis rate of briquetted meadow grass with/without KOH injection were enhanced significantly compared to untreated meadow grass. However, only slight correlation was found between hydrolysis rates and KOH concentration ($R^2 = 0.0252$) (Fig. 3b). According to first-order kinetic modeling, the hydrolysis rate of meadow grass briquettes ranged from 4.19×10^{-2} to 6.00×10^{-2} d^{-1}, with KOH injection ranging from 0.88 to 10.85. The injection of KOH had a higher effect on the hydrolysis rate of wheat straw than of meadow grass.

3.4. FTIR

FTIR spectroscopy is a non-destructive method for studying the physico-chemical properties of lignocellulosic materials. The peak at 1730 cm^{-1} in the wheat straw and briquetted wheat straw represents either the acetyl and uronic ester groups of the hemicelluloses or ester linkages between lignin and carbohydrates (Liu et al., 2009; Sain and Panthapulakkal, 2006), which were significantly reduced in briquetted wheat straw with 0.99 and 6.27% KOH injection. The peak at 1606 cm^{-1} (stretching of aromatic benzene ring in lignin) appeared from the KOH-treated briquetted wheat straw, indicating an increase in lignin due to the hemicellulose removal or lignin re-deposition (Mann et al., 2009). The intensity of the peak at 1510 cm^{-1}, which relates to the aromatic C=C stretch of the aromatic rings of lignin (Sain and Panthapulakkal, 2006), decreased from briquetted wheat straw with and without KOH injection, indicating part removal of lignin. Similar FTIR spectra of untreated meadow grass and briquetted meadow grass with KOH injection were observed, which indicates that the pretreatment did not effectively alter the lignocellulosic structure of meadow grass.

3.5. Alkaline distribution

Fig. 4 shows the measured pH and conductivity values with different KOH concentrations and capacities. The data present in Fig. 4 were mainly measured in wheat straw briquette since the trends from wheat straw and grass were very similar. pH and conductivity from briquettes with 10.85% KOH injection and (Fig. 4a) and treating capacity of 818 kg/h (Fig. 4b), which were higher than used in wheat straw, were obtained from meadow grass briquette. The average values and errors referring to single concentration/capacity were calculated from three different parts from same briquette (mentioned in Section 2.6). As shown in Fig. 4a, the measured pH and conductivity values are similar with a small standard deviation at injected KOH concentration lower than 1.35%. As the KOH concentration is increased, the pH value rises from neutral value to over 9.0, accompanied by a significant increase in conductivity. The increase in pH is mainly because the high KOH concentration cannot be totally consumed during

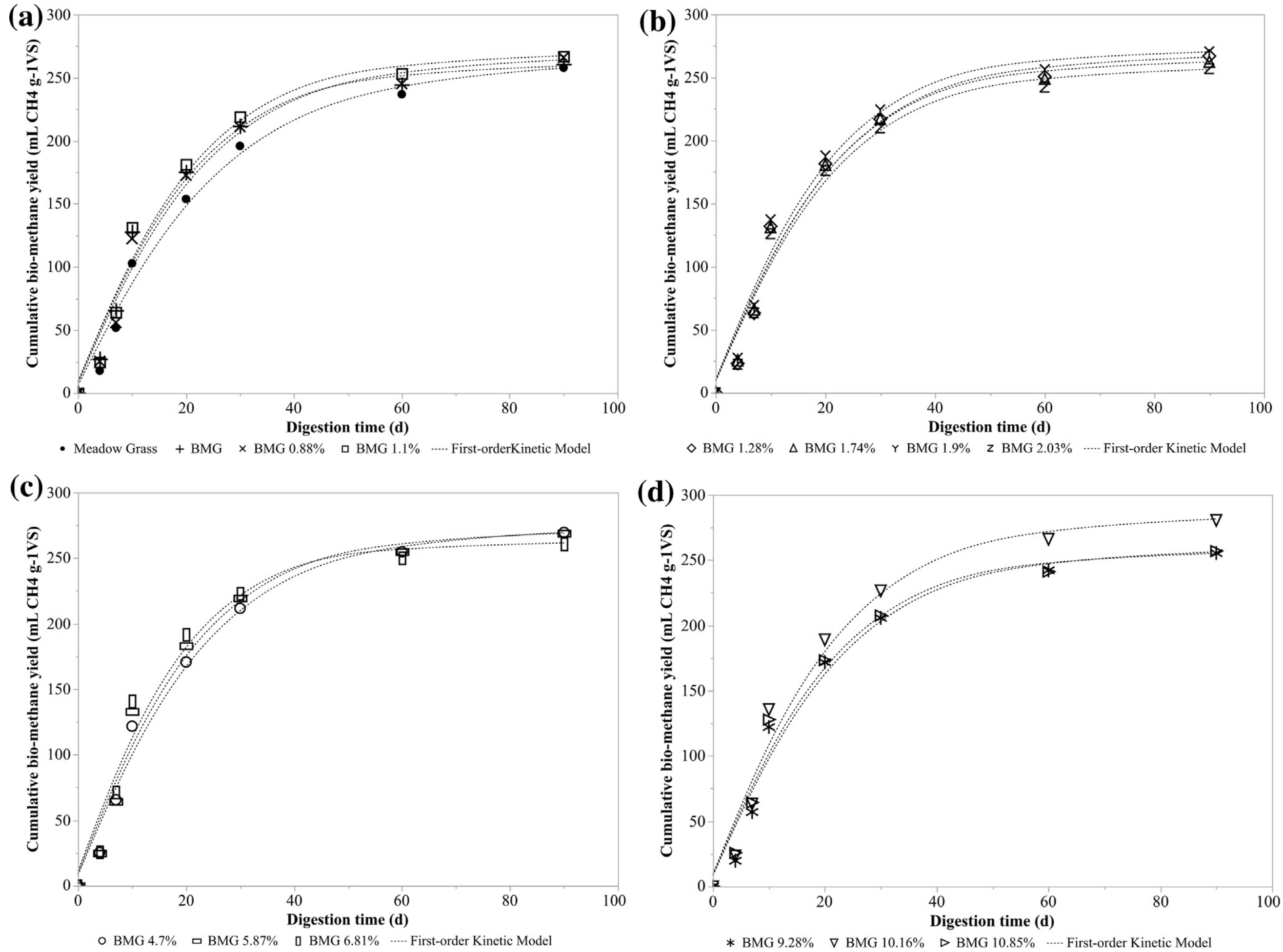

Fig. 2. First-order Kinetic plots of cumulative bio-methane yield of meadow grass and briquetted meadow grass (BMG) with KOH injection.

Table 4
Bio-methane yield at day 30, 60 and 90 of (briquetted) meadow grass with different KOH injection concentrations.

Substrate[1]	BMP_{30} (mL CH_4. g^{-1} VS)	Improved CH_4 yield (%)	BMP_{60} (mL CH_4. g^{-1} VS)	Improved CH_4 yield (%)	BMP_{90} (mL CH_4. g^{-1} VS)	Improved CH_4 yield (%)	B_0 (mL CH_4. g^{-1} VS)	k (d^{-1})
MG	$195.92^{b} \pm 5.68$	0	$236.87^{a} \pm 6.67$	0	$257.96^{a} \pm 6.57$	0.00	263.58 ± 7.02	0.0419
BMG	$211.73^{ab} \pm 1.63$	8.07	$244.53^{a} \pm 3.2$	3.23	$260.79^{a} \pm 3.66$	1.09	261.25 ± 6.29	0.0532
$BMG_{0.88\%}$	$211.17^{ab} \pm 7.95$	7.79	$245.21^{a} \pm 10.16$	3.52	$266.01^{a} \pm 10.11$	3.12	267.28 ± 7.69	0.0488
$BMG_{1.1\%}$	$219.02^{ab} \pm 2.17$	11.79	$253.26^{a} \pm 6.92$	4.86	$266.88^{a} \pm 4.16$	3.46	269.56 ± 7.17	0.0528
$BMG_{1.28\%}$	$217.07^{ab} \pm 1.24$	10.80	$250.74^{a} \pm 1.45$	5.86	$267.00^{a} \pm 1.46$	3.50	268.36 ± 7.44	0.0528
$BMG_{1.74\%}$	$216.97^{ab} \pm 1.45$	10.74	$248.82^{a} \pm 4.50$	5.05	$262.26^{a} \pm 3.06$	1.66	264.21 ± 6.79	0.0543
$BMG_{1.9\%}$	$224.72^{a} \pm 6.73$	14.70	$256.61^{a} \pm 8.55$	8.34	$270.74^{a} \pm 9.53$	4.95	272.02 ± 7.21	0.0556
$BMG_{2.03\%}$	$210.03^{ab} \pm 12.01$	7.2	$242.28^{a} \pm 14.54$	2.29	$256.99^{a} \pm 13.61$	−0.38	258.55 ± 7.87	0.0533
$BMG_{4.7\%}$	$211.70^{ab} \pm 7.13$	8.05	$254.78^{a} \pm 5.10$	7.56	$269.64^{a} \pm 5.83$	4.53	273.18 ± 6.60	0.0481
$BMG_{5.87\%}$	$219.45^{ab} \pm 1.90$	12.01	$254.85^{a} \pm 3.88$	7.59	$268.97^{a} \pm 3.56$	4.27	271.26 ± 7.27	0.0528
$BMG_{6.81\%}$	$223.09^{a} \pm 22.37$	13.87	$250.18^{a} \pm 33.30$	5.62	$260.80^{a} \pm 32.88$	1.10	262.76 ± 10.46	0.0600
$BMG_{9.28\%}$	$205.74^{ab} \pm 2.42$	5.01	$242.19^{a} \pm 4.35$	2.25	$255.42^{a} \pm 3.21$	-0.98	259.03 ± 7.47	0.0503
$BMGw_{10.16\%}$	$226.73^{a} \pm 4.82$	15.72	$266.31^{a} \pm 8.55$	12.43	$280.72^{a} \pm 9.22$	8.82	284.24 ± 8.17	0.0510
$BMG_{10.85\%}$	$207.56^{ab} \pm 3.16$	5.94	$241.22^{a} \pm 3.29$	1.84	$256.87^{a} \pm 3.33$	−0.42	257.22 ± 6.61	0.0535

[ab]Different letters indicate significant differences at $p < 0.05$.
[1] MG, meadow grass; BMG, briquetted meadow grass.

the pretreatment process. Fox et al. (1989) found that 35% of alkali remained after pretreatment with 0.1 g NaOH.g^{-1} biomass and could be recycled and reused for another round of pretreatment. As shown in Fig. 4b, negative correlation is observed from pH and conductivity to capacities. As the treated capacities increased from 354 to 818 kg.h^{-1}, the measured pH decrease from over 9.0 to neutral value, accompany with decrease of conductivity. That was because the higher treating capacity will reduce the injection KOH concentration of the briquette. Higher deviations of pH and conductivity values are observed from briquetted wheat straw/meadow grass at higher treatment capacity using spray nozzle B, which corresponds to a large flow rate of KOH. The results indicate that the pH and conductivity values were not affected greatly using low KOH concentration. However, as the flow rate changed when

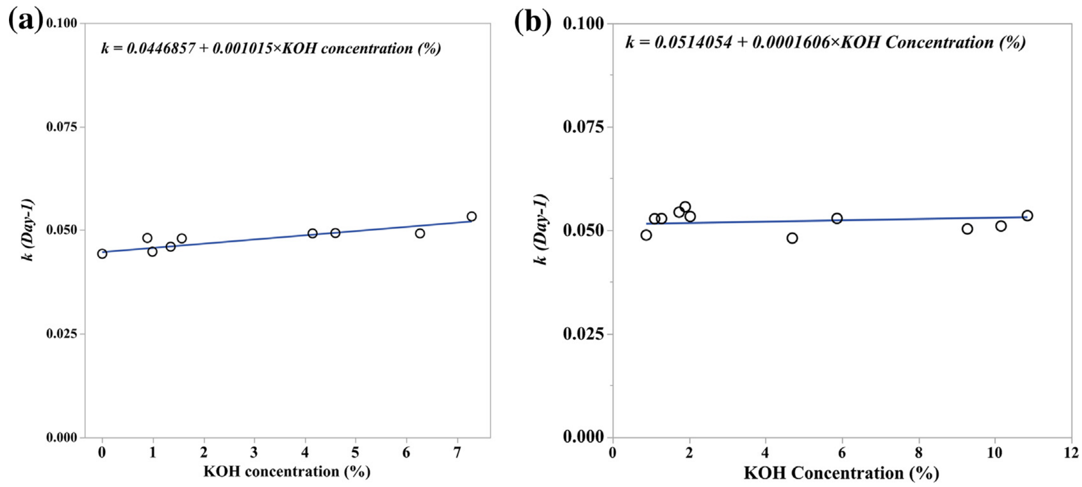

Fig. 3. Correlations between hydrolysis rate of a) wheat straw (R^2 = 0.8256) and b) meadow grass (R^2 = 0.0252) with different KOH concentrations (hydrolysis rate was calculated from first-order kinetic model (Hashimoto, 1989)).

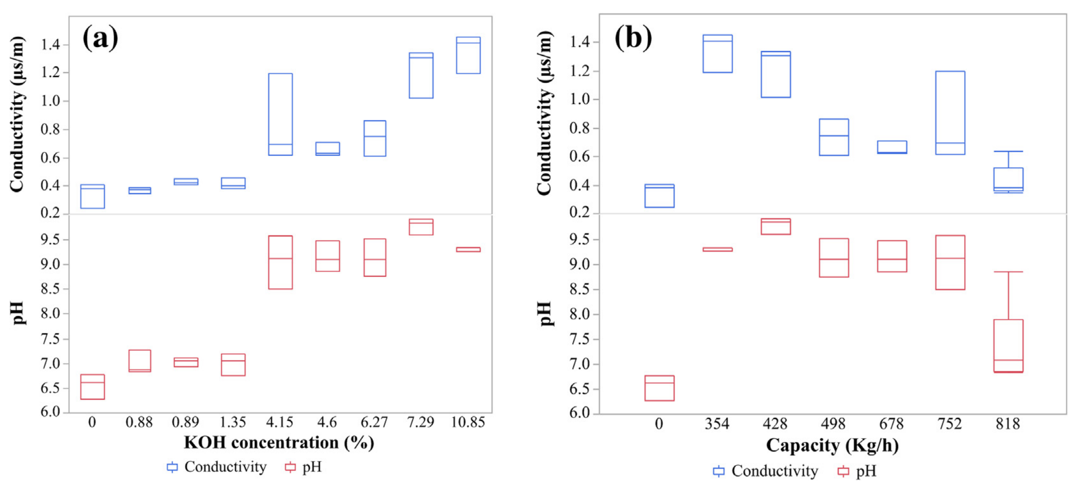

Fig. 4. Distribution of pH and conductivity from briquetted wheat straw with different a) KOH concentrations and b) briquetting capacities. (All data were measured from wheat straw except injected KOH concentration 10.85% and briquetting capacity 818 kg/h).

using spray nozzle B, an uneven alkaline distribution can be observed at the higher capacity, indicating that treating capacity higher than 700 kg/h is problematic.

4. Conclusion

This study presents a pretreatment method using direct injection of KOH during the briquetting process with low water usage and no wastewater production. An increased biomethane production as well as faster hydrolysis rates were achieved. This pretreatment method was found to have higher positive impact on treatment of wheat straw compared to grass. Pretreatment of briquetted wheat straw with 6.27% KOH injection increased the ultimate methane yield with 14% compared to un-treated wheat straw. This method is a promising technology which can easy be scaled up to industrial biogas plants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.05.032.

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