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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.