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Optimization of methane yield by using straw briquettes- influence of additives and mold size

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ABSTRACT

A combination of briquetting wheat straw (BWS) and additives is presented in this work. Two experiments were designed: firstly the mold size of the briquetting equipment and the additive addition were evaluated as an integrated pre-treatment promoting methane (CH_4) yield and hydrolysis rate (k). Secondly, two combinations from the first experiment were used in continuous stirred tank reactors (CSTR) in co-digestion with cattle manure (CM). In this second experiment, CH_4 yield, reactor performance and residual CH_4 production were measured. The addition of alkali to BWS had a more significant effect on k than on the CH_4 promotion. The CSTR results showed that the addition of 3% KOH to BWS had a positive effect on VS degradation, CH_4 production and energy and economic balances. In addition, the potential for CH_4 emissions during the subsequent storage was reduced.

1. Introduction

Lignocellulosic material like wheat straw is an abundant by-product in farming and may be interesting as a co-substrate for liquid animal manure to increase productivity in anaerobic digestion plants. However, wheat straw is a lignocellulosic substrate, its main components are cellulose (between 40 and 50%), followed by hemicelluloses (31–43%) and lignin (6–10%) (Motte et al., 2014). This fact not only means a slow microbial degradation, but also a low bulk density which significantly increases its cost of handling, transportation (Theerarattananoon et al., 2012), and storage (Rijal et al., 2012).

Briquetting of wheat straw is a pre-treatment technology where the straw is highly compressed. The reduction in storage, handling and transport costs can justify the associated cost of this process (Theerarattananoon et al., 2012). Briquetting compresses the straw to a density of 1000 kg m^3, preventing a floating layer and easing mixing in the digester to better achieve the potential biogas yield of the straw. The energy transferred from the piston during briquetting is both mechanical and kinetic which heats the straw up to a temperature proportional to the applied force. When the piston returns, the pressure drops momentarily from 2000 bar to atmospheric pressure which creates an autolysis of the straw, also known as steam explosion, from the natural water content in the straw. Through this steam formation, hydrolysis of hemicellulose and lignin could theoretically be promoted (Tumuluru et al., 2011). Previous studies have shown a 10% higher energy yield in terms of methane (CH_4) production from briquetting compared with shredded straw (Xavier et al., unpublished manuscript submitted for publication to Biosystems Engineering in November 2014).

Similar to briquetting, chemical pre-treatments may be used to promote the hydrolysis of lignocellulosic compounds. Chemical compounds are basically used to modify the structure of specific compounds mainly by changing the pH (alkali or acids) or by promoting enzymatic hydrolysis. The addition of a strong acid (H_2SO_4) has been broadly explored and it has been shown to effectively solubilize hemicellulose and lignin and to expose the cellulose component to hydrolysis (Liao et al., 2008). However, its practical implementation is limited due to technical problems, such as specific enzymatic inhibition caused by the sulfur concentration (Söderström et al., 2002), or other environmental aspects related to wastewater purification and product distillation (Zabihi et al., 2010). According to Zabihi et al. (2010), the use of acetic acid (HAc) as a catalyst for steam explosion is a better choice than strong acids, with no obvious detrimental effect on cellulytic enzymes or other environmental concerns.

Alkali pretreatments increase cellulose digestibility and they are thought to more effectively solubilize lignin than acid or hydrothermal processes (Carvalheiro et al., 2008). In fact, alkaline pretreatment has been shown as an effective pre-treatment for increasing the hydrolysis of agricultural residues, although this treatment appears less satisfactory for processing recalci-

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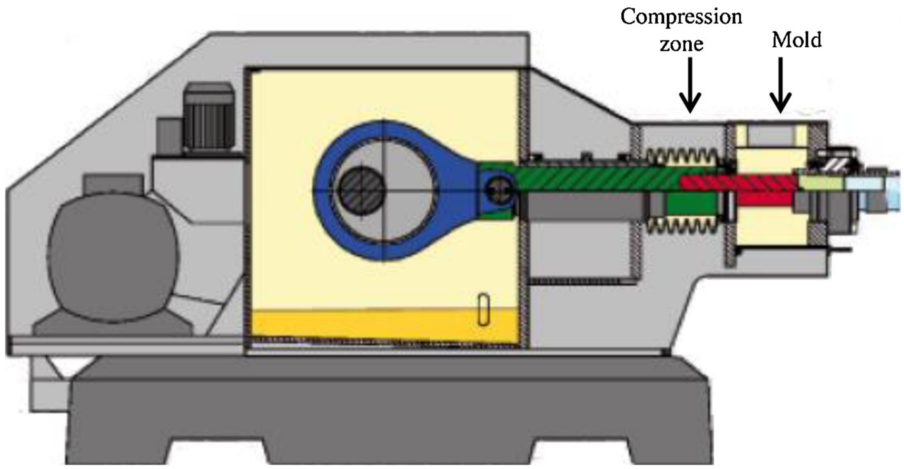

Fig. 1. Design of the briquetting unit CF Nielsen (Baelum, Denmark).
Source:http://www.cfnielsen.com/infoen/-1 (May, 2015).

trant substrates such as softwoods (Chandra et al., 2007). Alkaline conditions promote changes in the structure of the lignin, saponification of the uronic bonds between hemicelluloses and lignin, swelling of the fibers and increases in pore size (Sambusiti et al., 2013). These effects can increase the availability of the substrate to microorganisms and, therefore, hydrolysis and methane (CH_4) yield in the reactors could theoretically be accelerated. However, according to literature, alkali addition is an effective pretreatment only if effectuated over a longer period and at high alkali concentrations (Taherzadeh and Karimi, 2008). These conditions can increase the price of the process and create other problems associated with wastewater production. Therefore, a combination of an alkaline pre-treatment with a mechanical or physical pre-treatment is recommended to decrease the alkali concentration and to accelerate the process (Janker-Obermeier et al., 2012). In this regard, thermal chemical pre-treatments and microwave-assisted alkali treatment have been recommended for some lignocellulosic substrates (Janker-Obermeier et al., 2012; Monlau et al., 2012; Sambusiti et al., 2013).

In this paper we present a combination of briquetting with chemical additives as a pre-treatment for wheat straw prior to anaerobic digestion. Ideally this combined pre-treatment will achieve the benefits of both pretreatments to create maximum synergy. In addition, a complete reduction of wastewater production is achieved by this combined process where the additive is incorporated in the biomass during the briquetting process. The specific objectives of this work were to test the influence of briquetting mold size on CH_4 yield and to identify an optimal combination of briquetting and additive as a pre-treatment to promote CH_4 yield. Selected combinations were tested in continuous stirred tank reactors (CSTR) by measuring CH_4 yield, reactor performance and residual CH_4 production after the anaerobic digestion process.

2. Materials and methods

2.1. Substrates

The wheat straw was collected near Viborg (Denmark). The wheat straw was briquetted (BWS) with a BP 6500 briquetting unit (CF Nielsen, Baelum, Denmark). Before the briquetting process the straw was hammer-milled with a 20 mm sieve (Cormall HDH 770, Denmark). The capacity of the briquetting equipment was 900 to 1400 kg h^{-1}, producing briquettes with a 75 mm diameter. The briquetting technology developed by CF Nielsen is illustrated in Fig. 1 and consists of a mechanically-induced steam explosion motor of (55 KW) with repeated compression–decompression cycles at pressures between 1500 and 2000 bars and at atmospheric pressure. The explosion process can be extended for 40–120 min as appropriate. The C.F. Nielsen Mechanical press is an eccentric continuously rotating press connected to a plunger piston. The mechanical press receives raw material by a speed-controlled dosing screw. The speed of the dosing screw determines the output of the machine. The raw material is pushed through a conical die, where the counter pressure required can be adjusted by changing die conicity. After being compressed in the conical die, a cylindrical die retains pressure for a short duration.

Inoculum for the batch assay and for starting up the CSTR was obtained from the biogas plant of the agricultural Research Centre Foulum (Aarhus University, Denmark). The batch assay inoculum was pre-incubated for 15 days at mesophilic temperature in order to deplete the residual biodegradable organic material (degasification). This inoculum had 3.63% total solids (TS), 2.32% volatile solids (VS), 1.32% ash content, 3.34 g L^{-1} total ammoniacal nitrogen (TAN), 2.95 mg L^{-1} total volatile fatty acids (VFA) and a pH of 7.64.

The cattle manure (CM) used in the continuous experiment as a co-substrate was obtained from Research Centre Foulum (Aarhus University, Denmark).

2.2. Experiment 1: effect of different mold sizes and additives

A first pre-experiment was made to test the effect of mold size on CH_4 productivity; in this pre-experiment straw was sampled after the hammer milling and before the briquetting process (Hammer mill) and BWS samples were taken with three inner mold diameters of 54, 60 and 68 mm.

The effect of the addition of different additives during the briquetting process was also tested. For this purpose, two alkalis (NaOH, KOH) and one weak acid (HAC) were applied to the straw by a piston pump connected to a spray nozzle (B1/4LNND-SS.8, Spraying system Co, USA) in a mixing chamber prior to the briquetting process. The pump had a constant flow of around 76.7 kg h^{-1} and the concentrations added to the straw (0%, 0.5%, 1%, 2%, 3% and 5% on a dry matter basis) were adjusted using the flow settings of the briquetting machine.

Cumulative maximal CH_4 production of the wheat samples obtained from the different briquetting configurations were determined from three 0.5 L bottles. The different treatments are shown in Table 1.

Each bottle was filled with an inoculum-substrate ratio of approx. 1:1, based on VS. After filling, bottles were sealed with butyl rubber stoppers and aluminum crimps, and the headspace

Table 1
Pre-treatment conditions carried in experiment 1.

Name	Straw	Inner mold diameter (mm)	Alkali
Hammer mill	Wheat straw	–	–
BWS_{RAW}	Briquetted wheat straw (BWS)	68	–
BWS_{54}	BWS	54	–
BWS_{60}	BWS	60	–
$BWS_{5\%NaOH}$	BWS	68	NaOH 5%
$BWS_{3\%NaOH}$	BWS	68	NaOH 3%
$BWS_{2\%NaOH}$	BWS	68	NaOH 2%
$BWS_{5\%KOH}$	BWS	68	KOH 5%
$BWS_{3\%KOH}$	BWS	68	KOH 3%
$BWS_{2\%KOH}$	BWS	68	KOH 2%
$BWS_{1\%KOH}$	BWS	68	KOH 1%
$BWS_{0.5\%KOH}$	BWS	68	KOH 0.5%
$BWS_{1\%HAc}$	BWS	68	Acetic acid (HAc) 1%
$BWS_{0.5\%HAc}$	BWS	68	HAc 0.5%

was flushed with pure N_2 for two minutes. The bottles were then incubated at mesophilic conditions (35 °C) for 90 days.

Periodically, the total volume of biogas produced per bottle was measured. The measurement of biogas volume was done by inserting a needle connected to a tube with inlet to a column filled with acidified water (pH <2) through the butyl rubber. The biogas produced was calculated by the water displaced until the two pressures (column and headspace in bottles) were equal. The biogas was sampled and analyzed for CH_4, carbon dioxide (CO_2) and hydrogen sulfide (H_2S) content and the volume corrected to standard temperature and pressure (0 °C and 760 mm Hg).

The cumulative maximum CH_4 production after 90 days (BMP_{90}) can be considered as the ultimate CH_4 yield (B_0) of each substrate. In fact, an almost complete degradation process is considered in literature when incubation times are higher than 80 days (Vedrenne et al., 2008).

2.3. Experiment 2: Co-digestion of cattle manure and briquetted straw with and without alkali addition

In this experiment co-digestion of cattle manure and briquetted straw was tested in continuous stirred tank reactors (CSTR). Two different briquetted wheat straws from experiment 1 were used in this experiment: BWS_{RAW} and BWS with 3% KOH on dry matter basis ($BWS_{3\%KOH}$). For this purpose three CSTR with 15 L working capacity were used.

The three reactors were similar in design. The stirring was performed by a central shaft with two propellers, one at the bottom and one in the middle which was continuously rotating at 100 rpm. The three reactors were heated by electrical resistance at the bottom and the tank temperature was controlled by a temperature probe. The reactors were fed daily and unloaded manually. The biogas production was measured using an automatic biogas potential system (BRS BioReactor Simulator, Bioprocess Control, Sweden).

At the beginning of the experimental period, the three reactors were filled with a thermophilic inoculum from the biogas plant at Research Centre Foulum (Aarhus University, Denmark). During the first 15 days, the three reactors were fed a mixture of BWS_{RAW} and CM. After this period, one reactor continued with a fed of BWS_{RAW} and CM and the other two were fed a mixture of CM and pretreated BWS with 3% KOH ($BWS_{3\%KOH}$) for another 45 days. The total period of continuous feeding was 60 days. After end of the continuous experiment, the residual CH_4 production was measured from each reactor by measuring biogas production for 90 days without addition of new substrate.

The mixtures BWS with CM were made in order to feed the same amount of VS to all reactors (6.5 g VS L^{-1} day^{-1}). For this reason, the straw in fresh matter added to cattle manure was different in each mixture, 4.5% in BWS_{RAW} reactor and 5.5% in $BWS_{3\%KOH}$ reactors.

Temperature and hydraulic retention time (HRT) were kept constant for the three reactors during the whole experimental period, at 49 ± 1 °C and 15 days, respectively.

2.4. Analyses

The samples from feeding and unloading the CSTR were analyzed weekly for pH, dry matter and organic matter, following the TS and VS procedure (APHA, 2005), respectively. Dissolved VFA concentrations were determined using a gas chromatograph, according to the methodology described in 5560-D of APHA (2005) equipped with a flame ionization detector (HP 68050 series Hewlett Packard, USA). Total ammoniacal nitrogen was also determined from fresh samples using photometric kits (Spectroquant® kit, Merck, USA).

Samples from BWS with and without alkali addition used in the CSTR experiment were taken at the beginning of the experiment, dried (48 h at 60 °C) and milled using a mill with a 0.8 mm diameter (CyclotecTM 1093, Foss, USA). Fiber fractions of the dried milled samples (neutral detergent fiber (NDF), acid detergent fiber (ADF) and lignin (ADL)) were analyzed according to the Van Soest procedure (Van Soest, 1994); 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.

2.5. Calculations and statistical analysis

In experiment 1, the CH_4 production was determined in terms of L CH_4 per kg VS added to the bottles (specific CH_4 yield). The cumulative specific CH_4 yield as a function of time was modeled by fitting the experimental data obtained in the batch assay to the sigmoidal non-linear regression model described by Hashimoto (1989) (Eq. (1)):

$$BMP_t = BMP_{90}(1 - \exp^{-k \times t}) \quad (1)$$

where BMP_t denotes the cumulative specific bio-methane potential (L CH_4 kg VS^{-1}) at time (t) expressed in days; BMP_{90} is the ultimate specific BMP at 90 days (L CH_4 kg VS^{-1}); and k is the BMP degradation constant, expressed in the reciprocal of time (day^{-1}), which is substrate-specific and gives information about the time required to achieve a certain fraction of BMP_{90}; therefore it can be considered as the hydrolysis rate. The root mean squared error (RMSE) was used to calculate the k values combined with Eq. (1). The squared correlation coefficient (R^2) was used to evaluate the goodness of the model fit.

In the CSTR experiment, both the CH_4 yield obtained during the feeding period and the residual CH_4 production were calculated based on the initial composition of the mixture added to the

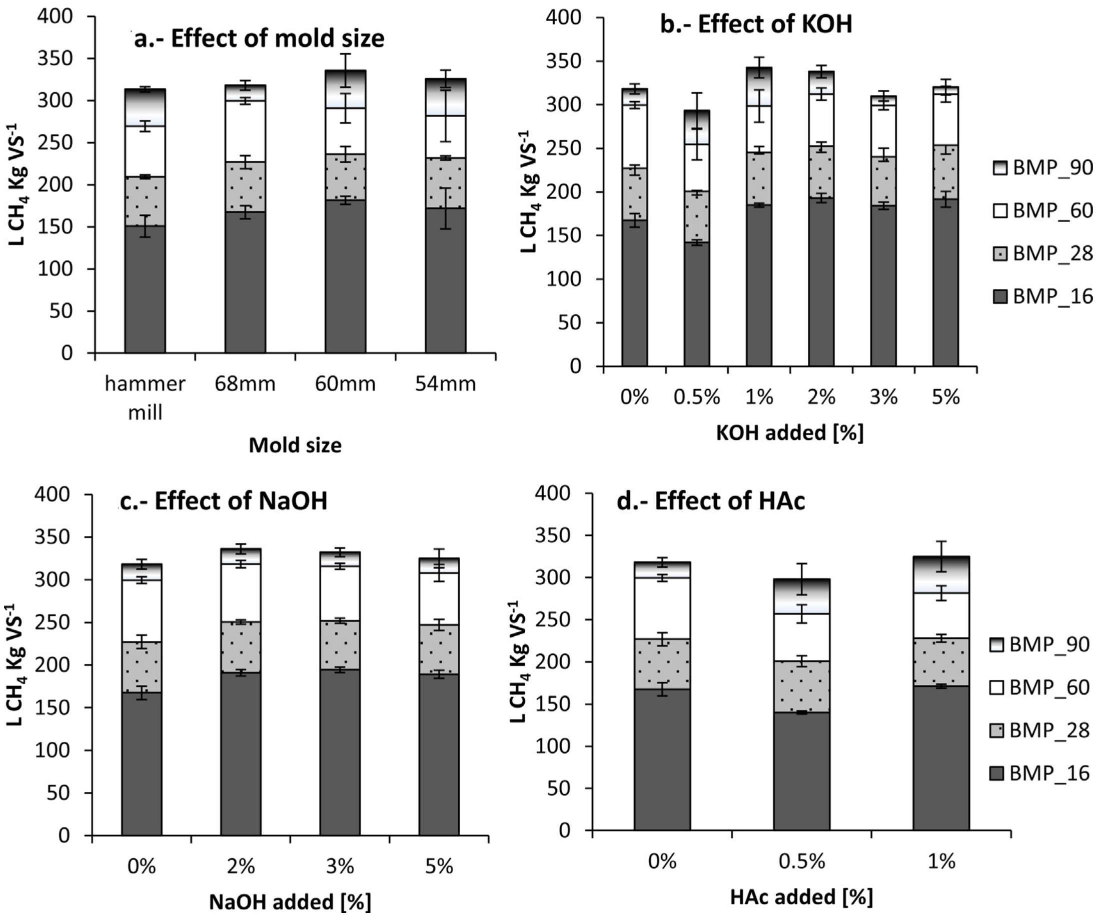

Fig. 2. Average of the cumulative methane production (BMP) at 16, 28, 60 and 90 days of the briquetted wheat straw made with different mold sizes (Fig. 2a) and different concentrations of additives: KOH (Fig. 2b), NaOH (Fig. 2c) and acetic acid (HAc) (Fig. 2d). Bars show standard deviation of the cumulative methane production at different times ($N = 3$).

reactors and expressed in terms of specific and volumetric CH_4 production (L CH_4 kg VS^{-1} and L CH_4 $kg_{substrate}{}^{-1}$, respectively). The ultimate CH_4 yield of the mixtures used to feed the reactors was then estimated in each reactor as the sum of the average CH_4 yield in the continuous feeding during the last HRT plus the residual CH_4 production, and subsequently the fraction of the ultimate CH_4 yield achieved in each reactor during the continuous feeding was calculated.

The residual specific CH_4 production was also calculated from each reactor in terms of the VS in the effluent, after the anaerobic continuous digestion process (LCH_4 kg $VS_{effluent}{}^{-1}$).

In the CSTR experiment, the percentage of VS degraded in the substrate during the continuous anaerobic digestion process (VS degradability) was calculated as a mass balance from the VS content in the substrate and in the reactor's effluent (Eq. (2)):

$$\text{VS degradability} = \frac{(\text{Corrected VS in the substrate} - \text{Corrected VS in the digestates})}{\text{Corrected VS in the substrates}} \times 100 \quad (2)$$

Corrected VS was calculated taking VFA losses during the drying process into account, as shown in Moset et al. (2012). The dissolved VFA content in the manure was added to the VS fraction when calculating the VS degradability in the following manner: 100% of the VFA was added to VS in manures with a pH below 7, 80% of the VFA was added to VS in manures with a pH between 7 and 8, and 10% of VFA was added to VS in manures with a pH higher than 8.

In the CSTR experiment, the average digestate composition and CH_4 yield were calculated with the corresponding values obtained after the second retention time in order to allow reactors to reach stability.

3. Results and discussion

3.1. Experiment 1: effect of different mold sizes and additives

Ultimate CH_4 yield of wheat straw increased with the use of briquettes (Fig. 2a). Although friction and pressure on the straw are higher with a smaller mold size, no clear relation between mold size and BMP was observed at any time. Considering these results and the lower energy consumption with the larger mold size, a mold size of 68 mm was used in the subsequent experiments.

Although in general the addition of additives to BWS enhanced BMP_{90} (Fig. 2b, c and d), a clear pattern between the type and the concentration of additive added and BMP was not observed during the different incubation times: 16, 28, 60 and 90 days.

The lowest KOH and HAc concentrations tested (0.5%) had no evident positive effect on BMP_{90} compared with no additive (Fig. 2b and d, respectively). This result contrasts with the work carried out by Sharma et al. (2002) who found that a 0.5% concentration of NaOH and a digestion period of 1.5 h was the most effective pretreatment for ethanol production from sunflower stalks, while a high alkali concentration (more than 3%) seemed to have a very adverse effect on B_0 promotion. Penaud et al. (1999) also observed a

Table 2
Chemical composition of the substrates (mean ± standard deviation) used to feed the reactors.

	Cattle manure	Raw briquetted wheat straw	Briquetted wheat straw plus 3% KOH
Total solids (%,[a]FM basis)	8.60 ± 0.13	84.86± 0.52	79.22 ± 0.84
Volatile solids (%,[b]DM basis)	80.12 ± 0.27	94.51 ± 0.43	84.55 ± 3.52
Ash (%,[b]DM basis)	19.88 ± 0.14	5.49 ± 0.23	15.45 ± 2.84
Cellulose (%,[b]DM basis)	[c]ND	45.74	42.56
Hemicellulose (%,[b]DM basis)	[c]ND	29.68	18.97
Lignin (%,[b]DM basis)	[c]ND	9.84	7.10

[a] FM: Fresh matter.
[b] DM: Dry matter.
[c] ND: Not determined.

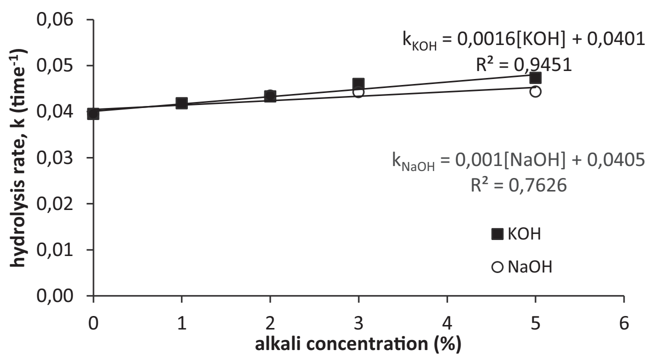

Fig. 3. Correlation between hydrolysis rate and alkali (KOH and NaOH) concentration. Hydrolysis rate calculated from model fit of the cumulative specific bio-methane potential (BMP) curve measured in L CH_4 kg VS^{-1} as a function of time $BMP_t = B0\,(1-\exp^{-k\times t})$ (Hashimoto, 1989).

reduction in complex carbon biodegradability at high alkali concentrations in a methanogenic activity test. These authors attributed this result to the nature of the solubilized molecules and the formation of recalcitrant compounds during the pre-treatment rather than to a toxicity effect of the high cation concentration. However, a comparison of bibliographic works is difficult, not only because of differences in the substrate composition and particle size, but also because of differences in processing pre-treatment parameters like temperature, time, additive concentration and additive source.

The rate of hydrolysis was enhanced at higher concentrations for both types of alkali used. In fact, a high and positive relationship was obtained between alkali concentration and hydrolysis rate, especially for KOH (Fig. 3).

When comparing the additives, HAc was the least able to promote BMP_{90} and k, especially at 0.5% (Fig. 2d). A slightly higher BMP was observed at different concentrations of NaOH compared with their respective concentrations of KOH, especially at 3% (Fig. 2c and b, respectively). In this regard, Penaud et al. (1999) observed slightly higher chemical oxygen demand solubility when using NaOH instead KOH as a pre-treatment of industrial waste activated sludge at ambient temperature.

The hydrolysis rate was, however, generally higher with KOH than with NaOH at any alkali concentration (Fig. 3), meaning that KOH can speed up the hydrolysis of the straw even at shorter retention times, which is important in CSTR where HRT often is below 30 days. Sodium hydroxide is the most studied alkali in the literature for the pretreatment of lignocellulosic substrates (Kaar and Holtzapple, 2000; Sharma et al., 2002), probably due to its low price and high efficiency (Kaar and Holtzapple, 2000). However in experiment 2, KOH was selected for testing in the CSTR because in addition to its higher k value, KOH has a positive side effect in that the digestate can subsequently be used as a fertilizer since potassium is a macro-nutrient in crop production, whereas sodium is only needed in small amounts and can be detrimental to soil and crop production if added in large amounts.

3.2. Chemical composition in experiment 2 (CSTR experiment)

The chemical composition of the substrates used is described in Table 2. The addition of alkali not only altered the distribution of solids in BWS by increasing the ash content and decreasing VS, but also significantly reduced the hemicellulose content in the BWS. However, slight differences were observed in lignin and cellulose content between briquetted wheat straws (Table 2). Janker-Obermeier et al. (2012) observed that hemicelluloses are the major affected fiber fractions to alkali in wheat straw. The sum of cellulose, hemicellulose and lignin represented 90% of the VS in BWS_{RAW} and only 81% in BWS pre-treated with 3% KOH, probably because of the solubility of hemicellulose.

The CSTR was fed mixtures of substrates of similar compositions in terms of VS, propionic acid and TAN (Table 3). However, slightly higher pH, ash, total VFA and acetic acid contents were noted in the mixture made with $BWS_{3\%KOH}$, probably because of the effect of the alkali on the mixture.

Although TS and VS content in feeding substrate were numerically higher in reactors fed $BWS_{3\%KOH,}$ a slightly lower TS and VS contents were obtained in the digestate from these reactors compared with BWS_{RAW}. In addition, VS degradability was higher in reactors using $BWS_{3\%KOH}$ (38.32 ± 2.30%) than in reactors using BWS_{RAW} (24.90 ± 5.65%). A pretreatment with 3% KOH could therefore be expected to increase VS degradation in the anaerobic co-digestion of cattle manure and BWS by more than 50%.

For the pH and VFA parameters, a lower VFA content and therefore higher pH was obtained in the reactors using BWS with 3% KOH compared with the reactor using raw BWS, which also indicates that the anaerobic digestion process was more efficient in reactors using BWS with 3% KOH.

3.3. Methane yield in experiment 2 (CSTR experiment)

Fig. 4 shows the evolution in CH_4 yield in reactors throughout the experimental period. The average specific CH_4 yield (±standard deviation) in the last 30 days was 239.7 (±17.95) L CH_4 kg VS^{-1} in the reactor fed CM + BWS_{RAW} and 291.9 (±15.69) L CH_4 kg VS^{-1} in reactors fed CM + $BWS_{3\%KOH}$. This means that around 22% more CH_4 per kg VS can be expected when BWS is pretreated with 3% KOH in the CSTR. Similar results were obtained in terms of volumetric CH_4 yield; in this case a 20% higher volumetric CH_4 yield was obtained in reactors fed CM + $BWS_{3\%KOH}$ than with CM + BWS_{RAW} (26.3 ± 1.42 and 21.7 ± 1.59 L CH_4 kg^{-1} of mixture added to the reactors, respectively) during the last 30 days of the experimental period. These results reflect the higher VS degradability found in reactors fed CM + $BWS_{3\%KOH}$.

Compared with the batch assay results, higher promotion in CH_4 yield was achieved with alkali addition in the CSTR than in the batch experiment, probably, as previously stated, because of an attenuation of the effect of alkali addition at increasing retention times, and therefore the effects of alkali addition could be higher at shorter retention times.

Table 3
Chemical composition of the substrates (mean ± standard deviation) and digestates in experiment 2 (continuous stirred tank reactors experiment).

	Substrates		Digestates	
	[a]CM + BWS_{RAW}	[b]CM + $BWS_{3\%KOH}$	[a]CM + BWS_{RAW}	[b]CM + $BWS_{3\%KOH}$
Total solids (TS) (%)	11.81 ± 0.64	12.38 ± 0.48	9.37 ± 0.25	8.77 ± 0.22
Volatile solids (VS) (%)	9.58 ± 1.09	9.59 ± 0.97	7.42 ± 0.54	6.54 ± 0.38
Ash (%)	2.24 ± 0.90	2.96 ± 0.90	2.16 ± 0.52	2.23 ± 0.22
[c]VS degradability (%)			24.90 ± 5.65	38.32 ± 2.30
pH	7.07 ± 0.29	7.48 ± 0.27	7.83 ± 0.03	7.93 ± 0.05
Acetic acid (g/L)	5.30 ± 1.63	5.99 ± 1.45	0.43 ± 0.12	0.21 ± 0.05
Propionic acid (g/L)	1.94 ± 0.36	1.95 ± 0.30	0.38 ± 0.05	0.23 ± 0.07
Total volatile fatty acids (g/L)	9.61 ± 2.23	10.30 ± 1.89	0.82 ± 0.33	0.48 ± 0.13
Total ammonia (g/L)	1.96 ± 0.39	1.79 ± 0.49	1.98 ± 0.45	1.75 ± 0.42

Corrected VS where calculated taking into account volatile fatty acid losses during drying.
[a] CM + BWS_{RAW}: Mixture made with cattle manure and raw briquetted wheat straw.
[b] CM + $BWS_{3\%KOH}$: Mixture made with cattle manure and briquetted wheat straw pretreated with 3%KOH.

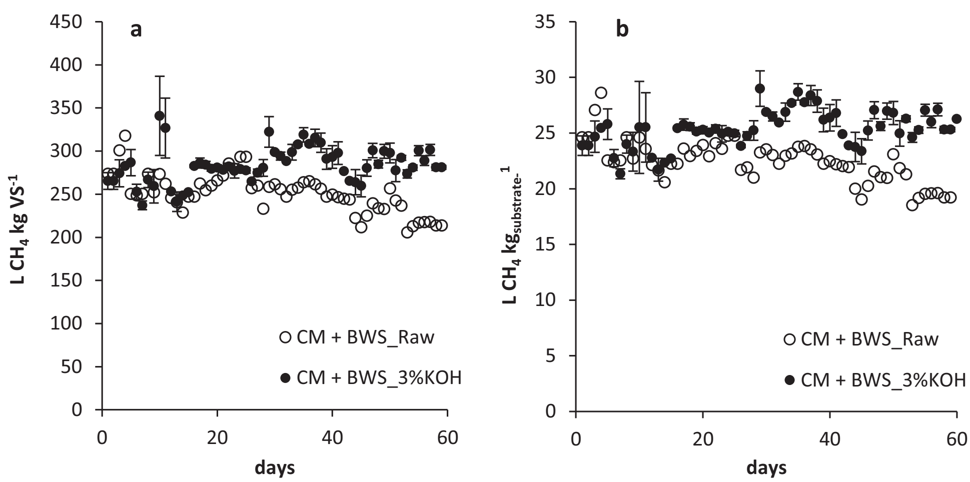

Fig. 4. Methane production in reactors in terms of L CH_4 per kg volatile solids introduced in the reactors (CH_4 kg VS^{-1}) (Fig. 4a) and in terms of L CH_4 per kilo of substrate introduced in the reactors (L CH_4 $kgsubstrate^{-1}$) (Fig. 4b). CM + *BWS_Raw* reactor fed with a mixture of cattle manure and briquetted wheat straw, CM + *BWS_3%KOH* average from two reactor fed with a mixture of cattle manure and briquetted wheat straw pre-treated with 3%KOH. Bars in *BWS_3%KOH* indicate the standard error of the mean from the two reactors.

In the CSTR experiment, a comparison between treatments from an energy and economic perspective was made to evaluate the consequences of alkali addition. For this, the extra energy input and economical cost were only related to the alkali addition itself, since this is the only difference between the treatments. The KOH used in $BWS_{3\%KOH}$ reactors was 1.31 g KOH kg^{-1} of fresh mixture (considering 5.5% of BWS in the substrate mixture and 3% of KOH on a dry matter basis in BWS), corresponding to 0.91 g K kg^{-1} fresh matter.

The energy balance was made with an assumption that the energy consumption of the potassium is 7 MJ kg^{-1} K (Møller et al., 2008), corresponding to an energy demand of 6.39 kJ kg^{-1} mixed substrate added to the digester (0.91 g KOH kg^{-1} × 7 MJ kg^{-1} K).

The extra CH_4 gained in the reactors with the addition of alkali is 4.6 L CH_4 kg^{-1} of mixture (26.3–21.7). The specific energy of methane is 35.96 kJ L^{-1}, which means an extra energy gain of 165.42 kJ kg^{-1} mixed substrate. This value is much higher than the calculated energy demand of alkali addition (9.17 J kg^{-1} mixed substrate); therefore, there is an evident energy surplus of more than a factor 20 by using this pre-treatment.

Concerning the economic cost, in Denmark it is assumed that the costs for KOH is 7 DKK kg^{-1}, which means an extra cost of 9.17 DKK ton^{-1} of mixed substrate added to the reactors (assuming 1.31 kg KOH ton^{-1} of mixture added). Furthermore, it is assumed that the investment in the piston pump is negligible in the overall economical evaluation. When calculating the extra income by using alkali it has been assumed that the value of methane coming from for biogas is around 5 DKK m^{-3} CH_4, according to Act No. 576 of 18.06.2012 (The law on the promotion of renewable energy) in Denmark. This means an extra income of 23 DKK ton^{-1} of mixed substrate (assuming 4.6 m^3 CH_4 extra ton^{-1} of mixture) and a net benefit of 13.83 DKK ton^{-1} of mixed substrate added to the reactor or around 251 DKK ton^{-1} of straw.

In these balances, the extra fertilizer value of a digestate rich in potassium has not been considered. If the farmers will value the fertilizer coming with the KOH the profit by using alkali will be even higher. In countries like Denmark, where potassium is imported, it is expected that farmers will be willing to put a value on the potassium returned with the digestate; otherwise, it has to be bought as a chemical fertilizer.

3.4. Residual methane production in experiment 2 (CSTR experiment)

Maximal specific and volumetric CH_4 potentials, calculated in the CSTR experiment by using the CH_4 yields (Fig. 4a and b) in CSTR and adding the subsequent residual CH_4 production (Fig. 5a and b), were very similar for the two mixtures at around 36 L CH_4 $kg_{substrate}{}^{-1}$ and 390 L CH_4 kg $VS_{in}{}^{-1}$, respectively. The CH_4 yield achieved in the CSTR reactors as a percentage of the potential differed, however, for the two mixtures: the reactor fed CM + BWS_{RAW} reached around 60% of its potential during the continuous feeding phase and 40% in the residual phase. The addition of an alkali to

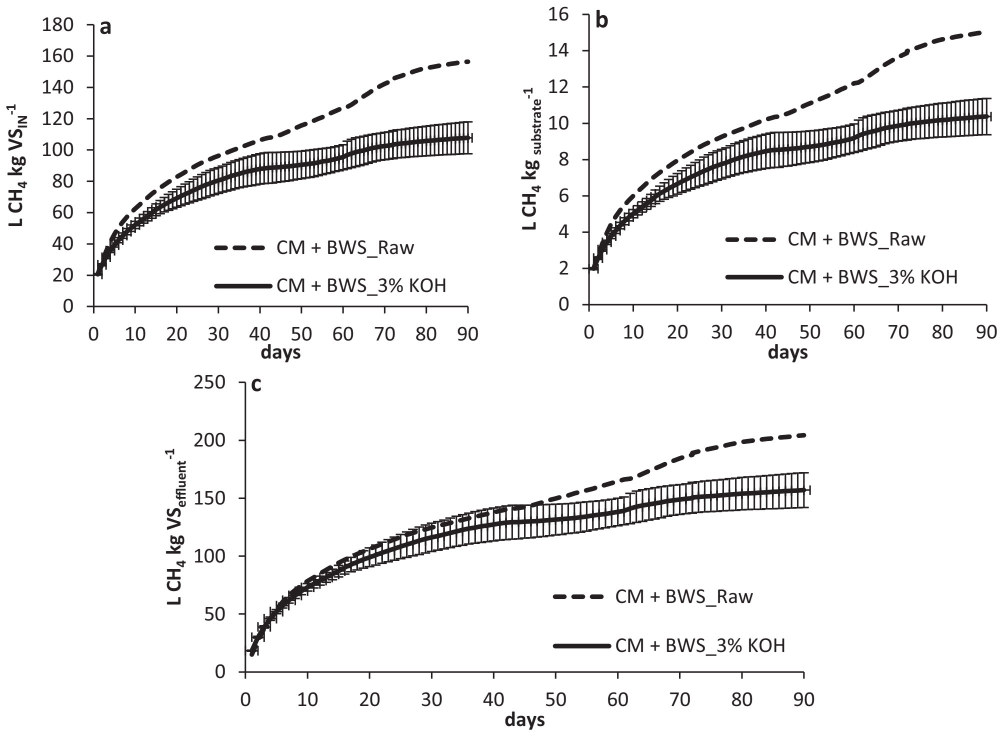

Fig. 5. Cumulative residual methane production in reactors. Fig. 5a: Specific residual methane production in terms of L methane per kg volatile solids initially introduced in the reactors (L CH_4 $^{-1}$); Fig. 5b: Volumetric residual methane production in terms of L methane per kg of substrate initially introduced in the reactors (L CH_4 kgsubstrate^{-1}); Fig. 5c: Specific residual methane yield in terms of L CH_4 per VS in the effluent (CH_4 kg VSeffluent^{-1}). CM + *BWS_Raw*: reactor fed with a mixture of cattle manure and briquetted wheat straw, CM + *BWS_3%KOH*: average from two reactor fed with a mixture of cattle manure and briquetted wheat straw pre-treated with 3%KOH. Bars in *BWS_3%KOH* indicate the standard error of the mean from the two reactors.

BWS increased yields in the reactors during the continuous feeding to around 74%, and as a consequence lowered residual CH_4 emissions to around 26%. These results confirm the results obtained in the batch assay, where only minor differences in the ultimate specific CH_4 yield were observed among treatments and the positive effect of an additive was mainly on the hydrolysis rate.

The effluent from the reactor fed a mixture CM + BWS_{RAW} gave a roughly 30% higher specific CH_4 yield than the effluent from reactors fed a mixture CM + $BWS_{3\%KOH}$ (204 and 157 LCH_4 kg $VS_{effluent}{}^{-1}$, respectively) (Fig. 5c). These results indicate that the digestate from the digestion of the CM + BWS_{RAW} contained a larger amount of undigested biodegradable VS than the digestate from reactors fed CM + $BWS_{3\%KOH}$, which potentially can be degraded during storage resulting in a considerable loss of CH_4 to the atmosphere.

Therefore pre-treatment with KOH 3% can both increase the CH_4 retrieved in the biogas plant and reduce the potential for CH_4 emissions to the atmosphere during the subsequent storage, without increasing the retention time. Hence, alkali pre-treatment of BWS may not only positively impact the economy of the biogas plants, but will also reduce the potential for CH_4 emissions during subsequent storage.

4. Conclusion

Different process configurations of briquetting and additive addition as a combined pre-treatment to improve biogas yield of wheat straw in anaerobic digestion plants are presented and discussed in this work. In terms of briquetting mold size, 68 mm is recommended due to its low energy consumption. In terms of chemical additive, KOH is recommended due its higher hydrolysis rate.

The addition of 3%KOH to BWS when used to feed CSTR in co-digestion with CM increased VS degradation, and CH_4 yield showing positive economic and energy balances; in addition, lower residual CH_4 emissions were observed when comparing with reactors working with BWS without a chemical additive.

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