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Research Paper

The efficiency of shredded and briquetted wheat straw in anaerobic co-digestion with dairy cattle manure

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Anaerobic co-digestion of cattle manure (CM) with shredded or briquetted wheat straw (SS and BS, respectively) was evaluated in thermophilic continuously stirred tank reactors (CSTR) in two experiments (lab and full-scale). Three lab-scale CSTR (15 l) were used with 20 days hydraulic retention time (HRT); one was fed with CM and the other two with mixtures of CM (95% of fresh matter, FM) and SS or BS (5% FM). In the second experiment, two full-scale CSTR (30 m^3) were operated with 25 days HRT; one reactor was fed with CM and the other with CM + BS (9% FM). Ultimate CH_4 yield was analysed from each substrate. Biochemical CH_4 potential at 21 days for CM, SS and BS were 128; 187 and 200 l_{STP} [CH_4] kg^{-1} [VS]. Anaerobic digestion of CM, CM + SS and CM + BS in lab-scale reactors yielded 165; 214 and 217 l_{STP} [CH_4] kg^{-1} [VS]. In full scale-reactors, CM and CM + BS yielded 264 and 351 l_{STP} [CH_4] kg^{-1} [VS]. Increments of 31 and 33% on CH_4 yield were achieved in CM + BS compared to CM in lab and full-scale reactors, respectively. Regarding the energy balance, the energy yields were the same for both reactors using straw as co-substrate (CM + SS and CM + BS) after subtracting the energy consumption of the pretreatment, corresponding to 1100 kWh of net energy output. However, briquetting technology could be advantageous for biogas plants where the straw might be transported over longer distances, due to reduction of the transportation costs.

1. Introduction

Anaerobic digestion is an interesting treatment for animal manure, not only because it can decrease the associated methane (CH_4) emission to the atmosphere, but also because the biogas produced can be used as renewable energy source (Sommer, Petersen, & Møller, 2004). However, anaerobic digestion using only animal manure produces a low CH_4 yield (Asam et al., 2011; Biswas, Ahring, & Uellendahl, 2012; Hamelin, Wesnæs, Wenzel, & Petersen, 2011). In order to

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Nomenclature

ADF	acid detergent fibre
ADL	acid detergent lignin
BMP	biochemical methane potential
BS	briquetted wheat straw
C:N ratio	carbon:nitrogen ratio
CM	cattle manure
CM + BS	reactor fed with cattle manure and briquetted wheat straw
CM + SS	reactor fed with cattle manure and shredded wheat straw
CO_2	carbon dioxide
CSTR	continuously stirred tank reactor
°C	temperature unit (Celsius)
DM	dry matter
HRT	hydraulic retention time
H_2S	hydrogen sulfide
kWh N m^{-3}	kilowatt-hour of energy per volume (m^3) of methane
l_{STP} CH_4	volume of methane (l) corrected for standard condition of temperature and pressure
SS	shredded wheat straw
NDF	neutral detergent fibre
ppm	parts per million by volume
$P < 0.01$	significance level
R_{straw}	percentage of straw (weight, weight)
TAN	total ammonia nitrogen
TKN	total Kjeldahl nitrogen
V_{CH4_CM}	volumetric methane yield of cattle manure
V_{CH4_mix}	volumetric methane yield of cattle manure and straw
V_{CH4_straw}	volumetric methane yield of straw
VFA	volatile fatty acid
VS	volatile solids

make this technology more attractive to farmers, an increase in CH_4 yield can be achieved by co-digesting animal manure with inexpensive and easy accessible agricultural by-products. Co-digestion, a process where two or more substrates are used together in a single anaerobic reactor, provides numerous advantages. Indeed, this process not only improves methane production, alkalinity and carbon to nitrogen ratio, but also promotes dilution of inhibitory compounds, and increases microbial diversity (García-Gen, Lema, & Rodríguez, 2013; Giuliano, Bolzonella, Pavan, Cavinato, & Cecchi, 2013; Wang, Yang, Feng, Ren, & Han, 2012).

Wheat straw is the most abundant crop by-product in Europe and the second in the world (Ferreira, Donoso-Bravo, Nilsen, Fernandez-Polanco, & Pérez-Elvira, 2013; Kim & Dale, 2004). However, due to its high lignocellulosic content, this by-product presents a low biodegradation degree (Pohl, Heeg, & Mumme, 2013). In addition, the low bulk density of the wheat straw greatly increases the cost of handling, transportation (Theerarattananoon et al., 2012), and storage (Rijal, Igathinathane, Karki, Yu, & Pryor, 2012). Briquetting and pelletising are the two potential processes that can increase biomass densification and help in solving logistic issues (Kaliyan & Morey, 2010; Larsson, Thyrel, Geladi, & Lestander, 2008).

Briquetting is a mechanical process in which biomass with a low initial density (0.1–0.2 kg l^{-1}) is first shredded and then submitted to high pressure, promoting its agglomeration and densification. The resulting product (briquettes) can achieve a density of around 1.2 kg l^{-1} (Grover & Mishra, 1996). Theoretically, this process can also alter the chemical structure of the biomass. Firstly, the reduction of the particle size of biomass by shredding process increases its surface area and it can reduce both the degree of polymerisation and cellulose crystallinity (Krishania, Vijay, & Chandra, 2013; Zheng, Zhao, Xu, & Li, 2014). In addition, vaporisation of liquid content in the lignocellulosic material can be expected during the briquetting process due to the high pressure. According to Tumuluru, Wright, Hess, and Kenney (2011), this can promote hydrolysis of the hemicelluloses and lignin into lower molecular weight carbohydrates.

Therefore, particle size reduction through shredding and the application of high pressure and temperature during briquetting process could both accelerate the hydrolysis and acidogenesis of the biomass, achieving a faster and higher CH_4 yield. However, to our knowledge, the effect of briquetting as pretreatment for lignocellulosic material in anaerobic digestion has been scarcely evaluated until now.

In general, prior to feeding anaerobic reactors, particle size reduction of straw is required in order to enhance biomass biodegradability, avoid problems of clogging and provide a homogeneous mixture during digestion. Reduction in particle size of straw can be accomplished by milling or grinding machines, extruders and shredders (Carlsson, Lagerkvist, & Morgan-Sagastume, 2012; Zheng et al., 2014). This process seems less expensive than briquetting as lower energy input is required. However, for more accurate recommendation, technical and economic aspects from both pretreatments should be studied.

Thus, the aim of this study was to evaluate the use of shredded and briquetted wheat straw in the anaerobic co-digestion with dairy cattle manure and the feasibility of biogas plant operation with the best pre-treated straw added to cattle manure.

2. Material and methods

2.1. *Substrates*

The cattle manure (CM) used in this experiment were collected from the animal facilities of the Research Centre Foulum (Aarhus University, Denmark).

The CM used to feed lab-scale continuously stirred tank reactors (CSTR) and also for the batch assay were the same. It was stored in a 1.5 m^3 tank for three months at ambient temperature. In order to feed full-scale reactors, CM was collected weekly from the animal facilities.

The wheat straw was collected near Viborg (Denmark). Before the experiment, the wheat straw was kept on the courtyard, piled in round or square bales and brought to the shredding and briquetting machines using a tractor. A portion of straw was fed manually into a quad shaft shredder equipped with electric control panel UNTHA RS 30 4-S (Kuchl, Austria) and a 20 mm sieve. This straw was named shredded straw (SS). The other portion of straw was briquetted with a BP 6500 briquetting unit CF Nielsen (Baelum, Denmark) linked to a hammer mill with 20 mm sieve (Cormall HDH 770, Denmark) and named briquetted straw (BS). The capacity of the briquetting was 900–1400 kg h^{-1} producing cylindrical briquettes with 68 mm diameter.

During the briquetting process, no external binding agent was used for biomass densification. Pressures applied during the process (compression–decompression cycles) ranged from 150 to 200 MPa above atmospheric pressure. The density of the briquettes was not measured. They ranged from 50 to 200 mm in length. Durability of the BS was not measured since they were used specifically for these experiments. For the batch assay and lab-scale CSTR, BS was prepared once, stored in a barrel and kept at ambient temperature. For the full-scale reactor, BS was prepared weekly. Before feeding the full-scale reactor, BS and CM were mixed in the tank and pumped to the reactor. Prior to this feeding, manual briquette disintegration was carried out in order to facilitate homogeneity in batch assay and lab-scale CSTR.

According to the manufacturer, energy consumption for the wheat straw briquetting process is 70.6 kWh t^{-1} and the shredding prior to the briquetting consumes an additional 30–60 kWh t^{-1}.

Thermophilic (50 °C) and mesophilic (35 °C) inoculums were used in the lab-scale CSTR and batch assay, respectively. Both inoculums were obtained from mesophilic and thermophilic reactors of the Agricultural Research Center in Foulum (Aarhus University, Denmark) which have been running for more than one year under these conditions.

2.2. *Ultimate methane yield*

Maximal biogas and CH_4 production were determined in CM, SS and BS samples in a batch assay at mesophilic temperatures (35 °C) and expressed in terms of l [biogas] kg^{-1} [VS] and l [CH_4] kg^{-1} [VS], respectively. Prior to starting the batch assay, mesophilic inoculum was pre-incubated for 15 days at 35 °C in order to deplete the residual biodegradable organic material (degasification). The composition of the inoculum used was: 3.81% of dry matter (DM), 2.63% of volatile solids (VS), 1.17% of ash content, 2.37% of total nitrogen, 1.59 g l^{-1} of total ammonia nitrogen and 0.13 g l^{-1} of total volatile fatty acids (VFA). The pH of the inoculum was 8.21.

Three bottles per substrate were filled with an inoculum: substrate ratio of approx. 1:1, determined on VS basis. In addition, three bottles were filled only with inoculum and used as blanks; their average cumulative biogas production (endogenous biogas production of the inoculum) was subtracted from the biogas production of the experimental bottles at each sampling time. After filling, each bottle was sealed with a butyl rubber stopper and aluminium crimps, and the headspace was flushed with pure N_2 for 2 min. The bottles were then incubated at 35 °C for 96 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.

2.3. *Lab-scale reactors*

This experiment was conducted during 64 days (more than three hydraulic retention time (HRT)) using three CSTR with 20 l total capacity and 15 l working capacity. Initially, the reactors were filled with thermophilic inoculum and from day 5 to 15, every reactor was fed 100% CM. During these 10 days, adjustments in temperature and stirring speed were carried out. In addition, the reactors were monitored to ensure no leaks during the process. Afterwards, each reactor was fed differently; the first reactor was fed 100% CM and is called the CM reactor, the second was fed a mixture of CM and SS and is called the CM + SS reactor and the third with CM and BS and called CM + BS reactor. The two different straws used to feed the reactor (SS and BS) were vigorously mixed with CM in a ratio 5% of straw and 95% of CM on fresh matter basis (mass $mass^{-1}$) before being introduced into the corresponding reactors. Temperature and hydraulic retention time (HRT) were maintained constant during the whole experimental period, at 49 ± 1 °C and 20 days, respectively.

In the three lab-scale reactors, mixing was performed by a central shaft with two propellers one at the bottom and one in the middle, continuously rotating at 100 rpm. The reactors were heated by electrical resistances 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 (AMPTS II, Bioprocess Control, Sweden).

2.4. *Full-scale reactors*

The full-scale experiment was run for 115 days (more than three times HRT) in two CSTR (30 m^3). The two reactors were similar in design, i.e. constructed in stainless steel and heated by an external water jacket. Both reactors operated under thermophilic conditions (50 °C). One reactor was fed 100% CM and is called the CM reactor, the other with a mixture CM and BS and called CM + BS reactor. In the CM + BS reactor, BS was added to a final concentration of 9% of fresh matter (mass $mass^{-1}$). Every Friday and Monday, the CM + BS reactor was fed double the amount of BS in order to compensate the lack of straw addition during weekends.

Continuous mixing of the digestate in the reactors was obtained using a central shaft with a propeller at the bottom, rotating at 60 rpm. Gas production was measured with a differential pressure transmitter device (EJX110A Yokogawa, Japan). Feeding and unloading the reactors was performed automatically by electric pumps. The load and unload were controlled by weighing the substrates and digestates in order to obtain an HRT of around 25 days.

2.5. *Analyses*

Samples from each reactor and from the substrates (CM, SS and BS) were collected and analysed weekly in both CSTR experiments; pH, DM as total solids (TS) and VS were analysed following the procedure described by APHA (2005). Dissolved VFA were determined using a gas chromatograph (5560-D procedure, APHA, 2005) equipped with a flame ionisation detector (HP 68050 series, Hewlett Packard). Total ammonia nitrogen (TAN) concentration was determined using photometric kits (Spectroquant® kit, Merck, USA). The total Kjeldahl nitrogen (TKN) was determined according to APHA (2005). Protein content was determined as (TKN − TAN) × 6.25.

In the last three weeks of the experimental period, samples from each lab-scale reactor were collected to determine fibre fraction and sugar availability. Samples for fibre analysis were dried (48 h at 60 °C) and milled to a particle size of 0.8 mm using CyclotecTM 1093 mill (FOSS North America). Fibre fractions (neutral detergent fibre (NDF), acid detergent fibre (ADF) and lignin (ADL)) were analysed according to the Van Soest (1994) procedure. From these fractions, hemicelluloses, cellulose and lignin were calculated. The hemicelluloses content was calculated as the difference between NDF and ADF, cellulose content was calculated as the difference between ADF and ADL, and lignin content was assumed to be equal to ADL.

For sugar availability, the fresh samples were extracted by enzyme hydrolysis method and the analysis was conducted in triplicates. Two types of enzymes, cellulase (Celluclast® 1.5 L, Novozymes) and mannanase (Novozym 51054, Novozymes) were added to promote the hydrolysis. The mixtures were then incubated at 150 rpm, 50 °C for 72 h using incubator shaker (Innova® 43). The samples were centrifuged at 4500 rpm for 5 min after incubation and only supernatant was used for the analysis. A glucose stock solution (1.0 g l^{-1}) was prepared and different concentrations of glucose (0.2, 0.4, 0.6, 0.8 g l^{-1}) were made by diluting the stock solution. Xylose standard solution (1.0 g l^{-1}) was also prepared to ensure the results obtained were reliable. Sugar availability in the samples was determined by using dinitrosalicylic acid method (Ghose, 1987) and absorbance of the samples was measured with Multiskan FC (Thermo Fisher Scientific, China) at 540 nm wavelength. Measurements were repeated in triplicate.

Biogas samples were taken from CSTR reactors and analysed twice a week and in each biogas measurement from bottles. In all cases, biogas was sampled by flushing a 22 ml sample bottle with 300 ml of biogas. The biogas was sampled and analysed for CH_4, carbon dioxide (CO_2) and hydrogen sulfide (H_2S) concentration using a gas chromatograph equipped with a thermal conductivity detector (Agilent technologies 7890A).

2.6. Calculations

Total volume of biogas and CH_4 produced in the batch assay and in the lab-scale and full-scale reactors was corrected for standard conditions (273.15 K and 101,325 Pa) and indicated as l_{STP}. In the batch assay, cumulative CH_4 yield as a function of time was calculated in terms of specific methane yield (l_{STP} [CH_4] kg^{-1} [VS]) and indicated as biochemical methane potential (BMP). The specific BMP at the end of the determination (96 days) was considered as the ultimate methane yield.

In the CSTR reactors, CH_4 production was determined both in terms of specific CH_4 yield (l_{STP} [CH_4] kg^{-1} [VS added]) and volumetric CH_4 yield (l_{STP} CH_4 kg^{-1} of substrate feeding added, on fresh matter (FM) basis).

Chemical composition of the substrates (average ± standard deviation) was calculated from data obtained throughout the daily load period for lab and full-scale CSTR. Chemical composition of the effluents, and specific and volumetric CH_4 yields (average ± standard deviation) from lab and full-scale CSTR were calculated from data obtained during the third retention time, day 43–63 and 91–115, respectively, to ensure steady state conditions had been achieved.

Volumetric CH_4 yield of straw subjected to the two pretreatment technologies (SS and BS) was calculated in terms of l_{STP} [CH_4] kg^{-1} [straw] according to Equation (1).

$$V_{CH4\_Straw} = \left(V_{CH4\_mix} - V_{CH4\_CM} * (100 - R_{straw})/100\right)/(R_{straw}/100) \quad (1)$$

R_{straw} is the percentage of biomass in the form of straw on a mass basis, V_{CH4_CM} is the measured volumetric CH_4 yield of cattle manure obtained under steady state conditions and V_{CH4_mix} is the measured volumetric CH_4 yield of the mixed biomass of cattle manure and straw obtained under steady state conditions.

Net energy of each straw pretreatment was calculated from the calculated volumetric CH_4 yield of each straw (SS and BS) considering an energy content of the 10 kWh N m^{-3} of CH_4 (Equation (2)).

$$\text{Net Energy}_{Straw}\left(\text{kWh t}^{-1}\right) = V_{CH4\_Straw}\left(\text{m}^3\ \text{CH}_4\ \text{t}^{-1}\right) * 10\ \text{kWh N m}^{-3} - \text{Energy consumed}\left(\text{kWh N m}^{-3}\right) \quad (2)$$

3. Results and discussion

3.1. Substrates composition

The CM, SS, BS and the mixtures used to feed the reactors were characterised and summarised in Table 1. As shown, similar TS, VS and ash contents were found between the two straw samples (Table 1).

No important differences were found in fibre composition between straw samples, especially in terms of lignin content. Cellulose, hemicelluloses and lignin content represented 74 and 75% (on DM basis) in the SS and BS, respectively. Cellulose and hemicelluloses contents of SS and BS obtained in this work were similar to those reported by Krishania et al. (2013) for wheat straw. In the present work, lignin content obtained in SS and BS was comparable to values in the literature (Buranov & Mazza, 2008). Higher TS, VS, ash, cellulose and hemicelluloses contents were observed in straw samples (SS and BS) than in the CM used in the lab-scale reactors. However CM presented a higher lignin and available sugar content than both straws.

No difference in the sugar availability was observed between straw samples. Similar sugar availability (7%, on DM basis) was found by Heiske, Schultz-Jensen, Leipold, and Schmidt (2013) in wheat straw samples.

Higher TS and VS content were found in the mixtures CM + SS and CM + BS compared with CM. In fact, the addition of straw increased the VS content in the influent used by

Table 1 – Chemical composition and ultimate methane yield of the substrates (mean ± standard deviation) used to feed the reactors.

	Shredded wheat straw	Briquetted wheat straw	Lab-scale reactors			Full-scale reactors	
			Cattle manure	Cattle manure + shredded wheat straw	Cattle manure + briquetted wheat straw	Cattle manure	Cattle manure + briquetted wheat straw
Total solids (%, FM[a] basis)	88.89 ± 1.15	87.46 ± 1.48	6.85 ± 0.92	10.80 ± 0.67	10.70 ± 0.92	6.18 ± 0.23	14.80 ± 2.70
Volatile solids (%, FM basis)	86.22 ± 1.05	83.21 ± 2.93	5.64 ± 0.69	9.35 ± 0.86	9.11 ± 1.15	5.07 ± 0.20	13.29 ± 2.58
Ash (%, FM basis)	2.80 ± 0.24	3.49 ± 1.08	1.21 ± 0.24	1.43 ± 0.46	1.56 ± 0.54	1.11 ± 0.06	1.30 ± 0.10
pH	ND[c]	ND	6.97 ± 0.14	7.19 ± 0.09	7.79 ± 0.14	7.10 ± 0.29	ND
Acetic acid ($g\ l^{-1}$)	ND	ND	3.60 ± 0.85	3.76 ± 0.96	3.87 ± 0.99	3.51 ± 0.38	ND
Propionic acid ($g\ l^{-1}$)	ND	ND	1.91 ± 0.35	2.03 ± 0.41	2.06 ± 0.41	1.81 ± 0.32	ND
Total volatile fatty acids ($g\ l^{-1}$)	ND	ND	6.93 ± 1.50	7.24 ± 1.64	7.40 ± 1.69	6.60 ± 0.87	ND
Total ammonia ($g\ l^{-1}$)	ND	ND	1.32 ± 0.18	1.28 ± 0.17	1.29 ± 0.20	1.34 ± 0.23	ND
Protein (%, DM[b] basis)	ND	ND	11.95 ± 1.27	6.95 ± 0.64	7.00 ± 0.87	10.97 ± 2.08	ND
Cellulose (%, DM basis)	44.98 ± 1.35	45.63 ± 1.26	23.76 ± 1.25	32.19 ± 0.68	32.80 ± 1.40	ND	ND
Hemicellulose (%, DM basis)	31.01 ± 2.95	33.44 ± 4.95	16.07 ± 1.13	22.01 ± 0.47	23.25 ± 1.04	ND	ND
Lignin (%, DM basis)	6.87 ± 0.25	6.46 ± 0.79	10.65 ± 0.22	9.01 ± 0.17	8.94 ± 0.18	ND	ND
Sugar availability ($g\ g^{-1}$, DM basis)	0.07 ± 0.02	0.07 ± 0.00	0.25 ± 0.01	0.17 ± 0.04	0.12 ± 0.02	ND	ND
Ultimate methane yield (96 days) ($l_{STP}\ CH_4\ kg^{-1}$ VS)	300.02 ± 4.02	303.21 ± 2.18	306.54 ± 4.35	ND	ND	ND	ND

[a] FM: fresh matter.
[b] DM: dry matter.
[c] ND: not determined.

approximately 64% in the lab-scale experiment and 162% in the full-scale experiment. The high standard deviation found in the TS and VS contents in CM + BS mixture used in the full-scale reactor could be explained by the double automatic straw load before and after the weekends.

In the lab-scale experiment, acetic acid, propionic acid, total VFA, and TAN concentrations in the CM substrate were close to those presented by mixtures used to feed CM + SS and CM + BS. Protein content however, was higher in the substrates containing only CM. In fact, protein content in the feeding substrates decreased more than 40% when adding straw, probably caused by the low protein content of the wheat straw (Krishania et al., 2013; Sambusiti, Monlau, Ficara, Carrère, & Malpei, 2013) and its high carbon: nitrogen (C:N) ratio (Chandra, Takeuchi, Hasegawa, & Kumar, 2012; Nkemka & Murto, 2013; Wang et al., 2012). According to Wang et al. (2012), animal manure can present a poor C:N ratio, due to its high TAN content which in some cases can be inhibitory for microbial growth. Co-digestion of manure and crop material can therefore, improve the C:N ratio avoiding ammonia inhibition. Mixtures containing CM + SS and CM + BS had higher cellulose and hemicellulose and lower lignin content than CM alone. Singh and Jain (1985) claimed that in the anaerobic digestion of lignocellulosic material like CM, a high percentage of the total CH_4 produced comes from cellulose degradation. Therefore, the addition of straw gave a higher cellulose and hemicellulose content in the feeding substrates which could improve the methanogenesis.

3.2. *Ultimate methane yield*

Ultimate CH_4 yields at 96 days for SS, BS and the CM were 300, 303 and 306 l_{STP} [CH_4] kg^{-1} [VS], respectively (Table 1 and Fig. 1). This means that no important differences were found in ultimate VS biodegradability (96 days) among the three substrates tested.

Cattle manure used in this work showed a higher ultimate CH_4 yield compared with other works found in the literature (Møller, Sommer, & Ahring, 2004; Moset, Cambra-López, &

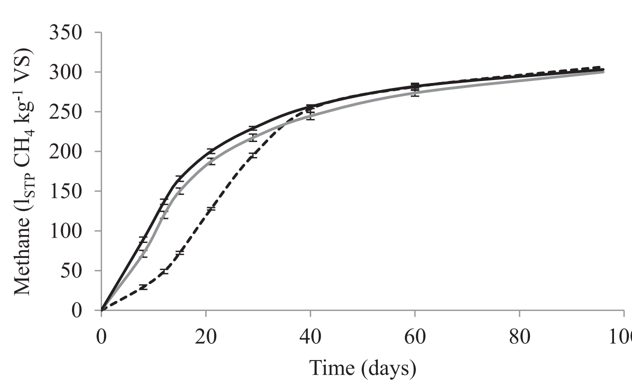

Fig. 1 – Cumulative methane yield from cattle manure (dotted line), shredded wheat straw (grey line) and briquetted wheat straw (black line) during the batch assay. Error bars: standard deviations.

Møller, 2012; Sommer et al., 2004). In the case of wheat straw, the high variability found in the literature complicates the comparison. In general, the values in the literature range from 70 to 404 l $[CH_4]$ kg^{-1} [VS] (Angelidaki & Ellegaard, 2003; Jackowiak, Bassard, Pauss, & Ribeiro, 2011; Krishania et al., 2013; Taherdanak & Zilouei, 2014). This variation could be explained by differences in chemical composition of the straws and the pretreatments used in these works.

During the first 21 days, BMP from both straws was higher than in CM (Fig. 1). In fact, BMP at 21 days obtained in the batch assay for CM, SS and BS was 128, 187 and 200 l_{STP} $[CH_4]$ kg^{-1} [VS], respectively. These yields correspond to 42, 62 and 66% of their respective ultimate CH_4 yield. Thus 32% and 36% more gas was produced from SS and BS, respectively, during the first 21 days comparing to CM. In this regard, Hjorth, Gränitz, Adamsen, and Møller (2011) also found higher specific CH_4 yield during the first 28 days in a batch assay with barley straw compared with the last remaining period. Therefore, important advantages in CSTR can be obtained if straw is used in co-digestion with animal manure; especially when retention times are lower than 30 days, as is usual the case in most North European countries. Comparing both straws, BS yielded 6% more CH_4 than SS at 21 days.

3.3. Continuous reactors: lab-scale and full-scale reactors

3.3.1. Chemical composition

The effluent from CM + SS and CM + BS lab-scale reactors presented a higher TS and VS content than effluent from CM reactor (Table 2). This can be explained by higher organic matter in the substrates containing straw (Table 1). Total VFA, acetic acid, cellulose and hemicelluloses content were higher in CM + SS and CM + BS reactors than CM reactor. The pH and sugar availability values were lower when CM was co-digested with SS and BS (Table 2). However, no differences were observed in ash, propionic acid, TAN, TKN, lignin and protein content among effluents from lab-scale reactors.

Results obtained in the full-scale experiment partially confirmed those obtained in the lab-scale experiment. In this regard, higher TS and VS content and lower TAN concentration were found in the effluent from CM + BS reactor compared to that obtained in CM reactor. In contrast, protein content decreased in full-scale reactors with the addition of straw and this could be explained by lower concentration of products from protein metabolism in the reactors working with straw. No differences were found in the pH, acetic acid and total VFA contents between full-scale reactors.

Despite the full-scale reactor having been operated at higher TS content and fed with highly compressed straw, which is not easy to disintegrate, no clogging problems or stirring difficulties were observed, and effluent from CM + BS full-scale reactor presented a homogeneous distribution. In fact, according to Smith, Probert, Stokes, and Hansford (1977), a rapid swelling of BS occurs on water immersion, leading to briquette disintegration within a few minutes. This mechanism can be explained by rupture of particle bonds formed during briquetting which are promoted by van der Walls and electrostatic forces (Tumuluru et al., 2011).

3.3.2. Biogas composition and methane yields

Concerning biogas composition, in full-scale reactors H_2S concentration in the biogas was higher in CM reactor than in CM + BS reactor (Table 2); in lab-scale reactors however, there was no differences in H_2S concentration in biogas among the reactors. Typically, biogas is composed of 55–80% CH_4 and 20–45% CO_2, with trace amounts of H_2S ranging between 0.005 and 1%, depending on the composition of the feed substrate (Pipatmanomai, Kaewluan, & Vitidsant, 2009). In reactors fed with animal manure, H_2S comes from anaerobic sulphate reduction and metabolism of sulphur-containing amino acids (Mackie, Stroot, & Varel, 1998). As stated above, the addition of straw decreased protein content in the full-scale reactor, and consequently lower H_2S concentration was found in the biogas. This is important in biogas plants because H_2S is an odorous and dangerous gas which must be removed from the biogas before it can be used because of its corrosive effect in combined heat and power engines (Cirne, Van der Zee, Fernadez-Polanco, & Fernandez-Polanco, 2008).

Volumetric CH_4 yields from lab-scale and full-scale experiments are shown in Figs. 2 and 3, respectively, and the average specific and volumetric CH_4 yields from both experiments are shown in Table 2. According to these results, CM presented higher specific and volumetric CH_4 yields in full-scale than in lab-scale experiment. This could be explained by the fact that in lab-scale reactors CM was collected at the beginning of the experimental period and losses of the easily degradable VS during manure pre-storage can be expected, as observed through the slight decrease of the CH_4 yield at third retention time (Fig. 2). In full-scale reactors however, CH_4 yield in CM reactor remained constant over time, probably because CM was taken from animal facilities regularly.

The specific CH_4 yields obtained for CM in this work are similar to those found by Linke, Muha, Wittum, and Plogsties (2013) who evaluated 24 German mesophilic biogas plants fed with CM and energy crops, grass silage or grain and found maximal CH_4 yield for CM of 270 l_{STP} $[CH_4]$ kg^{-1} [VS].

The highest specific CH_4 yields were obtained when co-digestion was used to feed reactors instead of CM as single substrate (Table 2 and Figs. 2 and 3). Co-digestion of CM and BS or SS increased the specific CH_4 yield by around 31 and 29%, respectively, when compared to CM alone, in lab-scale reactors. In full-scale experiment, BS addition increased the specific CH_4 yield approximately 33%. These results are in accordance with the ultimate methane yield test where the first 21 days yielded more than 30% extra biogas from straw compared to CM (Fig. 1). Comparing between the two straw types, the use of CM + BS increased the specific CH_4 yield by 2% compared to CM + SS in the lab-scale experiment. The CH_4 yield of BS on a fresh matter basis (l_{STP} $[CH_4]$ kg^{-1} [straw]) was 3% higher than shredding.

Concerning volumetric methane yield, co-digestion of CM and BS or SS increased the volumetric CH_4 yield by around 76 and 74%, respectively, when comparing with CM alone, in lab-scale reactors. In full-scale experiment, BS addition increased the volumetric CH_4 yield approximately 158%. Therefore, according to the results obtained in this work, more than double volumetric CH_4 yield can be expected in anaerobic reactors working with co-digestion compared to reactors running on

Table 2 – Chemical composition of the digestates and methane yields of the substrates (mean ± standard deviation) obtained during third retention time.

	Lab-scale reactors			Full-scale reactors	
	Cattle manure	Cattle manure + shredded straw	Cattle manure + briquetted straw	Cattle manure	Cattle manure + briquetted straw
Amount of straw (%, FM[a] basis)	0	5	5	0	9
Total solids (%, FM basis)	5.89 ± 0.72	8.28 ± 0.27	8.18 ± 0.22	4.99 ± 0.17	9.23 ± 0.15
Volatile solids (%, FM basis)	4.52 ± 0.63	6.74 ± 0.45	6.85 ± 0.19	3.73 ± 0.11	7.88 ± 0.15
Ash (%, FM basis)	1.36 ± 0.16	1.54 ± 0.37	1.33 ± 0.06	1.22 ± 0.05	1.31 ± 0.15
pH	7.90 ± 0.04	7.71 ± 0.03	7.70 ± 0.03	7.91 ± 0.04	7.91 ± 0.11
Acetic acid ($g\ l^{-1}$)	0.19 ± 0.05	0.28 ± 0.07	0.30 ± 0.05	0.21 ± 0.05	0.28 ± 0.09
Propionic acid ($g\ l^{-1}$)	0.02 ± 0.02	0.05 ± 0.01	0.05 ± 0.03	LD[c]	0.06 ± 0.02
Total volatile fatty acids ($g\ l^{-1}$)	0.22 ± 0.06	0.33 ± 0.07	0.35 ± 0.07	0.21 ± 0.05	0.29 ± 0.12
Total ammonia ($g\ l^{-1}$)	1.69 ± 0.13	1.49 ± 0.18	1.52 ± 0.10	1.65 ± 0.04	1.38 ± 0.13
Total nitrogen ($g\ l^{-1}$)	2.75 ± 0.32	2.83 ± 0.30	2.83 ± 0.16	2.63 ± 0.21	2.77 ± 0.05
Protein (%, DM[b] basis)	10.48 ± 1.66	9.82 ± 2.28	9.70 ± 1.08	12.06 ± 2.93	9.05 ± 0.60
Cellulose (%, DM basis)	23.46 ± 0.85	29.03 ± 0.34	29.01 ± 0.31	ND[d]	ND
Hemicellulose (%, DM basis)	8.11 ± 0.89	12.58 ± 1.43	13.14 ± 1.50	ND	ND
Lignin (%, DM basis)	16.45 ± 0.58	15.20 ± 0.89	15.74 ± 0.62	ND	ND
Sugar availability ($g\ g^{-1}$, DM basis)	0.21 ± 0.02	0.12 ± 0.01	0.13 ± 0.01	ND	ND
Specific CH_4 yield ($l_{STP}\ CH_4\ kg^{-1}$ VS)	165.72 ± 11.03	213.60 ± 6.46	217.08 ± 8.77	263.72 ± 37.77	351.33 ± 195.97
Volumetric CH_4 yield ($l_{STP}\ CH_4\ kg^{-1}$ substrate)	8.33 ± 0.58	14.46 ± 0.47	14.66 ± 0.63	13.36 ± 1.96	34.41 ± 5.24
Volumetric CH_4 yield ($l_{STP}\ CH_4\ kg^{-1}$ straw)	0	116.46 ± 12.33	120.23 ± 14.14	0	136.00 ± 23.91
H_2S in the biogas (ppm)	581 ± 305	387 ± 9	410 ± 25	2320 ± 350	410 ± 31

[a] FM: fresh matter.
[b] DM: dry matter.
[c] LD: lower than the detection limit.
[d] ND: not determined.

manure as the sole biomass. These results are important for the economy of the anaerobic digestion plants. The benefits of adding straw to anaerobic reactors working with animal manure have also been highlighted by Wang, Gavala, Skiadas, and Ahring (2009).

3.3.3. *Energy balance*

A positive energy balance is essential for the sustainability of implementing pretreatment of straw. During the experiments, the energy consumption was monitored and, on average, the energy consumption for the wheat straw briquetting process was 70.6 kWh t^{-1} and the shredding prior to the briquetting consumed an additional 30–60 kWh t^{-1}. In the latest setup, a total energy consumption of 100.6 kWh t^{-1} of wheat straw was estimated for the energy calculations of the briquetting process, including pre-shredding. The shredding unit for producing the SS in this experiment was an

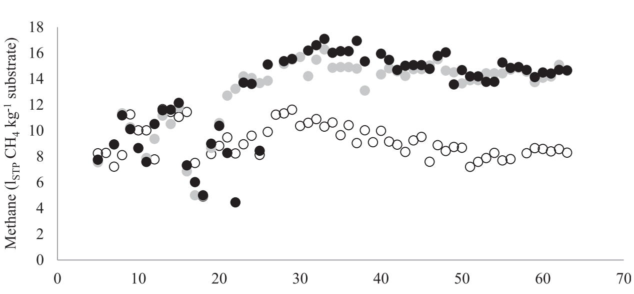

Fig. 2 – Volumetric methane yield obtained in the lab-scale CSTR from cattle manure (○), cattle manure + shredded wheat straw (●) and cattle manure + briquetted wheat straw (●).

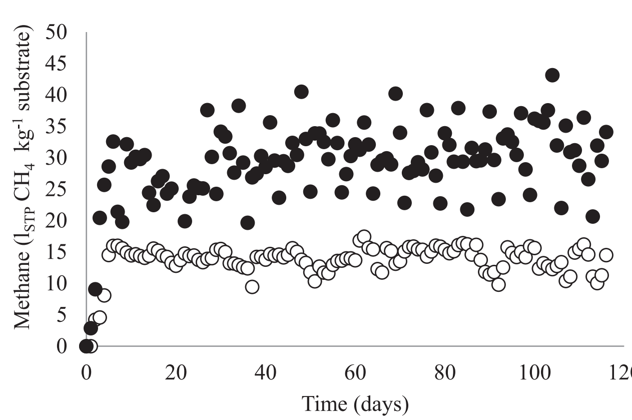

Fig. 3 – Volumetric methane yield obtained in full-scale CSTR from cattle manure (○) and cattle manure and briquetted wheat straw (●).

experimental setup fed by hand and the energy recorded will be higher than when used commercially. For this reason an energy consumption that would be expected in a commercial setup with a similar sieve size was used in the energy calculation of SS resulting in a consumption of 60 kWh t^{-1} of wheat straw. This means a total energy consumption of 100 kWh t^{-1} and 60 kWh t^{-1} is used for BS and SS, respectively.

The energy produced from the straw in the lab-scale digesters is around 116 and 120 m^3 CH_4 t^{-1} for SS and BS respectively (Table 2) corresponding to 1100 kWh t^{-1} of net energy for both straws after subtracting the energy consumption (calculated from Equation (2)).

Therefore, briquetting technology gave a similar net energy output compared to shredded straw when used for biogas production. However, the difference between buying baled or briquetted straw could entail important differences for farmers, since according to Singh, Panesar, and Sharma (2010) when lorries are used to transport biomass, a reduction of around 46% of the transport costs (in terms of US\$ t^{-1} km^{-1}) can be achieved if biomass is briquetted instead of baled. From an energy point of view, there will be savings in diesel consumption by transport as well, since the trucks can transport higher amounts of straw due to higher density obtained by briquetting. From Singh et al. (2010) it can be calculated that 0.83 l of diesel can be saved per kg of straw when the mean transport distance is 50 km, corresponding to approximately savings at around 8.3 kWh kg^{-1} [straw]. This means that the net energy output by briquetting can be improved if the straw has to be transported over longer distances.

The use of straw for co-digestion results in a positive net energy output for both technologies, since less than 10% of the energy produced from the straw would be used for shredding and briquetting.

4. Conclusion

Shredded or briquetted wheat straw as a co-substrate for anaerobic digestion of cattle manure increased TS and VS concentration in the reactors by increasing cellulose and hemicellulose concentration. This change in the chemical composition of the reactors resulted in higher specific and volumetric methane yields. Especially in full-scale reactors, where the mixture of CM and BS gave 33% higher specific CH_4 yield compared to cattle manure and 158% in terms of volumetric CH_4 yield. In addition, in full-scale reactors, biogas obtained from CM + BS had significantly lower H_2S concentration than from digestion of CM alone.

The net energy yields were the same for both pretreatments (1100 kWh), however the briquetting technology could still be more advantageous if the straw has to be transported over longer distances, due to the lower transportation costs.

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