Research paper

Pre-treatment methods for straw for farm-scale biogas plants

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Abstract

This study investigated the effect of five different pre-treatment methods (ammonia (NH_3), caustic soda (NaOH), dry milling, hot water and steam explosion) for straw for biogas production. The methods were selected based on their suitability for implementation in farm-scale biogas plants. The pre-treatment methods were applied to four different types of straw. Batch anaerobic digestion tests were carried out in bottles at mesophilic temperature (37 ± 1 °C). The straw was analysed for lignin, hemicellulose and cellulose. The results showed large variations in methane production following the different pre-treatment methods. There were also large variations between the pre-treatment methods in their effect on the different types of straw. Pre-treatment with NaOH on barley straw was particularly effective. The results also showed that the shorter the retention time in the reactor, the more important the choice of pre-treatment method. Different pre-treatment methods were found to be optimal, to some extent, for different retention times.

Keywords

Biogas production, lignocellulosic biomass, sodium hydroxide, steam explosion, barley.

Introduction

Today straw represents a large but largely unexploited resource for bioenergy production. Unlike purpose-grown energy crops, straw does not compete with food production. The grain is seen as the main product and much of the straw produced world-wide is left in the field after harvesting. Straw is therefore often available in large quantities at a low price. Only a small fraction of straw is collected for fodder, bedding material or incineration at heating plants. Burning straw in the field causes heavy air pollution and is forbidden in many regions and countries [1].

The yield of straw may vary due to several factors, such as water and nitrogen availability, crop seed rate and sowing date, fungicide treatment, crop species and crop cultivar [2]. The cutting height of the straw during harvesting influences also the amount of straw available for collection. The fraction of straw is often calculated as a ratio of the harvested grain, e.g. the straw:grain ratio for wheat was found to be within the range 0.34 - 0.65 in a Danish study [2]. A German study reported a straw:grain ratio of 0.8 for barley and wheat, 0.9 for rye and triticale and 1.1 for oats [3]. The world's grain production in 2014 was in total 144.3 Teragram (Tg) of barley, 23.0 Tg of oats, 15.3 Tg of rye, 17.1 Tg of triticale and 729.0 Tg of wheat [4]. Assuming an average straw:grain-ratio of 0.7, this represents 650 Tg of straw per year. In addition, annual production of rice straw is estimated to 810 Tg [5].

The lower heating value ($kJ \cdot g^{-1}$) of straw is reported to be: 17.3 for wheat, 17.6 for rye and 17.4 for barley [3], 17.4 for oats [6] and 17.1 for triticale [7]. The heating value of rice straw is reported to be 16.35 $kJ \cdot g^{-1}$ [8]. Together, the worldwide straw resources represent a total potential of approximately 24.5 Exajoules (EJ).

In Norway, total grain production in 2014 was 514.2 Gg of barley, 289.3 Gg of oats, 39 Gg of rye and 379.1 Gg of wheat [4]. Assuming a straw:grain-ratio of 0.7, this represents more than 855 Gg per year, with a total energy potential of 4.14 TWh. The biogas potential of the available straw in Norway has been estimated to be 575 GWh [9]. However, a Norwegian field study reported slightly lower harvest of straw dry matter of in average 2 $Gg \cdot ha^{-1}$. This mainly due to >10 cm cutting height and losses during harvesting [10]. The total available amount of straw in Norway in that study was estimated to be in the range of 0.5 Tg to 0.7 Tg dry matter per year [10].

Annual removal of straw may cause soil fertility depletion due to reduced soil organic carbon (SOC) input and increased soil erosion [11]. However, utilising the straw for biogas production, and thereby producing a digestate which can be used as a fertiliser in the field, can counteract many of the negative effects of removing the straw [12] [13]. In contrast to combustion, the nutrients in the straw are preserved during anaerobic digestion. The pressure from plant diseases is also reduced when the plant material is anaerobically digested compared with being left directly in the field after harvesting [14]; [15]; [16]; [17]. Anaerobic digestion of straw could therefore result in substantial production of renewable energy in a sustainable way.

Unfortunately, untreated straw is not considered as optimal substrate for biogas production [18]. This is mainly due to low degradability of the untreated straw, but also due to technical challenges regarding feeding the dry straw into the digester and problems with formation of floating layers due to the low density of straw. Moreover, the easily degradable cellulose in the straw is to some extent captured in lignin and hemicellulose structures, which makes degradation more difficult for microbial communities. To utilise the high biogas potential in straw, pre-treatment is necessary [19]. A number of pre-treatment methods have been tested, both laboratory-scale and full-scale, and many have shown promising results. Unfortunately, however, many of these methods are associated with high investment costs and are therefore not suitable for small farm-scale biogas plants. Pre-treatment of straw is also important for ethanol production [20], an application on which much research has been done. The structure and amount of lignin, hemicellulose and cellulose in straw varies between different crop species and cultivars [21]; [22]. The effect of pre-treatment methods may therefore differ for these different types of straw.

The aim of this study was to test different pre-treatment methods that are suitable for implementation in farm-scale biogas plants and determine their effect on different types of straw. Five pre-treatment methods were tested: ammonia treatment, NaOH treatment, dry milling, hot water treatment and a “high end” pre-treatment, steam explosion. Steam explosion is currently only profitable for large-scale biogas plants, but will hopefully also be available for smaller plants in the future. These pre-treatment methods were applied to four different types of straw, from the most common cereals grown in Norway: spring wheat, winter wheat, barley and oats.

2. Materials and methods

2.1. Straw

The four types of straw were tested were barley (*Hordeum vulgare* var. *Hexasticum*) cv. 'Heder', oat (*Avena sativa*) cv. 'Belinda', spring wheat (*Triticum aestivum*) cv. 'Zebra' and winter wheat (*Triticum aestivum*) cv. 'Mjølner'. The grain was cultivated on fields at or close to the Norwegian University of Life Sciences (NMBU), SE Norway (59°39'49.9''N 10°46'05.3''E). The grain was harvested by combine harvesters at ripening stage of the grain. After drying on the ground, the straw was baled by conventional round bale machines for agricultural tractors. After baling, the dry bales were stored in shelters. The straw for ammonia pre-treatment was treated and wrapped with plastic foliage in the field.

2.2 Pre-treatment of the straw

The pre-treatment methods were selected based on their suitability to be easily implemented on farm-scale biogas plants. This resulted in selection of ammonia (NH_3) pre-treatment, caustic soda (NaOH) pre-treatment, dry milling and hot water pre-treatment, which were compared with a high-end pre-treatment, steam explosion. Untreated straw was used as reference.

The ammonia pre-treatment was performed in the field and comprised the following steps. A tractor with an ammonia tank and a front loader with a weight and a hollow spear were used to insert ammonia into the bales at a ratio of 2.5 % of initial weight. The bales were then immediately wrapped with plastic foliage by a tractor driven wrapping machine. Ammonia treatment is the most common pre-treatment method for straw for cattle fodder in Norway today, although it is forbidden in many countries due to the high ammonia emissions to the atmosphere.

All other pre-treatment methods were performed in the laboratory. To facilitate use of the straw in bottle-based anaerobic digestion experiments, it was chopped manually with a paper knife into about 2.5 cm lengths before pre-treatment. The ammonia-treated straw was chopped after pre-treatment, before use in the experiments.

Pre-treatment with NaOH is the conventional pre-treatment method for straw used as cattle fodder in Norway. In the present study, this pre-treatment involved soaking 50 g straw in a 2 L solution for one hour. The solution was made by dissolving 1.5 g caustic soda ("Kaustisk soda, konsentrert 98/99 % NaOH", Stabil fabrikker, 1344 Haslum, Norway) per 100 g water. The straw was then ripened in air for at least four days at a temperature of ≥ 10 °C, as described previously [23]; [24]. After ripening, the NaOH-treated straw was stored in portion-packed plastic bags in a refrigerator until use. Before use, the NaOH solution had a pH of 13.10. After treatment, all the NaOH treatment solutions had a brownish colour, with the solution from the treatment of oat straw displaying the darkest colour.

Dry milling was selected as a pre-treatment method because smaller particles have a much larger surface area per unit mass and thus microorganisms and their enzymes have more contact area to work upon. Smaller particle diameter also reduces the time required to digest the whole particle. The dry milling was performed with a Retsch GmbH SM 2000 mill (Germany), at a rotating speed equivalent to 23.17 Hz. The bottom sieve selected in this experiment had a 0.5 mm mesh size. All the straw passed the sieve.

Hot water pre-treatment is a very simple method, with no need for additional chemicals. At biogas plants producing electricity and with no market for the excess heat, energy in the form of hot water is available in large quantities. During the hot water pre-treatment, the straw samples were contained in glass jars in a water bath. Each glass jar contained 50 g straw and 2 L distilled water. The temperature fluctuated from 85 °C to 99 °C during the hot water pre-treatment, which last for two hours. After hot water treatment, the beaker was allowed to stand for 20 minutes and then the water was drained off. The pH of the water was found to have increased during the treatment with hot water for oat straw, to 8.28 ± 0.03. For barley, spring wheat and winter wheat, the pH was 6.99 ± 0.03, 6.56 ± 0.02 and 6.54 ± 0.02, respectively.

Steam explosion, the high-end pre-treatment tested in this experiment, was performed at the Cambi test reactor (Asker, Norway) located at the Norwegian University of Life Sciences (NMBU). The straw was treated at 190 °C (1.16 MPa) for 15 minutes. During pre-treatment, the samples of straw were first inserted in the inlet chamber. The valves were automatically closed before the steam was added at the selected pressure. After the set time was reached, another valve was opened and the straw was forced by the high pressure to enter the flash-tank. This rapid pressure drop forced the structures of lignin, hemicellulose and cellulose to open up. The high temperature and release of acids from the organic material probably also had some effect on the pre-treatment. After the pre-treatment, the straw had a dark brown colour. During “flashing” of the straw samples, some volatiles from the material were observed escaping from the test reactor in the form of bluish smoke. An attempt was made to quantify this loss by comparing the ash content with that of the untreated samples, as increased ash content compared with untreated samples may give an indication of loss of volatiles. In a full-scale steam explosion unit these losses would not occur, as the steam is regenerated. For more details about the Cambi test reactor, see Horn et al., [25].

Untreated straw was used as reference for all pre-treatments. This straw was also cut into about 2.5 cm lengths before digestion.

2.3 Bottle experiment

For the anaerobic digestion experiments, glass bottles with a total volume of 1.125 L were used. Three replicates of each substrate and pre-treatment method were included. The anaerobic digestion was performed in an incubator room at mesophilic temperature (37 °C ± 1 °C), where the bottles were placed on a stirring bench agitating at a rotating speed equivalent to 1.33 Hz.

The bottles were first filled with 150 cm^3 inoculum and 450 cm^3 water. This was equal to 4 g volatile solids (VS) per bottle. The inoculum was collected from a mesophilic reactor running on cattle manure. The bottles were sealed and placed in the incubator room for some days for ripening. After ripening, the bottles were opened and the substrate, comprising 2 g VS, was added together with water up to a total mass of 100 g. A density of 1 g/cm^3 was assumed for the liquid. Bottles without added substrate were used as blanks.

Biogas formation was determined by measuring the increase in gas pressure in the bottles using a Greisinger GMH 3161-13 pressure meter. These measurements were carried out in the incubator room to ensure the correct temperature and thereby gas pressure, and were performed 1-2 times per week in the first stage of the experiment when gas production was high and whenever needed thereafter, when gas production was lower. The biogas was ventilated out by a syringe needle after the reading. A gas chromatograph (Agilent Technologies 3000A Micro GC) was used to determine the methane (CH_4) content for all the bottles on the same day as the pressure was measured, before the biogas was ventilated out.

Biogas production was calculated as:

$$Vb = \frac{n \times R \times 273}{Po} = \left(\frac{dP \times V}{R \times T}\right) \times \left(\frac{R \times 273}{Po}\right) = \frac{dP \times V \times 273}{T \times Po}$$

where Vb is the volume of biogas (L), at a standard condition of 273 K (0 °C) and 101.325 kPa total pressure. P_0 is 101.325 kPa, R is the ideal gas constant, V is the volume of headspace (L), T is the temperature in the incubator room (310 K) and dP is the over-pressure measured in the bottles (Pa) [26]. The gas production from the bottles with only inoculum was subtracted from the production in the bottles with substrate. In this way, the contribution from the vapour pressure of water and biogas production from the inoculum was removed. Biogas production was expressed per g VS of substrate, at a gas temperature of 273 K (0 °C) and 101.325 kPa total pressure.

2.4. Analyses and calculations

In order to add the correct amount of substrate, the mass fraction of total solids (TS) and VS in the inoculum and the substrates were analysed before the experiment started. The TS was determined by drying at 105 °C for 22 ± 2 h, while the VS was determined by measuring the ash content after incinerating the samples at 550 °C.

Further analyses were carried out at Eurofins (Moss, Norway). Milled straw was not analysed, as the chemical composition was assumed to be the same as for untreated straw. The analytical methods used were as following: acid detergent fibre (ADF) (AOAC 973.18, mod.), acid detergent lignin (ADL) (AOAC

973.18, mod.) and for neutral detergent fibre (NDF) (ISO/CD 16472). The methods used for ADF and ADL are standardised by the AOAC International, while the method for analysing NDF is an approved ISO standard. These analythical methods are well known for animal fodder analyses

The content of lignin, cellulose and hemicellulose in substrate were calculated as:

Lignin = ADL

Cellulose = ADF – ADL

Hemicellulose = NDF – ADF

At the end of the experiment, the pH and the concentration of total ammoniacal nitrogen in the digestate in the bottles were measured. As a result of the measurements no inhibition from low pH or high ammonia concentration was expected. The ammonium concentration was measured with a Thermo Scientific Orion Dual Star™ pH/ISE Meter, with an Orion 9300BNWP ammonium ion selective electrode, in 30 mL samples to which 3 mL of 10 % ISA water were added before measuring.

3. Results and Discussion

3.1 Effects of the pre-treatment methods on the composition of lignin, hemicellulose and cellulose

The effects of the pre-treatment methods on the composition of lignin, cellulose and hemicellulose are shown in Table 1. An increase of cellulose and reduced content of lignin and hemicellulose indicates improved biogas potential. Milled straw was not included in the analyses, as the milling was not expected to change the chemical composition compared with untreated straw. The results showed large differences between the different pre-treatment methods in terms of their effect on the different types of straw.

An especially noteworthy finding was a strong reduction in hemicellulose content in the steam-exploded and NaOH-treated straw. For barley straw, no hemicellulose was detected in the NaOH-treated sample. For all steam-exploded samples, there was an increase in the lignin mass fraction, ranging from + 22.7 % for spring wheat straw to + 38 % for winter wheat straw. This indicates formation of secondary lignin due to the harsh conditions in the pre-treatment step [25]. The cellulose content was relatively stable, with a small increase for oat and winter wheat straw and some reduction for straw from spring wheat.

On average, the NaOH pre-treated straw showed the highest reduction in hemicellulose and lignin. Unlike the other pre-treatment methods, there was an increase in the cellulose for all four types of straw with NaOH pre-treatment. For barley straw, the cellulose content showed a particularly marked increase, of 12.9 %. The NaOH pre-treatment also gave the highest methane production for the most relevant digestion time, 20-50 days.

Hot water as a pre-treatment method gave quite variable results depending on the type of straw. For example, there was an increase in the content of lignin in straw from barley, oats and winter wheat, while there was a reduction for spring wheat straw. In fact, hot water pre-treatment was the pre-treatment method that gave the greatest reduction in lignin for spring wheat straw. For hemicellulose, an increase following the hot water pre-treatment was found for all types of straw except winter wheat, for which there was a minor reduction. For cellulose, there was a reduction for barley and spring wheat straw, while there was an increase for oat and winter wheat straw. Based on these results, hot water pre-treatment seems to be a suitable alternative mainly for oats and to some extent for winter wheat.

Ammonia (NH_3) pre-treatment had the least effect on the content of lignin, hemicellulose and cellulose in the straw. A minor reduction in lignin content was observed for all straw types except spring wheat, where a minor increase was observed. There was also a minor reduction in the hemicellulose content, especially for the wheat varieties, and a minor reduction in the cellulose content in the four types of straw.

Table 1. here.

3.2 Other effects of the pre-treatment methods

The different pre-treatment methods had several other effects on the straw regarding how it behaved as a biogas substrate and the suitability of the digestate for fertilising farmers' fields. For example, the liquid pre-treatment methods made the straw wetter and softer, and to some extent degraded the structure. This made the straw easier to feed into the digester, as it could be blended more easily with liquid substrates and made it possible to pump. In general, the particle length of the different types of straw was reduced during several of the pre-treatment methods, which also made them easier to blend in the digester.

In this experiment NaOH was used as one of the pre-treatment methods. However, very high concentrations of sodium (Na) due to pre-treatment with NaOH have been found to have an inhibiting effect on the anaerobic process. E.g. Na and potassium (K) concentrations of 11 and 28 g/L, respectively, have been shown to have an 50 % inhibiting effect [27]. Too large fractions of NaOH-treated straw should therefore be avoided when blending substrate. When NaOH-treated straw is co digested with animal manure, inhibitory Na levels usually do not occur. It is also possible to pre-treat the straw with potassium hydroxide (KOH). The risk of inhibition is then lower, as the anaerobic process can tolerate a 2.5-fold higher concentration of KOH than of NaOH [27]. Although KOH is more expensive than NaOH, potassium is a valuable macronutrient for plants and pre-treatment with KOH would reduce the need for buying chemical potassium fertilisers.

When laboratory-scale pre-treatment methods are used, there may be some side effects that are not usually found at full-scale plants. For example, a coloured vapour was observed escaping the steam explosion unit during pre-treatment in the present study. In a full-scale plant, these losses would be captured in the liquid and digested at the plant. The other experimental pre-treatment methods that included liquids could also have suffered losses of organic material. The NaOH and to some extent the water from the hot water pre-treatment showed some discolouration, caused by organic substances from the straw. To check these losses, the ash fraction in the substrates was calculated (Table 2). The steam-exploded straw samples showed a slight increase in ash content, ranging from 1.3 to 6.5 %, compared with the untreated samples. Thus the total methane potential of steam-exploded straw could be expected to have been underestimated by this amount. However, addition of substrate to the bottles was based on the actual fraction of VS in the pre-treated substrates and therefore the underestimation in the bottle experiments was probably far lower, as it related to how easily degradable the remaining VS in the pre-treated straw were compared to those that escaped.

The NaOH-treated straw showed an increase in ash content, which was mainly due to NaOH from the treatment liquid being absorbed during the pre-treatment. There was also some loss of volatiles in the treatment process, especially of lignin and hemicelluloses, which may also have increased the ash content. This was observed as a brownish colour in the NaOH solution. For the boiled samples, there was a reduction in ash content of on average >50 % in most cases. This was probably caused by wash-out of the minerals from the straw [28].

Table 2 here.

The dry matter (TS) and organic dry matter (VS) content in the substrates also varied widely (Table 3). The lowest dry matter concentrations were found for the wet pre-treatment methods (hot water pre-treatment, NaOH-treatment and steam explosion). This reduction in DM content made it easier to blend the substrates in the digester.

Table 3 here.

3.3 Ammonia inhibition in the bottle experiment

Ammonium concentration in samples after the digestion test was found to be between 538 and 783 mg NH_4^+/L, with an average value of 659 ± 46 mg/L. As expected, this indicates that there was no ammonia inhibition in the bottle experiment.

3.4 Methane production

The bottle experiment showed large fluctuations in biogas yield between the different types of straw and between the different pre-treatment methods. Barley straw in particular showed large fluctuations for the different pre-treatment methods. The duration of digestion in the experiment was relatively long, more than 150 days. As expected, the increase in biogas production due to pre-treatment was reduced with longer digestion time, but the pre-treatment methods still had a positive effect on total biogas yield, except for steam explosion of barley, spring wheat and winter wheat straw. This was probably due to formation of secondary lignin and losses of the most easily degradable VS during pre-treatment.

As the summation curves indicate (Figures 1-4), the speed of degradation was heavily dependent on the pre-treatment method. The steeper the summation curve, the more rapid the production of methane and the better the pre-treatment method. This was seen most clearly for the barley straw, for which the methane production was very different with the different pre-treatment methods (Figure 1).

Figure 1 here.

Figure 2 here.

Figure 3 here.

Figure 4 here.

3.5 Selection of pre-treatment method based on expected hydraulic retention time and straw type

The different pre-treatment methods gave different daily methane production rates. Some substrates fulfilled most of their potential during the early weeks, while others produced smaller amounts of methane over a longer period. The most appropriate pre-treatment is one which makes the straw so easily degradable that it reaches most of its potential production within very few days. This is especially important for single-step semi-continuous reactors with low hydraulic retention times, where a larger fraction of the substrate, included substrate added on the same day, is removed. For batch reactor systems, for example “garage” systems, which are dry batch anaerobic digesting systems, the situation may be slightly different. The very rapid degradation may cause acidification in the digesters and inhibition of the process. On the other hand, rapid degradation enables digestion of more batches per year, hopefully improving the operating economics for the plant owner. It is of course also important that the pre-treatment makes the straw so degradable that it gives very high total methane production per g VS. From a practical point of view, it is often better if most of the methane production potential is fulfilled within a very few days, rather than having higher methane production after a relatively long retention time.

It may be difficult to identify the optimal pre-treatment method for a particular type of straw using only the summation curve. Therefore in Figures 5-8 the increase in methane yield resulting from pre-treatment of the straw is plotted against retention time in the bottles. The retention times selected for the calculations were 15, 20, 30, 50 and 100 days in the bottles. A bottle experiment is of course not directly comparable to a semi-continuous reactor, due to low dry matter concentration, not fully activated and adapted microbial communities etc., but it may give some indication of trends. The hydraulic retention time of farm-scale semi-continuous reactors fed with animal manure and easily digestible materials is often in the range of 20-30 days, although some have slightly shorter hydraulic retention time. For reactors fed with purpose-grown energy crops, the retention time is often longer, sometimes more than 100 days, as it is more important to utilise as much of the potential as possible.

As can be seen in Figures 5-8, milling proved to be the best option with a very short retention time. When the retention time was longer, NaOH treatment gave the highest methane production. The different types of straw also exhibited different responses to the pre-treatments. For example, oat straw showed a good response to milling at all retention times tested. Barley straw showed the best response to NaOH treatment, with an increase in methane production of 83.3 % compared with untreated straw after 20 days of digestion. Oat straw showed the least response to NaOH treatment, with an increase of 49.5 % compared with untreated straw after 20 days of digestion.

Figure 5 here.

Figure 6 here.

Figure 7 here.

Figure 8 here.

3.6 General comments about the results

According to the results presented in this study, it is important to know the main type of straw to be treated before a pre-treatment method is selected. The expected hydraulic retention time may to some extent also play a role in the selection of pre-treatment method.

For steam explosion, the total methane yield was found to be lower than for the untreated straw. This was probably mainly due to losses of organic vapours during the pre-treatment and to some extent to formation of secondary lignin caused by the high temperature in the steam explosion unit. At a full-scale plant the total methane production would probably be higher, as the lost vapours would be trapped and fed back into the digester. Today, a steam explosion unit may often be too expensive for smaller farm-scale biogas plants.

Hot water pre-treatment of the straw was found to be the least effective pre-treatment. This was probably due to loss of easily degradable materials to the water. Hot water pre-treatment can to some extent be recommended as a pre-treatment for straw from oats and winter wheat, based on the positive effect it appears to have on the cellulose fraction.

Ammonia pre-treatment demonstrated very little effect on the composition of lignin, hemicellulose and cellulose. However, the bottle digestion experiment showed quite good results in terms of methane production, especially for longer retention times. Ammonia pre-treatment is a method which may also suit smaller farm-scale biogas plants, as it is performed in the field. On the other hand, the method may not be legal in all countries, due to emissions of ammonia.

All four types of straw showed very good responses to milling, especially for the shorter retention times but also in terms of total methane production. However, a milled particle size of <0.5 mm, as tested here, is very small and quite fine machinery is needed to achieve it. The energy costs may also be relatively high. Moreover, the straw has to be of relatively good quality, dry and without stones and soil. If the milled particle size is increased, a relatively quick reduction in pre-treatment effect can be expected, as the surface area per unit mass decreases drastically with even a small increase in particle size.

4. Conclusions

Pre-treatment of straw generally improved the methane production level over the relevant retention time. The shorter the retention time for the substrate, the more important the use of a pre-treatment. However, there were large variations in the effect of the different pre-treatment methods, with the response to NaOH pre-treatment being particularly good. The effect of the different pre-treatment methods also varied with the type of straw, with barley straw in particular showing a good response to NaOH pre-treatment and steam explosion. The results indicated that methods applicable for farm-scale biogas plants may be as effective as large-scale methods.

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Tables

Table 1: Concentration ($g \cdot kg^{-1}$) of lignin, cellulose and hemicellulose in untreated and treated straw (excluding milled straw).

		Untreated	Steam-exploded	NaOH-treated	Boiled	Ammonia-treated
Barley	Lignin	86	106	76	93	82
	Cellulose	464	464	524	417	448
	Hemicellulose	220	23	Nd	331	216
Oats	Lignin	64	81	56	81	62
	Cellulose	436	439	454	489	418
	Hemicellulose	236	56	31	261	220
Spring wheat	Lignin	75	92	74	67	77
	Cellulose	435	408	436	353	413
	Hemicellulose	261	60	61	287	228
Winter wheat	Lignin	71	98	66	88	65
	Cellulose	449	452	464	492	435
	Hemicellulose	289	52	69	282	245

Nd = not detectable, negative value for NDF-ADF.

Table 2: Ash mass fraction of dry total solids (%) of untreated and treated straw (St. dev. = standard deviation). N = 3 for all samples.

		Untreated	Steam-exploded	NaOH-treated	Boiled	Ammonia-treated	Milled
Barley	Ash cont.	4.7	5.0	18.8	1.9	4.2	4.5
	St.dev.	0.05	0.09	1.27	0.21	0.06	0.07
Oats	Ash cont.	7.7	7.8	18.8	2.5	6.8	7.1
	St.dev.	0.12	0.20	1.77	0.02	0.07	0.05
Spring wheat	Ash cont.	3.5	3.6	17.2	1.4	3.1	3.5
	St.dev.	0.06	0.03	1.04	0.03	0.07	0.03
Winter wheat	Ash cont.	3.9	4.1	17.3	2.0	5.3	4.1
	St.dev.	0.20	0.04	0.84	0.05	0.14	0.06

Table 3: Mass fraction of total solids (%) and volatile solids (% of TS) in untreated and treated straw (St. dev. = standard deviation). N = 3 for all samples.

		Untreated	Steam-exploded	NaOH-treated	Boiled	Ammonia-treated	Milled
Barley	TS (%)	92.67	25.83	18.09	17.58	89.29	93.05
	St.Dev.	0.15	0.75	0.84	0.48	0.17	0.13
	VS (% of TS)	95.26	95.04	81.19	98.06	95.82	95.54
	St.Dev.	0.05	0.09	1.27	0.21	0.06	0.07
Oats	TS (%)	92.05	19.59	19.11	15.39	90.29	93.24
	St.Dev.	0.05	0.26	0.34	0.68	0.04	0.09
	VS (% of TS)	92.25	92.17	81.16	97.54	93.24	92.90
	St.Dev.	0.12	0.20	1.77	0.02	0.07	0.05
Spring wheat	TS (%)	91.91	25.24	18.55	16.99	89.39	93.31
	St.Dev.	0.04	0.68	0.26	0.58	0.31	0.07
	VS (% of TS)	96.51	96.40	82.82	98.64	96.87	96.49
	St.Dev.	0.06	0.03	1.04	0.03	0.07	0.03
Winter wheat	TS (%)	91.36	24.55	17.43	17.28	90.84	92.97
	St.Dev.	0.13	0.63	0.43	0.20	0.02	0.09
	VS (% of TS)	96.05	95.91	82.67	98.00	94.70	95.91
	St.Dev.	0.20	0.04	0.84	0.05	0.14	0.06

Figures

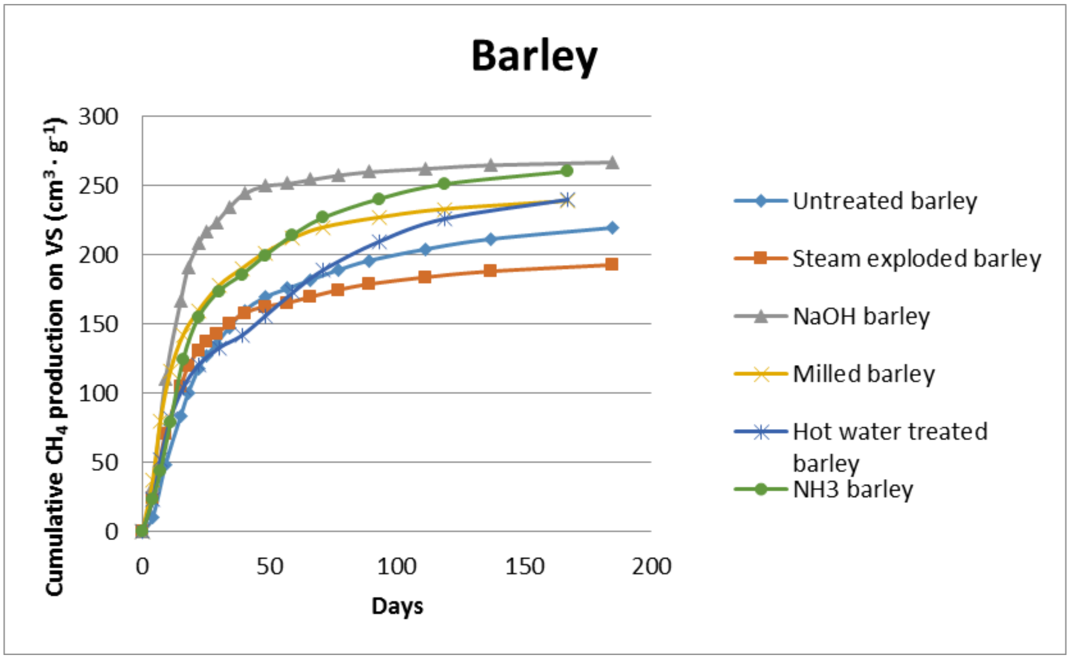

Figure 1: Cumulative CH_4 production on VS ($cm^3 \cdot g^{-1}$) from treated and untreated barley straw.

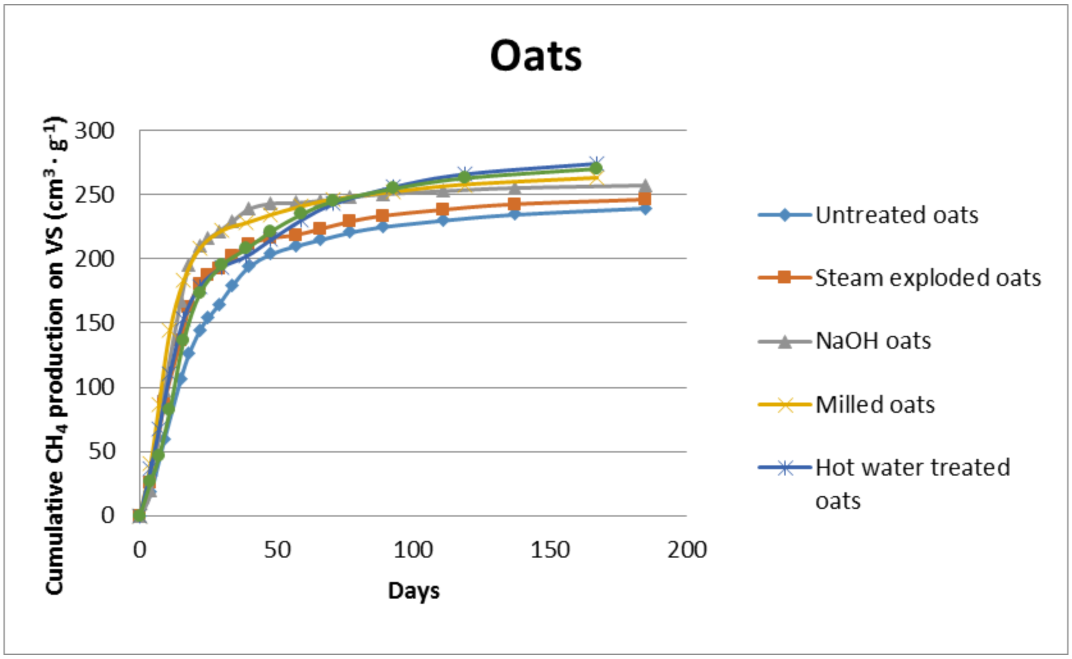

Figure 2: Cumulative CH_4 production on VS ($cm^3 \cdot g^{-1}$) from treated and untreated oat straw.

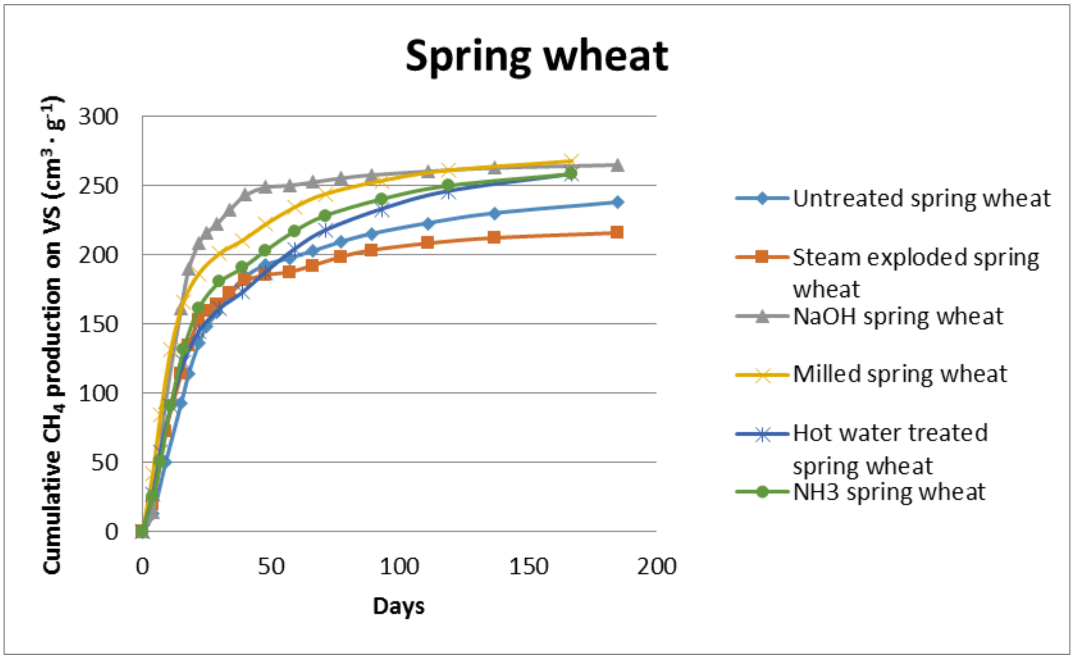

Figure 3: Cumulative CH_4 production on VS ($cm^3 \cdot g^{-1}$) from treated and untreated spring wheat straw.

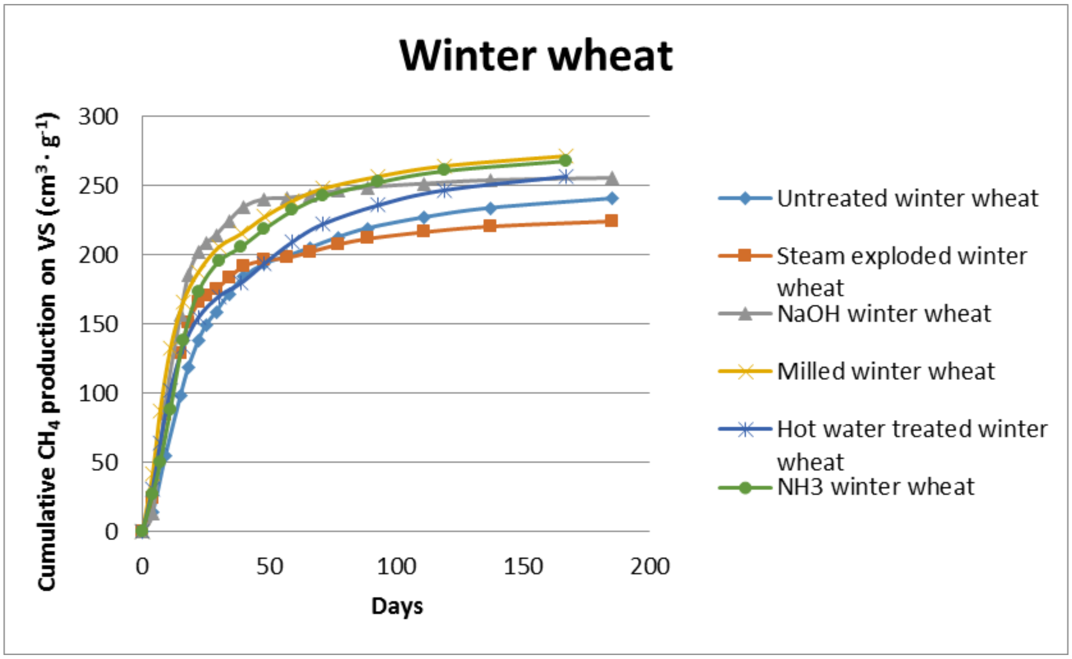

Figure 4: Cumulative CH_4 production on VS ($cm^3 \cdot g^{-1}$) from treated and untreated winter wheat straw.