THE EFFECT OF THERMO-CHEMICAL PRE-TREATMENT ON THE ULTIMATE BIOGAS POTENTIAL OF STRAW

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1 INTRODUCTION

Second generation biofuels derived from sources such as agricultural residues are gaining importance these days, although converting them to energy poses certain difficulties. Agricultural wastes, like straw or husk for example, have a high content of lignin, whose function is to provide structural support, defence against microbial attacks, and impermeability (Pérez et al, 2002). Lignin is closely associated with cellulose and hemicellulose, making them inaccessible for microbial degradation. Thus there is a difference between the total organic content of a biomass that can theoretically be converted into biofuels and the amount that can actually be converted by micro-organisms. Breaking down the association between lignin, cellulose and hemicellulose makes the latter two parts more available to the micro-organisms. This can be achieved by chemical, mechanical, biological or thermal means.

Most of the research in pre-treatment of lignocellulosic biomasses has been for ethanol production. The same pre-treatments can also be applied to biogas production. Earlier studies have shown that lignocellulosic materials undergo hydrolysis at temperatures between 150°C and 230°C (Garotte et al 1999). There are also many studies that point out that alkali pre-treatment at ambient temperatures enhance the biogas yields (Pang et al 2008). Paper pulp sludge pretreated with sodium hydroxide increased the methane by 54-88% (Yunqin L., et al 2009). Chang et al (1997) studied the effects of thermo-chemical pre-treatment on switchgrass using calcium hydroxide as the alkaline reagent and found that about 29% of the lignin was solubilised. The alkalis commonly used in pre-treatments are sodium hydroxide and calcium hydroxide. The use of sodium hydroxide poses a problem if the digestate after anaerobic digestion is to be spread on agricultural land as it could increase the soil salinity.

The objective of this study is to quantify, at a laboratory scale, the effects of high temperatures, alkali treatment and a combination of alkali and thermal pre-treatments on the ultimate biogas yield of straw.

2 MATERIALS AND METHODS

2.1 Experimental design

The experimental treatments can be classified into thermal treatment, thermo-chemical treatment, holding period and chemical treatment. The treatment scheme followed is as shown in table 1:

TABLE 1 **Treatment scheme**

Pre-treatment	Temperature in °C							
	20	75	100	125	150	175	200	225
Thermal		X	X	X	X	X	X	X
Thermo-chemical, 1.5% $Ca(OH)_2$		X	X	X	X	X	X	X
Thermo-chemical, 0.75% $Ca(OH)_2$			X		X		X	
Thermo-chemical, 3% $Ca(OH)_2$			X		X		X	
Chemical, 1day, 1.5% $Ca(OH)_2$	X							
Chemical, 5days, 1.5% $Ca(OH)_2$	X							
Chemical, 10days, 1.5% $Ca(OH)_2$	X							
Chemical, 15days, 1.5% $Ca(OH)_2$	X							
Holding time, 5 min			X		X		X	
Holding time, 10 min			X		X		X	
Untreated	X							

2.2 Pre-treatment methods

The substrate used was straw (obtained from a Danish company called Dansk Dyrestimuli). The composition of the straw was 75% wheat straw and 25% rapeseed straw. The straw was cut to pieces of 4 cm average, and the dust removed. This ensured a near homogeneous sample for each of the treatments. The straw had a dry matter content of 83%. The straw was treated in a high temperature and pressure vessel (Parr 4524). The system consisted of a stainless steel reaction chamber fitted with temperature and pressure measurement devices, a mechanism for mixing, and safety valves. The system also has an insulated external heating element which when raised surrounds the pressure vessel. The pressure vessel is completely sealed with no mass transfer occurring with the surroundings. The measurement devices from the pressure vessel are connected to a controller that controls the thermal output of the heating element according to the desired temperature that has been set. The controller is in turn connected to a computer where the settings can be changed and the process can be monitored and recorded in real time.

The range of temperatures for the thermo-chemical pre-treatment were between 20°C and 225°C to see if pre-treatment at lower temperatures with the addition of an alkali will have the same effect as a pre-treatment at higher temperatures. The same temperature range was used for the thermal pre-treatment to facilitate a direct comparison with the thermo-chemical pre-treatment. Another aspect that was investigated in this study was the effect of holding time on anaerobic biodegradability. Holding time is the time the sample was held at a particular pre-treatment temperature. It does not include the heating time to reach the correct temperature. Laboratory grade calcium hydroxide (Merck) was used as the alkali reagent. The concentration of calcium hydroxide in this study was 1.5% w/w of the dry matter and was based on a previous study by Møller, (2008). To examine the effect of a change in the concentration of alkali, two sets of thermo-chemical pre-treatments were carried out at 3% w/w concentration and 0.75% w/w concentration.

Each pre-treatment was carried out on 1 kg of material. The straw was mixed with deionised water to make the dry matter content 5% by weight. This was done mainly to facilitate efficient mixing and heat transfer in the pressure vessel. The straw and water were mixed just before the mixture was introduced into the pressure vessel. The solubility of lime in water is low; hence wherever lime was used, it was dissolved into the deionised water before being mixed with the straw. After a sample was put into the reaction chamber, the chamber was sealed, and the heating element was raised. The temperature was maintained within ± 2.5 °C of the desired temperature. The holding period for all samples was 15 minutes unless otherwise specified in the treatment scheme. After the pre-treatment, the material was cooled down to 30 °C before being taken out of the pressure vessel.

2.3 Biogas batch assays

The complete digestion period in this experiment is 90 days, and the total amount of biogas accumulated during this period will be considered as the ultimate biogas potential of the material.

After pre-treatment, 200 grams of the material was put into a glass bottle with a capacity of one litre and 500 grams of inoculum was added to it. The inoculum was sourced from a pilot scale digester operating on pig manure and was incubated for 15 days prior to the start of the batch experiment at 38°C to reduce the amount of digestible material. This ensures that the amount of biogas produced by the inoculum itself is very low and thus reducing errors. The bottle was then sealed with a rubber stopper and a screw cap. The empty space in each of the bottles was flushed with nitrogen gas for four minutes, so that the conditions in the bottle were made anaerobic. Each of the samples was tested in triplicate. The bottles were placed in an incubation chamber that was maintained at a mesophilic temperature of 38°C. The quantity and the quality of the biogas produced in each of the bottle were measured at regular intervals. The volume of biogas produced was measured by acidified water displacement. A sample of the biogas was collected and the composition was determined using a gas chromatograph (HP-5890 Series II).

3 RESULTS AND DISCUSSION

The total net biogas produced after 32 days has been tabulated in table 2. The results are presented in the same order as the treatment scheme. Some of the results are discussed in detail in the following sections.

TABLE 2 **Total net biogas produced in L/Kg of VS after 32 days of anaerobic digestion**

Pretreatment	Temperature in °C							
	20	75	100	125	150	175	200	225
Thermal		400	407	411	365	374	357	317
Thermo-chemical								
1.5% Ca(OH)2		384	446	437	366	351	361	305
0.75% Ca(OH)2			452		435		420	
3% Ca(OH)2			397		384		340	
Chemical, 1.5% Ca(OH)2								
1day	474							
5days	398							
10days	455							
15days	463							
Holding time								
5 min			357		331		338	
10 min			336		331		275	
Untreated	290							

3.1 Effect of concentration of calcium hydroxide on thermo-chemically pretreated samples

The addition of calcium hydroxide in general increased the biogas production when compared to the untreated sample. From figure 1 it can be seen that the higher concentrations of calcium hydroxide seem to inhibit the biogas production especially as the pre-treatment temperature was increased. Only the samples pre-treated with 0.75% calcium hydroxide and the sample pretreated with 1.5% calcium hydroxide at 100°C produced more biogas than the samples pre-treated at the same temperatures with no calcium hydroxide.

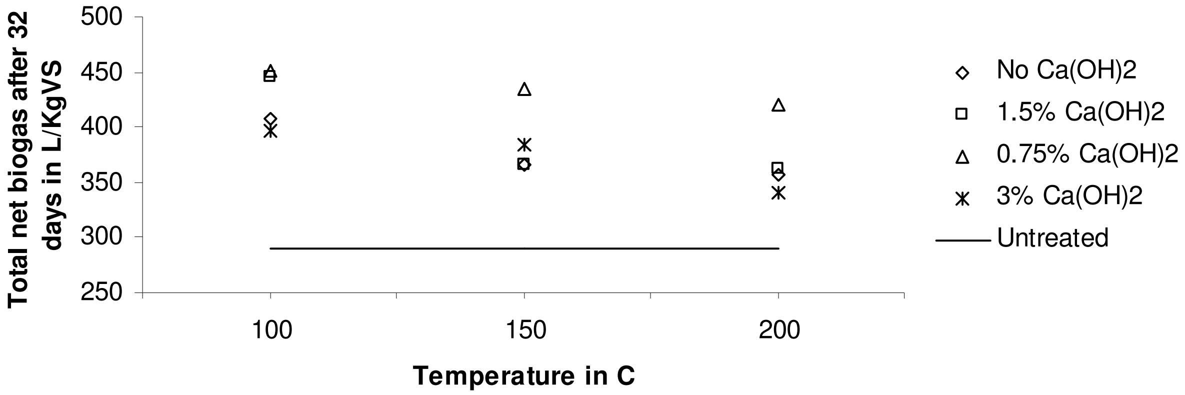

FIGURE 1 **Comparison of the total net biogas obtained after 32 days from samples thermally pretreated with different concentrations of $Ca(OH)_2$ against straw samples pretreated at the same temperatures without $Ca(OH)_2$ and the untreated straw. (The untreated straw here is shown as a line across the graph and has no relation to the temperature scale on the X-axis)**

3.2 Effect of thermal and thermo-chemical pretreatment

A comparison of the samples pretreated at the same temperatures but with and without addition of calcium hydroxide shows that at lower temperatures i.e. 100°C and 125°C the biogas production increases with the addition of calcium hydroxide (figure 2). As seen in the previous observation, pre-treatment at higher temperatures leads to lower biogas production when compared to lower temperatures. A similar observation was made by Gossett et al (1982). They suggested that temperatures above 160°C caused the solubilisation of lignin, which being a phenolic polymer solubilised into phenolic compounds. These compounds usually have an inhibitory effect on the anaerobic digestion process.

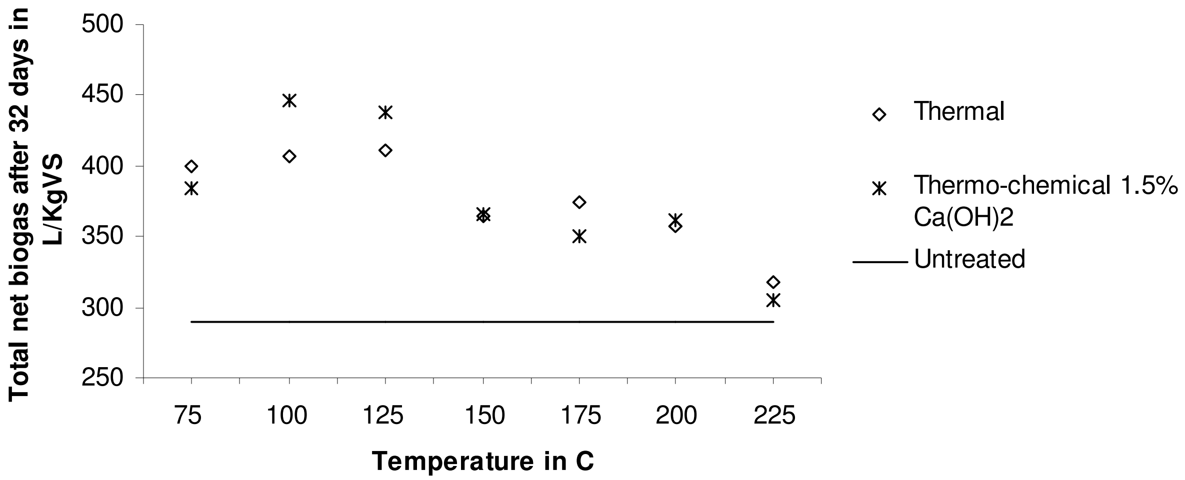

FIGURE 2 **Comparison of the total net biogas produced after 32 days from samples that have been pretreated between the temperatures 75°C to 225°C with and without the addition of calcium hydroxide against the untreated sample. (The untreated straw here is shown as a line across the graph and has no relation to the temperature scale on the X-axis)**

4 CONCLUSIONS

Based on preliminary results after 32 days of anaerobic digestion it could be seen that thermo-chemical pre-treatment in general increased the biogas yield of all the pretreated samples from a minimum of 5 % to a maximum of 63% except the sample that was treated at 200°C with a holding time of 10 minutes which showed a 5% decrease. At this stage the sample that was treated with 1.5% calcium hydroxide for 1 day gave the highest yield of biogas compared to the other pre-treatments.

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