

EXTREME THERMOPHILIC PRE-TREATMENT OF MANURES FOR IMPROVED BIOGAS PRODUCTION

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1 INTRODUCTION

The increase in the biogas production of animal manures when co-digested with organic agricultural, municipal or industrial wastes is well documented (Kaparaju *et al.* 2002; McDonald *et al.* 2008). In Denmark, the decreasing availability of organic waste products for biogas production and the high prices of these products have made economic production of biogas difficult. This is especially the case when the relatively low price paid for the electricity produced in Denmark (0.1 euros / kWh) is taken into account. These factors have been at least partly responsible for the stagnation of the production of new Danish biogas plants over the last ten years (Raven and Gregersen, 2007). However, the Danish government proposes to use 50% of livestock manure for energy production by 2020. Manure has low degradability and consequently low biogas yields (Møller *et al.* 2004). In order to increase the production of biogas from manure without co-digestion, pre-treatment processes are necessary.

Extreme thermophilic pre-treatment has been shown to improve biogas production by up to 30% during continuous digestion of sewage sludge (Ferrer *et al.* 2008) and by up to 56% during batch digestion of cattle manure (Nielsen *et al.* 2004).

This study examined the effect on biogas and methane yield of pilot scale reactors by the addition of an extreme thermophilic (68°C) pre-treatment stage at different retention times. Two experiments are described here; the first used a co-digestion mix of pig slurry with maize silage to examine the effect of pre-treatment on an agricultural digester using energy crops to boost biogas production. The second experiment used cattle slurry as a single substrate to represent an agricultural biogas plant with lower output but also significantly reduced feedstock costs.

2 MATERIALS AND METHOD

2.1 Experimental biogas reactors

Two thermophilic (52°C) methanogenic continuously stirred tank reactors (CSTR) of 30 m³ (R1 and R2) and a pre-treatment CSTR of 10 m³ maximum (R3) were used for experiments 1 and 2. All reactors were very similar in design, constructed of stainless steel and heated by an external water jacket. R3 working volume was lowered during the experiment to decrease the pre-treatment time, the minimum volume being dictated by the height of the lower of the two central mixing blades. One of the methanogenic reactors (R2, control) and R3 were fed directly from a feeding vessel of 800 litres maximum capacity and the other methanogenic reactor (R1) was fed from the output of R3. The feeding vessel functioned as a pre-heating unit in addition to the dosing and mixing of feedstock in experiment 1. The volumetric gas production was measured on-line using pressure differential gas meters. All pumping of slurry and digestate was carried out by Mono eccentric screw pumps.

2.2 Experiment 1: Pig slurry with maize silage

During experiment 1 the HRT of R1 and R2 methanogenic reactors was 12 days, which is common full scale Danish practice for pig manure with or without energy crop co-substrate. Feeding of the reactors occurred ten times per day. The operational parameters and pre-treatment HRTs are summarised in Table 1.

2.3 Experiment 2: Cattle manure

The second experiment used a longer methanogenic HRT of 14.6 days. This is to mimic Danish full scale experience where cattle manure is given a longer digestion time than pig manure or energy crops due to the fibrous nature of cattle manure. The combination of longer retention time and reduced dry matter and volatile solids per litre of material resulted in a lower organic loading rate than experiment 1. Feeding of the reactors occurred ten times per day. The operational parameters and pre-treatment HRTs are summarised in Table 1. Changes in the flow rate as a

result of a longer methanogenic HRT than that used in experiment 1 meant that the minimum pre-treatment HRT was also increased from 35 to 38 hours. This was because R3 had a minimum capacity of *ca.* 30% full.

As the cattle manure was more fibrous in nature than the pig slurry with maize silage used in experiment 1, it was decided to include a longer pre-treatment HRT of 110 hours.

TABLE 1 Operational parameters.

	Parameter	Value
Experiment 1	Substrate volatile solids (VS) and mix ratio	Pig slurry 6.7% VS (56 % of VS input)
		Maize silage 33 % VS (44 % of VS input)
	Methanogenic reactors retention time	12 days
	Pre-treatment reactor retention times	96 hours
		35 hours
Organic loading rate	8.5 kgVS / m ³ / day	
Experiment 2	Substrate volatile solids	5.5 % VS
	Methanogenic reactors retention time	14.6 days
	Pre-treatment reactor retention times	110 hours
		77 hours
		38 hours
Organic loading rate	3.41 kgVS / m ³ / day	

2.4 Analytical methods

Gas composition was measured at-line with an infrared gas analyser (Visit 03, Messtechnik GmbH). Total and volatile solids were measured by heating to 105°C and 550°C respectively. Volatile fatty acids (VFA) were measured by gas chromatograph (HP 6859).

3 RESULTS AND DISCUSSION

3.1 Experiment 1

The biogas and methane yields are shown in Figure 1. Clearly, including the biogas produced by the pre-treatment reactor had no effect on the overall methane yield, although biogas yield increased as a result of adding the pre-treatment gas production. The biogas produced in the pre-treatment reactor was less than 7% methane on average therefore it contributed little to the overall methane yield. This was ascribed to the acidic conditions (pH 5.8-6.0) inhibiting methane production, which in turn was ascribed to high VFA levels (Table 2) from the hydrolysis of easily digestible material in the maize silage.

Changing the HRT of the pre-treatment process had little effect on biogas or methane yields. Therefore the shorter retention time is preferable as this reduces construction and heating costs. Methane yield was found to be increased by a maximum of *ca.* 8.5% when compared to the control reactor. Mean yields at 35 hours HRT were lower than expected (as demonstrated by the change in the control reactor yields in Figure 1), due to technical problems but the problem affected both reactors so a direct comparison was considered valid.

Examination of the mean VFA concentrations (Table 2) shows that pre-treatment increased acetic acid by *ca.* 30% and propanoic acid by *ca.* 13% when compared to the raw feedstock. R1 was therefore fed a higher concentration of VFA than R2. However, R2 VFA levels were at least 50% greater than R1. This suggests better utilisation of VFA by R1 which is consistent with the biogas and methane yield data.

The VFA concentrations during the experiment showed little change at different HRT, which is also consistent with the biogas and methane yield data. These results suggest that enhanced VFA production by extreme thermophilic pre-treatment of pig manure with maize silage has no appreciable effect above 38 hours HRT.

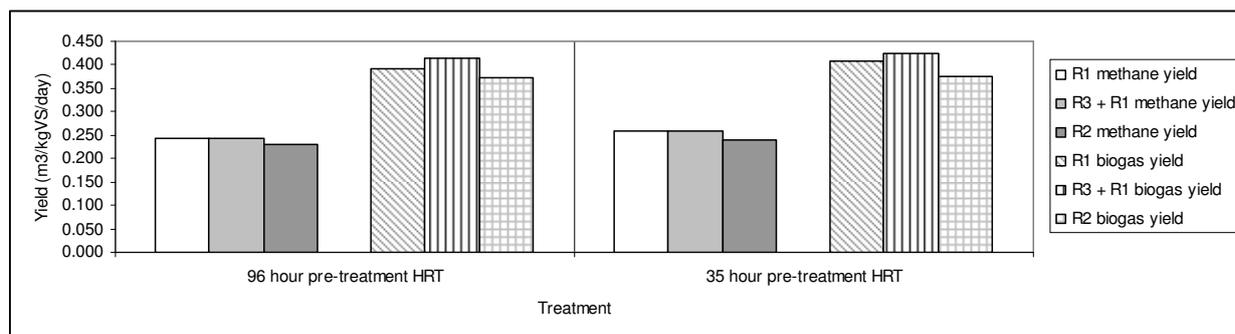


FIGURE 1 Biogas and methane yields of a methanogenic reactor fed pre-treated pig slurry with maize silage (R1), of the pre-treatment reactor combined with the methanogenic reactor (R3+R1) and a control reactor (R2).

TABLE 2 Mean VFA levels during experiments 1 and 2.

	Feedstock acetic acid (mg.L ⁻¹)	Feedstock propanoic acid (mg.L ⁻¹)	R3 acetic acid (mg.L ⁻¹)	R3 propanoic acid (mg.L ⁻¹)	R1 acetic acid (mg.L ⁻¹)	R1 propanoic acid (mg.L ⁻¹)	R2 acetic acid (mg.L ⁻¹)	R2 propanoic acid (mg.L ⁻¹)
Expt 1	6100	2300	8200	2600	600	200	900	350
Expt 2	5300	1900	7500	2100	270	60	500	70

3.2 Experiment 2

Figure 2 shows the experiment 2 methane and biogas yields. In this experiment, a slight improvement in methane yield was gained by including the gas produced by R3. This was ascribed to the pre-treatment pH being more favourable for methanogenesis in this experiment (pH 7.4-7.8), which in turn was ascribed to less easily digestible material than was the case in experiment 1. Mean yields at 77 hours and 38 hours pre-treatment HRT were lower than expected, again due to technical problems. Pre-treatment at HRTs of 77 or 110 hours returned very similar results, suggesting that pre-treatment was optimal at less than 77 hours HRT with no gain in yield at longer pre-treatment times. This is in disagreement with Neilsen *et al.* (2004) who found optimum yield of liquid cattle manure at 108 hours HRT but little HRT dependant change in the yield of separated fibres when treated for between 36 and 168 hours. The highest gain in methane yield from R1 alone was 27.3% above that produced by R2, and 55.7% greater than R2 when the pre-treatment reactor biogas was included. The maximum increase was at the shortest HRT of 38 hours. The VFA data (Table 2) was similar to experiment 1 in that there was an increase due to pre-treatment and higher VFA levels in R2 than R1, although the values were lower in experiment 2.

The increase in both biogas and methane yields as a result of a reduction in HRT makes the data difficult to interpret. The VFA concentrations in R3 were fairly stable throughout the experiment, yet the concentrations were high. It is tentatively suggested that the methanogenic organisms in R3 were inhibited slightly by the high VFA concentrations at the start of the experiment and became acclimatised during the later (shorter HRT) part of the experiment.

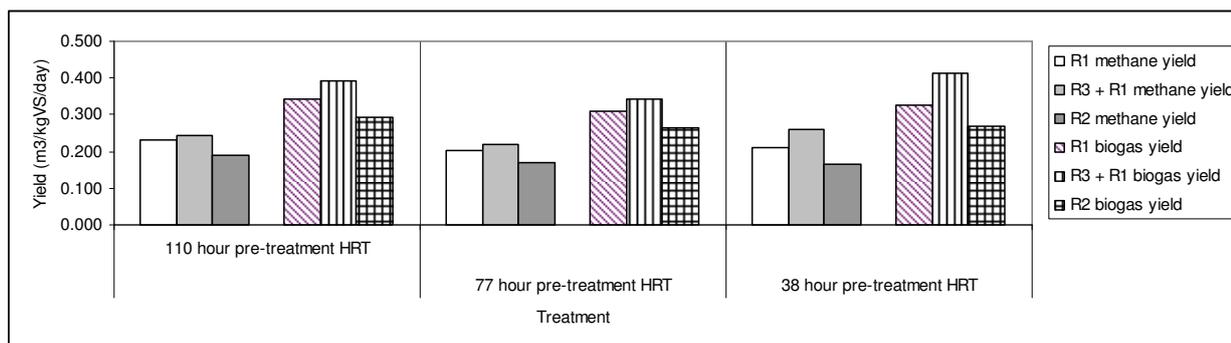


FIGURE 2 Biogas and methane yields of a methanogenic reactor fed pre-treated cattle manure (R1), of the pre-treatment reactor combined with the methanogenic reactor (R3+R1) and a control reactor (R2).

4 CONCLUSIONS

The pre-treatment reactor provided a steady source of VFA, particularly acetic acid, to the methanogenic reactor R1. It can be concluded that pre-treatment at 68°C is particularly effective when cattle manure is used as a single substrate. The biogas produced in the pre-treatment reactor in experiment 1 was of a low methane concentration and as a result did not add substantially to the methane yield, but the gas from the experiment 2 pre-treatment was found to make a significant contribution to the overall yield. It was also found that a reduced pre-treatment HRT provided an increased methane yield. The reason for this is uncertain and will require further work although it has been proposed that some VFA inhibition was possible. Based on the results shown, a smaller pre-treatment reactor is optimal, thus reducing capital costs and also the energy required for heating. However, the pre-treatment times have yet to be optimised correctly and this is the aim of the next stage of this work. The cost of heating to 68°C will also be calculated and balanced against the energy gained by increased methane yield, although much of the extra energy input can be recycled *via* heat exchangers.

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REFERENCES

- Ferrer I, Ponsa S, Vazquez F, Font X 2008. Increasing biogas production by thermal (70°C) sludge pre-treatment prior to thermophilic anaerobic digestion. *Biochemical Engineering Journal* 42, 2 186-192.
- Kaparaju P, Luostarinen S, Kalmari E, Kalmari J, Rintala J 2002. Co-digestion of energy crops and industrial confectionery by-products with cow manure: batch scale and farm-scale evaluation. *Water Science and Technology* 45, 275–80.
- McDonald T, Achari G, Abiola A 2008. Feasibility of increased biogas production from the co-digestion of agricultural, municipal, and agro-industrial wastes in rural communities. *Journal of Environmental Engineering and Science* 7, 4, 262-273.
- Møller HB, Sommer SG, Ahring BK. 2004. Methane productivity of manure, straw and solid fractions of manure. *Biomass and Bioenergy* 26, 485-495.
- Nielsen HB, Mladenovska Z, Westermann P, Ahring BK 2004. Comparison of two-stage thermophilic (68°C/55°C) anaerobic digestion with one stage thermophilic (55°C) digestion of cattle manure. *Biotechnology and Bioengineering* 86, 3, 291-300.
- Raven R P J M, Gregersen K H 2007. Biogas plants in Denmark: successes and setbacks. *Renewable and Sustainable Energy Reviews* 11, 116-132.