Study of thermal hydrolysis as a pretreatment to mesophilic anaerobic digestion of pig slurry

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Abstract Feasibility of anaerobic digestion of pig slurry is dependent, among other factors, on the biogas production rate, which is low compared with other organic wastes, and on the profitable uses of surplus thermal energy produced, a limiting factor in warm geographical areas. The objectives of this work are determining whether low temperature thermal pretreatment (<90°C) improves pig slurry anaerobic digestion, and determining whether organic matter degradation during the thermal pretreatment is due to thermal phenomena (80ºC) or to enzymatic ones (60ºC). The thermal degradation tests showed that hydrolysis occurring during the thermal pretreatment is due to thermal phenomena. The increase in soluble substances were significantly larger at 80ºC than at 60ºC (both during 3 h). Two types of slurry were used in the batch anaerobic digestion tests. The effect of thermal pretreatment differed with the type of slurry: it was positive with almost non-degraded slurries containing low NH_4^+-N concentration, and negative (inhibition of the anaerobic digestion process) when using degraded slurries with high NH_4^+-N content.
Keywords Anaerobic digestion; hydrolysis; inhibition; pig slurry; thermal pre-treatment

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Introduction

A treatment strategy for a given waste is a combination of processes with the objective of obtaining profitable products, minimising emissions and recovering energy and raw materials. For pig slurry, the inclusion of anaerobic digestion in the treatment strategy reports some advantages: to avoid volatile organic compound emissions, to control odours, to mineralise nutrients and to recover energy through methane production. However, its low hydrolysis and biogas production rates can limit its economic feasibility.

When energy cogeneration is applied, process feasibility is also dependent on profitable uses of the recovered heat. The main form, in which the energy is recovered (<50%), is as water at or below 90ºC. Profitable uses of this energy fraction are a limiting factor in warm countries.

Early studies (Hang *et al*., 1978), reported the use of thermal energy to increase the available soluble organic matter of sewage sludge previous to its anaerobic digestion. When using temperatures higher than 150ºC, they concluded that this process could lead to an increase in methane yield and biodegradability with an optimum near 175ºC, beyond which gas production decreased. Recent studies reported similar results. Delgenès *et al*. (2000) studied a thermo-chemical pretreatment of an industrial biomass. A COD solubilization of 70% was found when temperature was set at 140ºC; however, anaerobic biodegradability did not improve. Pinnekamp (1989) defined different optimal temperatures (135–180ºC) depending on the kind of sewage sludge, and stated that temperatures above 200ºC resulted in a clear reduction of biogas yield. The solubilization and/or formation of recalcitrant or toxic compounds by Maillard reactions, which act as anaerobic digestion inhibitors, can explain this decrease (Müller, 2000).

The use of low temperature pre-treatments (<100ºC) offers the advantage of low energy requirements, an easy operation, and can be a good way to avoid the generation of Maillard compound (lower reaction rates). However, a larger contact time is required. Li and Noike

(1992) and Wang *et al*. (1997) reported an increase in biogas yield and biodegradability when thermally pre-treating sewage sludge at low temperatures. No references have been found using heat sources at the available temperatures in cogeneration (<90ºC), and pre-treating pig slurry.

Among all inhibitors, ammonia nitrogen is described as the main one during pig slurry anaerobic digestion (Van Velsen, 1979; Angelidaki and Ahring, 1993; Bonmatí, 1998; Hansen *et al*., 1998). Many investigations have dealt with the threshold ammonia inhibitory concentration, but results are diverse and have been obtained under different conditions. Since free-ammonia concentration has been suggested to be the active component causing ammonia inhibition (Hashimoto, 1983), pH and temperature must be taken into account to describe it. Free-ammonia concentration is calculated according to the following equation:

$$\left[NH_3\right] = \frac{\left[NH_3 + NH_4^+\right]}{1 + \left[\frac{H^+}{Ka}\right]} \quad (1)$$

where $[NH_3]$ is the free-ammonia concentration, $[NH_3 + NH_4^+]$ is the total ammonia concentration; $[H^+]$ is the hydrogen ion concentration, and Ka is the ionisation constant of ammonia. The higher the pH and temperature are, the higher the free-ammonia concentration is.

Moreover, anaerobic digestion of complex substrates, such as pig slurry, can be limited by its initial hydrolysis phase. There is a loss of energetic potential since a large percentage of the organic matter is not hydrolysed. Relating the normally achieved yield from manure (200–250 L CH_4/kgVS) to the theoretical yield (400–450 L CH_4/kgVS), an unused potential of up to 25% is found in the particulate organic matter (Hartmann *et al*., 2000).

The objectives of the present work are to determine whether a low temperature thermal pre-treatment (<90ºC) improves the hydrolytic phase of anaerobic digestion and the anaerobic digestion of pig slurry as a whole, and to determine whether organic matter degradation during the thermal pre-treatment is due to thermal phenomena (80ºC) or to an enzymatic one (60ºC).

Methods

The tests performed to achieve the objectives of this work and the methods used are described below.

Thermal degradation tests

Two temperatures (60ºC and 80ºC) were tested with the objective of determining whether the degradation observed when thermally pre-treating pig slurry are due to enzymatic or to thermal processes. The test is based on the hypothesis that most enzymes are denatured at 80ºC and that at 60ºC their activity is not hindered. The experimental set-up and the methodology are described hereunder.

Five litres useful volume reactor containing 4-L substrate, tight closed, was used. A thermostatic water bath was used as heating system. The reactor temperature was controlled with a temperature probe. Two temperatures (60ºC and 80ºC) were tested to determine if hydrolysis was due to enzymatic or to thermal process. Hydrolysis was evaluated with the following parameters: NH_4^+-N, soluble COD (SCOD), soluble TKN (STKN), soluble TS (STS), and total volatile fatty acids (TVFA). The pre-treatment lasted for 3 h according to the results of previous experiments (results not shown), showing that degradation was maximum after 3 h of thermal pre-treatment at 80ºC temperature. Three replications were done.

Batch anaerobic tests

Batch anaerobic digestion tests were performed as described hereafter, in order to determine if thermal pre-treatment has a positive effect on further anaerobic digestion of the slurry.

The batch reactors were 120 mL glass vials filled with 54 g of substrate and 6 g of inoculum, flushed with N_2/CO_2 during 3 minutes, tightly closed with rubber stoppers and aluminium crimps, and placed in a incubator at 35ºC for 80 days. The inoculum used came from a steady-state sewage sludge anaerobic reactor. Every 3–4 days the headspace gas composition was analysed. Volatile fatty acids (VFA) were analysed every week. At the beginning and at the end of the experiment a complete analytical characterisation (see below) was done.

Four treatments were done: (P1) fresh pig slurry (low NH_4^+-N/TKN ratio) and low ammonia content; (P3) old pig slurry (high NH_4^+-N/TKN ratio) and high ammonia content; (P2) the same pig slurry as in P1 but thermally pre-treated at 80ºC for 3 h; and (P4), the same pig slurry as in P3 but also thermally pre-treated at 80ºC for 3 h. Four replications per treatment were used.

Analytical methods

The complete analytical characterisation consisted of: pH, Kjeldahl-N (TKN), NH_4^+-N, total solids (TS), volatile solids (VS), and COD. These parameters were analysed by standard methods (APHA, 1995). VFA were analysed by capillary gas chromatography with a FID detector. Biogas composition was determined with a packed column gas chromatography with a TCD detector. For the analysis of SCOD (S stands for soluble), STKN and STS, the sample was previously filtered through a 0.45 µm membrane.

Results and discussion

The discussion is presented separately for the results of each experiment.

Thermal degradation tests

A summary of the initial and final contents of soluble compounds of the thermally treated pig slurry, at 60ºC and 80ºC for 3 h, is shown on Table 1. A significant increase (5% significance means separation test) in all parameters is observed except for STS for which the increase is not significant. This fact can be explained by the high dispersion observed in the analysis, because of the heterogeneous nature of pig slurry, and supports the need for statistical significance tests in all experiments for these kind of substrates.

The concentration of soluble compounds after the pre-treatment is larger than before it, both at 60ºC and 80ºC, indicating that degradation occurs at both temperatures. However, the increase in soluble compounds is significantly larger at 80ºC than at 60ºC (Table 2).

In spite of the observed generation of VFA, there is a pH increase through the process. When treating at 60ºC, pH increased by 0.2 (from 7.1 to 7.3). When treating at 80ºC, pH increased by 0.7 (from 7 to 7.7). This suggests that thermal hydrolysis of pig slurry results

Table 1 Initial and final contents of the soluble compounds of the thermally treated pig slurry at 60°C and 80°C for 3h (average of 3 replications)

	NH_4^+-N (g/kg)		STKN (g/kg)		STS (g/kg)		SCOD (g/kg)		TVFA (g/kg)	
	60ºC	80ºC	60ºC	80ºC	60ºC	80ºC	60ºC	80ºC	60ºC	80ºC
Initial	1.24 b	1.21 b	1.41 b	1.35 b	4.9 a	4.9 a	5.34 b	7.07 b	1.11 b	1.15 b
Final	1.30 a	1.35 a	1.67 a	1.69 a	5.2 a	5.5 a	6.93 a	11.12 a	1.24 a	1.30 a

Note: different letters, in columns, show statistically significant differences between means (5% significance). The statistical analysis was done for every variable and by pairs

Table 2 Increase of NH_4^+-N and the soluble compounds concentrations through the thermal degradation tests (average of 3 replications)

	NH_4^+-N (% increase)	STKN (% increase)	STS (% increase)	SCOD (% increase)	TVFA (% increase)
Thermal treatment 60°C	4.0 b	18.2 b	5.9 a	29.7 b	12.2 a
Thermal treatment 80°C	12.1 a	24.7 a	12.6 a	57.7 a	13.4 a

Note: different letters, in columns, show statistically significant differences between means (5% significance). The statistical analysis was done for every variable and by pairs

in a solubilization and/or generation of basic substances (i.e. ammonia nitrogen) that results in a pH increase. A high final pH can cause problems during further anaerobic digestion since free-ammonia concentration increases or because of inhibition due to pH when higher than 8 (Clark and Speece, 1989).

Thermal treatment enhances hydrolysis of organic matter mainly due to thermal phenomena. Batch anaerobic tests, described below, were done with the slurry pretreated at 80°C for 3 h because this was the treatment where the largest hydrolysis was observed.

Batch anaerobic tests

Two types of slurry were used to test if the thermal pretreatment (80ºC for 3 h) improves anaerobic digestion (Table 3). The slurries were characterised according to its NH_4^+-N content (possibility of anaerobic digestion inhibition) and the NH_4^+-N/TKN ratio (degree of degradation).

The slurry used in P1 and P2 treatments (Table 3) has a low NH_4^+-N content and its NH_4^+-N/TKN ratio is close to 50%. This slurry is called *low NH_4^+-N content slurry – little degraded*. Differences in the content of organic matter between P1 and P2 can be explained by its degradation to volatile organic compounds through the thermal hydrolysis treatment (small amounts of CH_4 in the headspace were detected). However, the large decrease observed, pointed out that some volatile organic loss had happened, due to the non-completely airtightness of the lab-scale thermal hydrolysis system used. The NH_4^+-N content in the slurry of P3 and P4 treatments is much higher and its NH_4^+-N/TKN ratio is close to 70%. This slurry is called *high NH_4^+-N content slurry – very degraded*. Another main difference between these two types of slurry is that the pH of the slurry used in the P3 and P4 treatments is higher than the slurry used for the other two treatments.

The results of P1 treatment were statistically analysed against the results of P2, and those of P3 treatment against those of P4. The volumetric methane production rates referred to the initial TS, VS and COD concentrations, as well as the substrate conversion rates, according to Field *et al*. (1988), to methane (M%), VFA (VFA%), and acidification (A%), were used for the comparative analysis of the results.

P1 vs P2 treatments. The evolution of gas and VFA production is shown in Figure 1. In both treatments, there is an initial VFA accumulation, which is rapidly consumed (Figure 1(b)).

Table 3 Characterisation of the substrates used on batch anaerobic tests

Treatment	Thermal treatment	pH	TS (g/kg)	VS (g/kg)	COD (g/kg)	NH_4^+-N (g/kg)	% (NH_4^+-N /TKN) (g/kg)
P1: Low NH_4^+-N content	NO	7.19	45.3	33.9	56.23	1.23	43.7
P2: Low NH_4^+-N content	YES	7.76	23.6	16.9	31.05	1.31	55.9
P3: High NH_4^+-N content	NO	8.15	49.8	31.1	47.87	3.72	69.4
P4: High NH_4^+-N content	YES	9.05	47.1	28.6	48.30	3.63	69.9

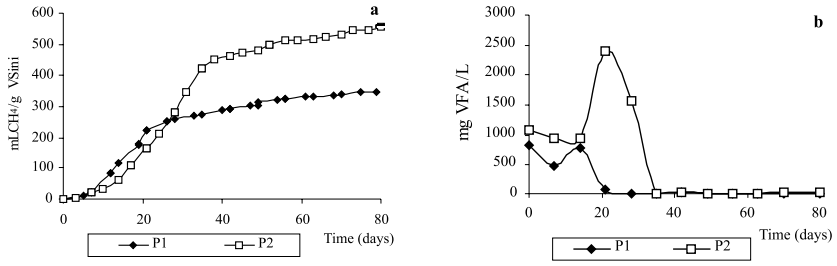

Figure 1 Evolution of methane production (a) and VFA concentration (b) in treatments P1 and P2 during batch anaerobic tests (average of 4 replications)

In treatment P2, the VFA accumulation is larger and it is delayed a few days. This delay is consistent with a longer lasting *lag phase* in treatment P2 (Figure 1(a)).

The volumetric methane production rates are shown on Table 4. There are significant differences in the indexes between the treatments for those rates. The production rates are higher in treatment P2 than in P1. However, the volumetric methane production is higher for the non-pretreated slurries. This fact can be explained by the organic matter volatilisation during the pre-treatment and by not accounting for the methane generated during the pretreatment.

Substrate biodegradability is good since the methanisation rates obtained were high and the VFA rate was practically null in both treatments (Table 4).

The methanisation rates of treatment P2 is remarkably higher than those of P1. This result may be due to organic matter solubilization during the pretreatment making it more available to microorganisms. This is also shown by the higher VFA increase (Figure 1(b)) and by a final organic matter conversion rate to methane, which is larger in treatment P2 (Table 4).

The total removal of organic matter (measured as volatile solid concentration) was 40% in P1 treatment and 46% in treatment P2. An increase in organic matter reduction of 18% is reported when pig slurry is thermally pretreated. The overall performance of the thermal pretreatment and anaerobic digestion led to a total organic matter removal of 74%. Otherwise, the loss of volatile organic matter through the thermal pretreatment will result in a loss of methane potential that can be avoided at a full-scale plant.

These results indicate that the thermal pretreatment has an important positive effect on the initial hydrolytic phase of anaerobic digestion.

P3 vs P4 treatments. The evolution in methane production and VFA accumulation (Figure 2) in treatments P3 and P4 is very different from that of treatments P1 and P2.

The almost lineal (absence of the exponential phase) methane production (Figure 2(a)),

Table 4 Methane production and substrate conversion rates for treatments P1 and P2

Treatment	Methane production rates				Substrate conversion rates		
	CH_4/ Substrate (L/kg)	CH_4/TSi (L/kg)	CH_4/VSi (L/kg)	CH_4/CODi (L/kg)	%M (COD_{CH4}/ COD_i)	%VFA (COD_{VFA}/ COD_i)	%A ($COD_{CH4+VFA}$/ COD_i)
P1	13.1 **a**	260.2 **b**	347.5 **b**	209.7 **b**	54.89	0.01	54.90
P2	10.4 **b**	400.2 **a**	557.5 **a**	304.1 **a**	79.60	0.08	79.69
% Increase	–19.9	53.8	60.4	45.0	39.5	–	45.1

Note: different letters, in columns, show statistically significant differences between means (5% significance)

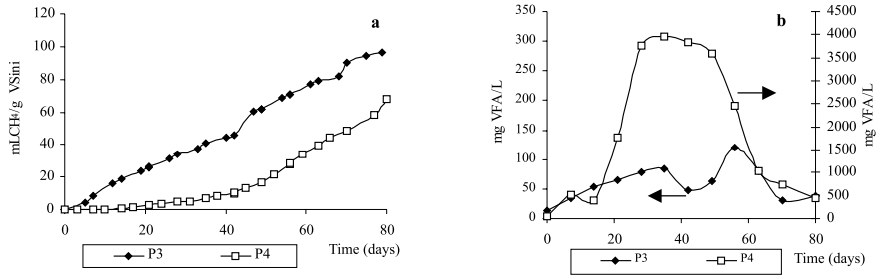

Figure 2 Evolution of methane production (a) and concentration (b) in treatments P3 and P4 (means of 4 replications)

the low methane production rates and substrate conversion rates (Table 5), in treatment P3, indicate that the substrate is already degraded. In the same way, the high NH_3-N content (0.521 g/kg) together with a slight VFA accumulation through the process (Figure 2(b)), indicates that the process is also partly inhibited by free-ammonia.

However, treatment P4 suffered considerable inhibition. The VFA accumulation is between 10 and 15 times higher, through the process, than in treatment P3. The methane production rates in P4 are significantly lower that those of the P3 treatment. Inhibition can be explained by the pH (9.05, see Table 6) and the high NH_3-N content of the slurry.

The VFA accumulation through the anaerobic digestion slightly decreases the pH. Therefore, there is a lower inhibition degree due to a decrease in the NH_3-N content (Table 6) and a decrease in pH itself. This agrees with the start of methane production on day 40 of digestion, and with the large VFA consumption observed from day 50 on (Figure 2(b)). However, the final VFA% shows that the system could not consume all the generated VFA (Table 5).

In spite of this, the measured removal of organic matter is slightly higher in treatment P4 (8.8% volatile solids reduction) than in treatment P3 (7.2% volatile solid reduction). This can be explained by the accumulation of VFA shown in treatment P4 that was not converted to methane. The overall performance of the whole treatment (thermal hydrolysis and anaerobic digestion) led to a total organic matter removal of 16%.

Ammonia inhibition. The initial and final values of total ammonia nitrogen, pH and calculated free-ammonia (by Equation 1), are shown in Table 6.

The NH_3-N threshold concentration described in the literature as inhibiting anaerobic digestion is between 0.1 g NH_3/kg (Henze, *et al.*, 1995) and 0.7 g NH_3/kg when inoculum has been previously adapted to high ammonia nitrogen concentrations (Angelidaki and Ahring, 1994). Regarding treatments P1 and P2, although the slight increase of pH and total ammonia nitrogen through the process, free-ammonia concentration remained below the inhibition levels in both treatments (Table 6).

Table 5 Methane production and substrate conversion rates for treatments P3 and P4

Treatment	Methane production rates				Substrate conversion rates		
	CH_4/ Substrate (L/kg)	CH_4/TSi (L/kg)	CH_4/VSi (L/kg)	CH_4/CODi (L/kg)	%M (COD_{CH4}/ COD_i)	%VFA (COD_{VFA}/ COD_i)	%A ($COD_{CH4+VFA}$/ COD_i)
P3	3.32 **a**	59.9 **a**	96.1 **a**	62.3 **a**	25.16	0.14	25.30
P4	2.15 **b**	41.1 **a**	67.7 **a**	40.1 **b**	16.32	2.46	18.78
% increase	–35.2	–31.4	–29.5	–35.6	–35.1	–	–25.8

Note: different letters, in column, show statistically significant differences between means (5% significance)

Table 6 Initial and final concentration of total ammonia nitrogen, pH and free-ammonia in the batch anaerobic test

Treatment	Initial			Final		
	[N-NH_3+N-NH_4^+] (g/kg)	pH	[N-NH_3] (g/kg)	[N-NH_3+N-NH_4^+] (g/kg)	pH	[N-NH_3] (g/kg)
P1	1.23	7.19	0.022	1.32	7.95	0.103
P2	1.31	7.76	0.082	1.44	8.03	0.144
P3	3.72	8.15	0.521	3.84	8.25	0.633
P4	3.63	9.05	2.047	3.86	8.49	0.970

In treatments P3 and P4, the high ammonia concentration, together with the high pH, results in a free-ammonia concentration above the concentrations reported as inhibitory. Process instability due to ammonia resulted in VFA accumulation (Angelidaki and Ahring, 1993), which led to a lowering of the pH, thus decreasing the concentration of free-ammonia. This pattern is shown in both treatments. The differences in methane production rates between P3 and P4 can be explained by the higher degree of inhibition in treatment P4 than in P3. The initial free-ammonia concentration in treatment P4 was 2.047 g NH_3/kg and 0.521 g NH_3/kg in treatment P3. The large accumulation of VFA in treatment P4 led to a lowering of the pH at the end the digestion, resulting in a free-ammonia concentration lower than the initial one. However, its concentration still remained above the inhibitory values.

It can be concluded that thermal pretreatment of degraded slurry with high ammonia content increases anaerobic digestion inhibition phenomena that can be explained by the pH increase of the slurry during the pretreatment, with the corresponding increase on free-ammonia and its inhibition effect (see Table 6).

Energy considerations. Although thermal hydrolysis of pig slurry requires energy, the need for heat is very low. The consumption of energy can be optimised so that the total energy balance is positive. Considering a combined heat and power engine (CHP) with a conversion to thermal energy of 50% and a thermal energy recovery, by heat exchangers, in the whole treatment process of 80%, the methane yield increase obtained in the P2 treatment is higher than the equivalent surplus energy needed for the described thermal pretreatment. Taking into account previous figures, the minimum amount of organic matter concentration needed for having an energy surplus is 10 g VS/kg. Pig slurry volatile solids concentration is normally higher than this value.

Conclusions

Thermal pretreatment at 80ºC for 3 h accelerates organic matter hydrolysis because of thermal processes. The thermal pretreatment has different effects depending on the pig slurry type. On type P1, fresh pig slurry (low NH_4^+-N/TKN ratio) and low ammonia content, the methane production rates increase significantly, and a positive energy balance is obtained. The thermal pretreatment does not seem appropriate for P3 pig slurry type, old pig slurry (high NH_4^+-N/TKN ratio) and high ammonia content, since the pH increase leads to larger inhibition by free-ammonia.

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