The Effect of Low-Temperature Thermal Pre-Treatment on Methane Yield of Pig Manure Fractions

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Abstract. The aim of the present study was to evaluate the effect of low-temperature thermal pre-treatment on the methane yield of pig manure fractions. Four different temperatures ranging from 65°C to 80°C were applied for 20 h to whole pig manure and the solid fraction of pig manure derived from solid-liquid manure separation. The results showed significant improvements in methane yield both in pig manure and solid-fraction pig manure at 11 d of the batch digestion test. The improvement was between 9.5-22.5% for pig manure and 6.1-25.3% for solid fraction pig manure. However, at 90 d of the batch digestion assay the effect of low-temperature pre-treatment on methane yield was significant only for the 65°C treatment. Application of low-temperature thermal pre-treatment appears to be a promising method to improve methane yield of pig manure fractions, particularly when surplus thermal energy is available.

Key words: biogas, anaerobic digestion, thermal pre-treatment, pig manure, methane.

Abstrak. Penelitan ini bertujuan untuk mengevaluasi pengaruh pre-treatment pada suhu rendah terhadap produksi methan dari bagian manure babi. Perlakuan pre-treatment yang digunakan berupa empat level temperatur mulai dari 65°C sampai dengan 80°C selama 20 jam yang diterapkan pada manure babi dan bagian padat manure babi yang diperoleh dari pemisahan bagian cair dan bagian padat manure babi. Hasil penelitian menunjukkan adanya peningkatan produksi methan secara signifikan setelah 11 hari inkubasi dengan digester model batch. Produksi methane meningkat antara 9,5-22,5% pada manure babi dan 6,1-25,3% pada bagian padat manure babi. Namun demikian setelah 90 hari inkubasi, pengaruh dari penggunaan pre-treatment pada suhu rendah hanya berpengaruh siginifikan pada temperatur 65°C saja. Penggunaan pre-treatment pada suhu rendah menunjukkan bahwa metode tersebut merupakan metode yang menjanjikan untuk meningkatkan produksi methan dari manure babi khususnya apabila terdapat surplus energi.

Kata kunci : biogas, digesti secara anaerob, pre-treatment dengan pemanasan, manure babi, methan

Introduction

Anaerobic digestion (AD) is a multistep process that includes hydrolysis, acidogenesis, acetogenesis and methanogenesis, with different microbial consortia active at each stage (Batstone et al., 2002). Hydrolysis, the first step of AD, is known as a limiting step in the AD treatmentof many solid wastes.Thepresence of biofibres is the main reason for the restricted hydrolysis rate of AD-processing of animal manure. Therefore,a focus ofthe pre-treatmenthas been to break downthe lignocellulosic structure of biofibres,thus accelerating the degradation process in the biogas reactor (González-Fernándezet al., 2008).

Of the pre-treatment strategies available, thermal pre-treatment including steam explosion and liquid hot water pre-treatmentseemsto havea largerpositive effect in terms of energy balance (Hendriks and Zeeman, 2009). The effect of thermal pre-treatment of enhancing biogas production is due to the solubilisation of particulate organic matter in the substrate, subsequently increasingthebiodegradability of the substrate

(Bougrier et al., 2008). Other studies have usedlow-temperature thermal pre-treatment prior to AD.Bonmati et al. (2001) reported that thermal pre-treatment at 80°Cfor 3 h can accelerate the hydrolysis rate of pig manure and significantly increase methane production in batch assays. Carrère et al. (2009) centrifuged pig manure after thermal pre-treatment at 70°C for 3 h and found thatmethane yield wasincreased by 70% in the liquid phase but decreasedby 12% for the particulate fractions when compared to whole pig manureafter a 40 d mesophilic batch assay.However, there is limited information abouttesting theeffect of different low temperaturesin the thermal pre-treatment of pig manure fractions. Thermal pre-treatment of the solid fraction of animal manure, which is rich in energy content in terms of fresh weight of substrate (Hjorth et al., 2010), can reduce energy demand per kg volatile solids (VS)during thermal pre-treatment when compared to whole animal manure that has high water content. Additionally, utilization of the solid manure fractionas a co-substrate in AD can reduce transport costs to centralized biogas plants (Asam et al., 2011) and increase methane production per unit fresh weight of substrate (Møller et al., 2007).

Menardo et al. (2011) reported that the unused fraction of heat in the form of hot water from combined heat and power production (CHP) is usually wasted to the atmosphere. Therefore,the objective of this study was to evaluate the effects of low-temperature thermal pre-treatment (65°Cto 80°C) on the methane production ofwhole and solid-fractionpig manure.The temperatures were chosen to correspond with the expected exit temperatures of cooling water from CHP plants.

Materials and Methods

Experimental. Low-temperature thermal pre-treatment was conducted using 500 ml sealed glass bottles. Samples weighing 300 ± 1 g were pre-treated at temperatures ranging from 65 to 80°C at 5°C intervals using a water bath for 20 h. Following pre-treatment, the material was cooled down to ambient temperature using a water bath at room temperature for 1.5 h and subsequently transferred to the 500 ml sealed plastic bottle which was kept at -20°C until use. Untreated sample were prepared and kept under the same conditionsas the pre-treated samples and used as reference.

The batch digestion experiments were performed using 0.5 L infusion bottles with the method described by Møller et al. (2004). The ratio of inoculum to substrate was 0.98 ± 0.04 in terms of VS. Batch reactors containing solely inoculum served as a control to measure the inoculum gas production, which was subtracted from the gas production of the experimental batch reactors. Prior to batch digestion, each reactor was sealed using butyl rubber stoppers and aluminium caps. In order to remove oxygen the headspace of each bottle was flushed with 99.9% nitrogen for 2 min. Batch assays were done in triplicate, maintained at 35°C and ran for a period of 90 d.

Inoculum and Substrate. Inoculum for the batch assay was sourced from the active commercial biogas reactor at Research Centre Foulum, Denmark, which operates at a thermophilic temperature (52°C). The commercial digester treats pig manure, cattle manure, maize silage and industrial organic by-products. To ensure that most of the residual organic material in the digested slurry was converted to biogas, it was kept at 35°C for three weeks. In order to get a uniform inoculum, digested slurry was separated using a sieve (500 µm serial number 5564470 D-42759 Haan, Germany). To further minimize the inoculum biogas production, only the liquid fraction was subsequently used to inoculate the batch tests. Total solids (TS), volatile solids (VS) and pH of the inoculum for the batch digestion experiments were 3.56, 2.35 and 7.5%, respectively.

The substrate for this study was pig manure from the fattening growth stage. Pig manure was collected in a single batch from the storage tank at Aarhus University, Foulum, Denmark. The solid fraction of pig manure was obtained by manual separation using a sieve (500 µm serial number 5564470 D-42759 Haan, Germany). TS and VS of pig manure were 7.2 and 6.1%, respectively with corresponding figures for the solid fractions of 15 and 13.7%, respectively. The substrate properties can be seen in Table 1.

Analytical procedures. The gas composition was analysed using a gas chromatograph (Agilent Technologies, serial number CN 11041099). Volatile fatty acid (VFA) (C_2-C_5) concentrations were determined by means of gas chromatography with a flame ionization detector (Agilent Technologies serial number CN 11041020).TS was determined by drying at 105°C for 24 h. Ash was determined by combusting the dried sample at 550°C for five hours and VS was calculated by subtracting the ash weight from the TS. Total ammonia nitrogen (TAN) was measured colorimetrically at 690 nm with a spectrophotometer (Merck®NOVA 60, NH_4^+ test 1.00683.0001). pH was measured using a pH meter (Knick Type 911, Germany). Total nitrogen was analysed using the Kjeldahl standard method (APHA, 1995) and a Kjell-Foss 16200 auto analyzer (Foss Electric, Hillerod, Denmark). Data were statistically analysed using the General Linear Model (GLM) procedure in SAS(SAS® software, Cary, NC). Duncan multiple range tests were used in the post ANOVA analysis, when differences were found to be significant at the $P \leq 0.05$ level.

Results and Discussion

Effects of Low-Temperature Thermal Pre-Treatment on Substrate Properties

Substrate properties in the batch assay are presented in Table 1. The pH value of the pre-treated sample was slightly higher than in the control (Table 1). This phenomenon may be caused by the solubilisation of macromolecules such as protein (Carrère et al., 2009) and/or formation of a basic substance (i.e. ammonia nitrogen) due to thermal pre-treatment (Bonmatí et al., 2001). This fact is confirmed by a higher TAN concentration in the pre-treated sample compared to TAN in the untreated sample. Moreover, TAN in all samples was below the inhibition threshold of about 2.5 g/L as reported by Hashimoto (1986). Total VFA concentrations of pre-treated samples also showedthe same trend as the pH value. A higher total VFA concentration in the pre-treated sample than in the untreated sample may be because there was increased microbial hydrolytic and acidogenic activity, since the low-temperature thermal pre-treatment was performed for 20 h. Nielsen et al. (2004)

Table 1. Substrate properties

Sample	Pre-treatment (°C)	TAN (g/L)	Total VFA (mg/L)	TN (%)	pH	I : S ratio
Pig manure	No	2.24	6391.75	3.64	6.75	1
Pig manure	65	2.61	11551.13	3.47	6.78	1
Pig manure	70	2.48	9134.18	3.46	6.78	0.9
Pig manure	75	2.43	9564.76	4.09	6.79	1
Pig manure	80	2.28	9106.80	3.56	6.80	0.9
Solid fraction pig manure	No	1.95	5928.90	3.65	6.63	1
Solid fraction pig manure	65	2.29	9768.82	4.20	6.64	1
Solid fraction pig manure	70	2.10	6982.88	3.93	6.66	1
Solid fraction pig manure	75	2.00	8975.55	4.17	6.84	1
Solid fraction pig manure	80	1.98	9824.56	3.45	6.82	1

suggested that the application of extreme thermophilic temperatures (>65°C) in the first stage of a two-stage reactor would lead to a broader spectrum of thermophilic lignocellulose-fermenting microorganisms becoming involved in the degradation process. Moreover, the increase of the individual VFAs after low-temperature thermal pre-treatment was dominated by acetic acid, propionic acid and butyric acid. The highest improvement in VFA contents of pig manure was at 65°C with 65, 62.8 and 11.1% increases for acetic, propionic and butyric acids, respectively. For the solid fraction the largest increases in VFA were seen at 80°C with 62.8; 126.2 and 11.1% increases of acetic, propionic and butyric acids, respectively, compared to the control.

Methane Production of Pig Manure

The effect of low-temperature thermal pre-treatment on methane yields of pig manure can be seen in Fig. 1. The ultimate methane yield (B_0) of pig manureranged from 383.3 to 402.6 L/kg VS (Table 2). These values were in accordance with other studies inthe literature reporting B_0 values of pig manure between 327 and 403 L/Kg VS added (Chae et al., 2008; Cuetos et al., 2011). There was a significant (P<0.05) improvement in methane production of pig manure following low-temperature thermal pre-treatment. The greatest increase of methane production was in the beginning of the batch assay (11 d) and the improvement was in the range of 9.5% to 26.4% (Table 2) compared to the control. Since the increase in methane production was greatest in the early part of the batch test, this would suggest an increased rate of methane production, which would be of interest to a commercial continuous stirred tank reactor (CSTR). In addition, Ward et al. (2010) reported that in Denmark AD-processorsof pig manure without co-digestion with energy crops commonly operate with a short hydraulic retention time (HRT) of approximately 12 d. However, the significant positive effect (P<0.05) of low-temperature thermal pre-treatment on the methane yield of pig manure at 90 d of a batch assay digestion was only found at 65°C pre-treatment. This may due to microbial hydrolytic and acidogenic activity within the temperature, therefore the effect of pre-treatment was not only from low-temperature thermal pre-treatment but also from these microorganisms activity.This result suggested that this pre-treatment could increase the reaction rate but has little effect on the overall yield at infinite HRT, as represented by $B_{0.}$

The lack of positive effects at 70, 75 and 80°at the end of experiment (90 d) may be explained by evaporation of VFA during the pre-treatment process and/or emergence of toxic substances due to the Maillard reaction which can cause inhibition (Müller, 2000). Moreover, the total VFA concentration of pre-treated pig manure at 65°C was higher than at the other tested temperatures (Table 1). This can explain the higher B_0 of this pre-treated sample compared to the othersamples since acetic acid can be used directly by acetoclastic methanogens to produce methane (Bruni et al., 2010).

Methane Yield of Solid-Fraction Pig Manure

Methane production of the solid fractionfollowing low-temperature thermal pre-treatment is presented in Fig. 2. In general, there was a linear improvement in methane yield as the temperature in the thermal pre-treatment was increased from 65 to 80°C, although the effect was not statistically significant on the B_0 of solid fraction pig manure (Table 2). The greatest improvement in methane yield was 25 at 80°C after 11 d of batch digestion.

The significant ($P<0.05$) improvement of the methane yield of the solid-fraction pig manure at 11 and 28 dof the batch testbut not at 90 d indicateda release of easily degradable organic material. This was then easily digested by microorganisms resulting in a higher methane production in the early days of the batch assay.

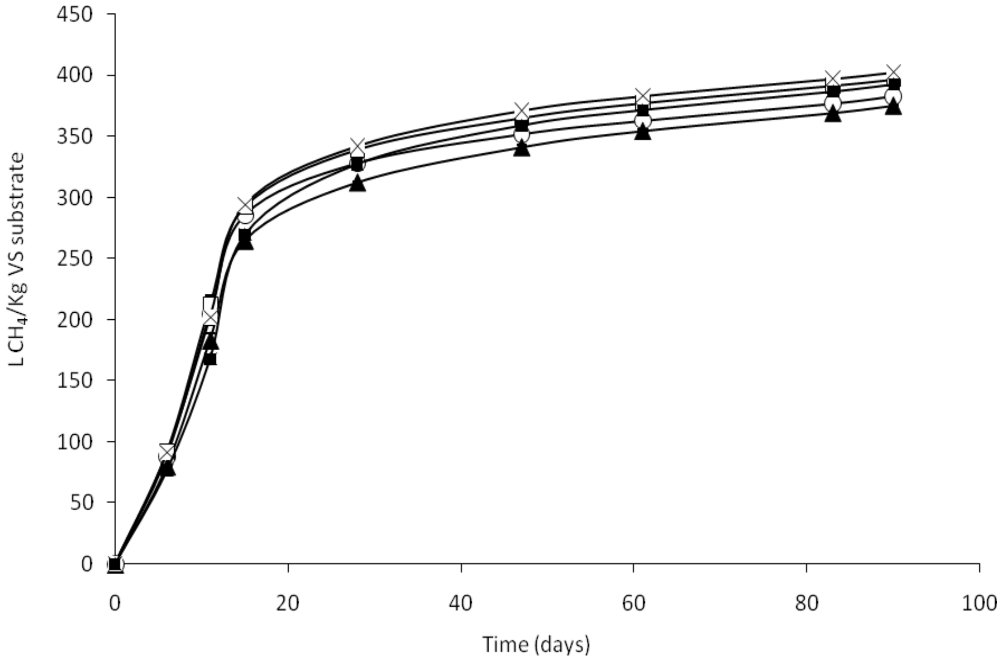

Fig. 1. Methane production of pig manure (■ : pig manure, × : pre-treated pig manure 65°C, ▲: pre-treated pig manure 70°C, □ : pre-treated pig manure 75°C, ○ : pre-treated pig manure 80°C).

Table 2. Cumulative methane production of batch assay

Sample	Pretreatment temperature	At 11 days	% increase	At 28 days	% increase	At 90 days	% increase
Pig slurry	control	167.48[a]	-	327.26[a]	-	392.36[a]	-
Pig slurry	65°C	201.84[b]	+20.52	342.35[b]	+4.61	402.63[b]	+2.62
Pig slurry	70°C	183.39[c]	+ 9.50	312.65[c]	–4.46	375.57[c]	–4.28
Pig slurry	75°C	211.64[d]	+26.37	338.86[ab]	+3.54	396.20[ab]	+0.98
Pig slurry	80°C	205.17[bd]	+22.50	328.41[a]	+0.35	383.29[a]	–2.31
Solid fraction pig manure	control	163.60[a]	-	265.05[a]	-	330.54[ab]	-
Solid fraction pig manure	65°C	173.54[ab]	+6.08	258.90[a]	–2.32	316.12[b]	–4.36
Solid fraction pig manure	70°C	181.87[bc]	+11.17	272.71[ab]	+2.89	337.07[ab]	+1.98
Solid fraction pig manure	75°C	193.91[cd]	+18.53	280.48[ab]	+5.82	344.31[a]	+4.17
Solid fraction pig manure	80°C	205.06[d]	+25.34	289.86[b]	+9.36	351.60[a]	+6.37

[a,b,c,d] Values bearing different superscript at the same column shows significant

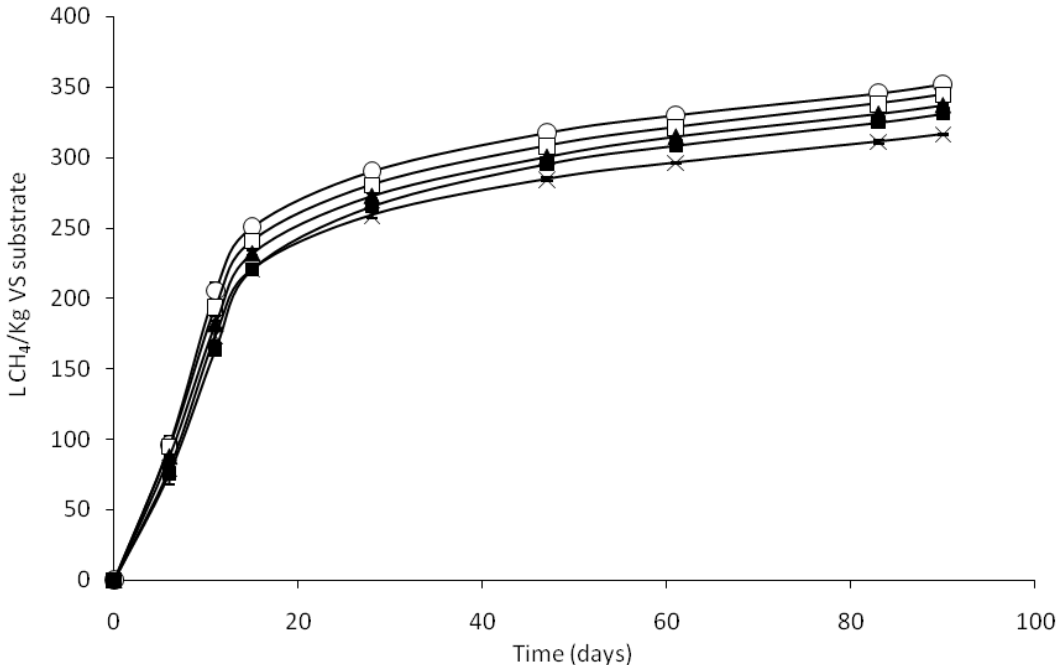

Fig. 2 Methane yield of solid fractions pig manure (: ■ : solid fraction pig manure, × : pre-treated solid fraction pig manure 65°C, ▲: pre-treated solid fraction pig manure 70°C, □ : pre-treated solid fraction pig manure 75°C, ○ : pre-treated solid fraction pig manure 80°C)

Table 3. Energy consideration per tonne substrate

Sample	Treatment (°C)	TS (%)	VS (%)	Methane yield at 11 d batch digestion** (L/kg VS)	Net energy gain*** (kWh)
Pig manure	Control*	7.24	6.09	148.45	-
Pig manure	65	7.32	6.01	187.59	– 34.56
Solid fraction pig manure	no (15)	15	13.70	145.01	-
Solid fraction pig manure	80	15.43	13.50	205.06	– 23.21

*: Assuming average ambient temperature 15°C, pig manure was stored in barrel tank in room temperature before pre-treatment. **: STP condition. ***: Energy gain due to thermal pre-treatment– energy required for thermal pre-treatment

Energy Considerations

When applying thermal pre-treatmentat full-scale AD plants, it is to consider the energy balance of the whole process. The energy calculations per tonne of substrate are presented in Table 3. The value used for specific heat of pig manure was taken from Chen (1983) as 4.19-0.00275 TS (TS content in the substrate) J/g/°C$^-$ and 1 m^3 CH_4 = 36 MJ and 1 MJ = 3.6 kWh (Raju et al., 2012). The calculations were based on the greatest improvements in methane yield for both whole pig manure and solid-fraction pig manure, which were at 11 d digestion and 65°C in the case of pig manure and 80°C for the solid fraction of pig manure (Table 2). The energy gained from the extra methane yield following thermal pre-treatment was found to be insufficient to cover the process energy requirements. However, to overcome this problem, Raju et al. (2012) suggested 1) using a relatively cheap energy source from the CHP unit that was often part of industrial biogas plants andin some cases wasted to the atmosphere (Menardo et al., 2011), and 2) recovering the energy required during the pre-treatment process by heat exchangers that transfer much of the heat to the incoming substrate. In addition, thermal pre-treatment of solid-fractionpig manure has a better energy balance than thermal pre-treatment of whole pig manure, since the solid fraction hasa higher VS content.

Conclusions

Low-temperature thermal pre-treatmentat 65 to 80°C for 20 hgave significant improvements in the methane production of pig manure up to day 28 of the batch digestion but at the end of the batch assay (90 d) the effectwas only significant following the 65°C pre-treatment. These treatments also improved the methane production from solid-fraction pig manure throughout the 90 d batch assay and a higher temperature gave an increased effect. Applications of low-temperature thermal pre-treatment of pig manure fractions in AD could be a useful method to increase methane yields, particularly when applied to solid fractions, although the energy balance was not favorable unless either the heat energy required was easily and cheaply available or effective of heat exchangers was employed.

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