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Enhanced methane production from ultrasound pre-treated and hygienized dairy cattle slurry

Sami Luste [a,*], Sari Luostarinen [b]

[a] University of Eastern Finland, Department of Environmental Science, Yliopistonranta I E, FI-70211 Kuopio, Finland
[b] MTT Agrifood Research Finland, Bioenergy and Environment, Lönnrotinkatu 5, FI-50100 Mikkeli, Finland

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ABSTRACT

The effect of hygienization (70 °C, 60 min) and ultrasound (6000 ± 500 kJ/kg total solids (TS)) pre-treatments on hydrolysis and biological methane (CH_4) potential (BMP) of dairy cattle slurry was studied. The BMP of the untreated slurry (control) was 210 ± 10 N m^3 CH_4/ton volatile solids (VS) added; after ultrasound pre-treatment it was 250 ± 10 N m^3 CH_4/ton VS_{added} and after hygienization 280 ± 20 N m^3 CH_4/ton VS_{added}. The specific methanogenic activity (SMA) of the inoculum increased from 22 (untreated) to 26 (ultrasound treated) and up to 28 N ml CH_4/g VS d, after hygienization. However, only hygienization achieved a positive net energy balance. Both pre-treatments increased the VS-based hydrolysis of slurry (10–96%), soluble nitrogen (N_{sol}) content in digestates (20 ± 5%) and biodegradability of the slurry (8 ± 3%) as estimated via elevated VS removal.

1. Introduction

Anaerobic digestion (AD), i.e. biogas technology, is a microbiological process during which organic material is converted into two end-products: methane-rich biogas and nutrient-rich digestate. This technology offers several advantages, including controlled stabilization of organic material with minimized environmental emissions, production of renewable energy (methane which can be converted to electricity, heat and/or vehicle fuel) and recycling of carbon and nutrients via the reuse of digestate.

Cattle slurry is an accepted organic fertilizer and thus also a suitable raw material for AD (e.g. high buffering capacity and produced steadily throughout the year). During the AD process, the slurry becomes more soluble and homogeneous as particulate material is degraded. Moreover, its nutrient balance (carbon/nitrogen ratio) and content of soluble nutrients (ammonium, phosphate, dipotassium oxide) are improved (Kapuinen et al., 2008). For these reasons, the digestate is technically easier to spread and better absorbed into soil, making nutrients more readily-available for plants when compared to raw slurry. Still, correct spreading time (vegetative phase) and methods (injection/mulching) are required to minimize ammonia volatilization and nutrient run-off (Joki-Tokola, 1998; Kapuinen et al., 2008; Knudsen and Birkmose, 1997). The adoption of AD techniques in dairy farms can also reduce greenhouse gas emissions (GHG) from dairy cattle slurry by more than 60% from the 92.4 kg carbon dioxide (CO_2) equivalents (eq.)/m^3 from storing, composting and field application of raw slurry (Amon et al., 2006; Clemens et al., 2006). Moreover, the yearly GHG emissions of Finnish dairy farms are estimated to be 180,000 kg CO_2 eq. (Kaparaju and Rintala, in press). As most of agricultural GHG emissions is methane from storing and use of raw slurry, which could be easily harvested and utilized in a more efficient and controlled manner in biogas plants and used for energy purposes.

BMP of cattle slurry is relatively low (130–240 m^3 CH_4/ton VS_{added}; Ahring et al., 2001; Amon et al., 2006; Angelidaki and Ahring, 2000; Lehtomäki et al., 2007; Mladenovska et al., 2006; Møller et al., 2004; Nielsen et al., 2004), as the primary energy content has already been utilized in the digestive tract of the cow and the amount of recalcitrant materials is high (e.g. lignin compounds; Lehtomäki et al., 2007). To improve the economical feasibility of slurry-based biogas plants, it is recommended that slurry is co-digested with other organic materials, such as plant biomass or organic wastes or by-products (Alvarez and Lidén, 2008; Lehtomäki et al., 2007; Luste et al., unpublished results).

It is also possible that some pre-treatments are able to improve the degradation of slurry and improve the stability of the digestate. Thus, pre-treatments aim at enhanced hydrolysis and subsequently a more complete degradation of the slurry (defined as higher removal of VS). During the hydrolysis, solid materials are transformed into the soluble phase. The increased content of soluble material may allow bacterial cells (which are only able to take up small molecules) to exploit the substrates more efficiently

* Corresponding author. Tel.: +35 8405143694; fax: +35 8153556513.
E-mail addresses: sami.luste@uef.fi, sami.luste@uku.fi (S. Luste).

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and thus to achieve higher biogas yields, supporting further hydrolysis (Miron et al., 2000; Palenzuela-Rollon, 1999).

Ultrasound is a potential pre-treatment technique; it has been reported as being an effective way to degrade particulate material for AD. Ultrasound evokes cavitation in the organic material by bubble formation in the liquid phase. The collapse of these bubbles produces high local heating and pressure, formation of radicals and high-rate shearing phenomena which degrade the particulate material. Ultrasound treatments with energies below 10,000 kJ/kg total solids (TS) and with low frequencies (20–40 kHz; Tiehm et al., 1997) have been found to be optimal for hydrolysis of waste activated sludge (Bougrier et al., 2005; Dewil et al., 2006) and for improved efficiency of hydrolyzing enzymes (Chu et al., 2002). Though, ultrasound pre-treatment has been widely studied for sewage and waste activated sludge (Bougrier et al., 2005; Dewil et al., 2006; Khanal et al., 2006), as far as we are aware, it has not been previously evaluated for pre-treatment of dairy cattle slurry.

The primal function of hygienization (animal by-product (ABP) regulation of the European Union (EU): 70 °C, 60 min, particle size <12 mm; European Parliament and Council (EC), 2002) is to destroy the pathogens, but it can also be considered a thermal pre-treatment with the following advantages: (1) separating liquid organic material from solids to solubles, (2) loosening of the structures via pressure changes and (3) concentrating the material via evaporation of water (Bougrier et al., 2005). In previous studies, low pre-treatment temperatures (<100 °C), as in hygienization, have been found as being more effective in increasing biogas production than higher temperatures (Gavala et al., 2003). Hygienization has previously been studied as a pre-treatment for co-digestion of cattle manure and biowaste, of cattle slurry and ABPs, and of sewage sludge and ABPs with 12–24% increased methane yields (Luste et al., unpublished results; Luste and Luostarinen, 2010; Paavola et al., 2006).

In this paper, the effect of ultrasound and thermal pre-treatments on the BMP of dairy cattle slurry has been studied. The selected ultrasound energy was estimated from the highest increase of solubilization during the screening experiments, while the thermal pre-treatment was performed as the hygienization of EU ABP regulation.

2. Methods

2.1. Materials

Cattle slurry was collected from a dairy farm housing 40 dairy cows (Mikkeli, Finland) and kept at 4 °C prior to processing. Characteristics of the cattle slurry are reported in Table 1. The inoculum was collected from a farm-scale biogas plant (Laukaa, Finland) digesting cattle slurry, plant biomass and confectionery waste (TS 4.4%, VS 3.5%; pH 7.5).

Table 1
Characteristics of raw, ultrasound pre-treated and pre-hygienized cattle slurry and the increase (%) in hydrolysis parameters when compared to the raw slurry (/).

	Raw slurry	After ultrasound	After hygienization
TS (%)	5.8 ± 0.1	6.0 ± 0.1	6.1 ± 0.1
VS (%)	4.4 ± 0.2	4.5 ± 0.1	4.6 ± 0.1
COD_{sol} (g/l)	14 ± 1.0	17 ± 1.0	21 ± 1.0
COD_{sol}/VS	3.1	3.7	4.5
VFA (g/l)	6.0 ± 0.2	6.7 ± 0.2	8.5 ± 0.5
NH_4-N (g/l)	1.3	1.4	1.7
N_{sol} (g/l)	1.6	1.7	2.1
LRC_{sol} (g/l)	1.9	2.5	3.8
pH	7.2	7.1	6.9
COD_{sol}/VS (%)	/	15	44
VFA/VS (%)	/	10	37
N_{sol}/VS (%)	/	10	33
LRC_{sol}/VS (%)	/	32	96

Amount of parallel analysis TS, VS, COD_{sol} and LRC_{sol}: 3 (min); VFA, N_{sol} and NH_4-N: 2.

2.2. Pre-treatments

Optimal ultrasound treatment (Hielscher UP100H ultrasound processor, Germany; 30 kHz, pulse range of 80%) was screened as defined by the highest hydrolysis ratios of chemical oxygen demand (COD_{sol})/VS and volatile fatty acids (VFA)/VS received at 22 ± 5 °C using specific energy (Es) inputs of 1000, 3000, 6000, 9000, 14000 (±500) kJ/kg TS. The thermal pre-treatment applied was the hygienization treatment required according the ABP regulation (70 °C, 60 min, particle size ≤12 mm; European Parliament and Council (EC), 2002). First, the slurry was heated up to 70 °C (Heidolph MR 3001, Germany) and then set in an incubator (Termaks TS 8056, Norway) for one hour.

2.3. Batch experiments

BMPs were determined in duplicate in two liter glass bottles incubated statically at 35 °C. BMP of the raw slurry was compared to those of ultrasound pre-treated and pre-hygienized slurries. The methane production of the inoculum was measured and subtracted from the methane yield of the slurries. Inoculum (600 g/batch) and slurry were added into the bottles in a $VS_{substrate}/VS_{inoculum}$ ratio of 1. Distilled water was added in order to achieve a liquid volume of 1.2 l. The pH value of each batch was adjusted to 7.0 (2 M NaOH and 6 M HCl), and sodium bicarbonate ($NaHCO_3$, 3 g/l) added as the buffer. Headspaces of the bottles were flushed with nitrogen gas for 5 min, after which the bottles were sealed with rubber septa. The produced biogas was collected into aluminium gas bags (Tesseraux Spezialverpackungen GmbH, Germany). The bottles were static except for manual mixing during gas measurements.

2.4. Analyses and calculations

Biogas volume and methane content, TS, VS, COD_{sol}, VFA, N_{sol}, ammonium nitrogen (NH_4-N^+), pH and specific methanogenic activity of inoculum (SMA) were analysed as described previously (Luste et al., 2009; Luste and Luostarinen, 2010). Biogas results are given at in normal (NTP) conditions (0 °C, 1 atm). Hydrolysis of soluble lignin related compounds (LRC_{sol}) was estimated from filtered (Whatman GF/A glass microfibre-filters, 1.6 μm) samples and analyzed in a Perkin Elmer Lambda 45 UV/VIS spectrometer (absorbance of 280 nm; Larrea et al., 1989), with the lignin-model-compound and the dissolution product 4-hydroxymethyl-2-methoxyphenol (Merck, purity >98%) as the standard (Crestini et al., 2005; Lahtinen et al., 2009) to monitor the degradation of lignin structures.

VS-based hydrolysis parameters (COD_{sol}/VS, VFA/VS, N_{sol}/VS, LRC_{sol}/VS) were used in the calculations of the results to avoid the changes in VS occurring during the pre-treatments (evaporation, dilution) and to enable comparisons of hydrolysis and degradation between the slurries with different viscosities. The Es input for ultrasound treatments was calculated with Formula (1), also enabling economical estimates and further energy balance calculations of the biogas process:

$$E_s\left[\frac{kJ}{kgTS}\right] = \frac{Pt}{VTS_0} \tag{1}$$

where P = ultrasound power, t = duration, V = volume of ultrasound pre-treated material and initial TS (Bougrier et al., 2005). The Es input for hygienization was calculated with Formula (2).