Biogas from cattle manure as an alternative energy source

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Abstract
Research into alternative renewable energy sources is a global objective aimed at sustaining the current standard of living in developed countries. Biogas production offers a very promising option for generating renewable energy. Asturias, a region in the north of Spain, has a large population of dairy cattle. The industrialization of cattle farming in the region has led to surplus manure, around 696400 t/year. The objective of this research was to study the co-digestion of cattle manure with glycerine. A series of experiments were carried out under mesophilic conditions using batch reactors (CSTR) containing mixtures of cattle manure with different amounts of glycerine. The effect of pre-treatment by the application of ultrasound was also analysed. Results indicate that the addition of glycerine (4%) increases biogas production up to 4-fold. If sonication is applied as a pre-treatment, the production of biogas can be increased up to 8-fold with respect to untreated manure.
Keywords: cattle manure, glycerine, biogas, ultrasound, energy

1. INTRODUCTION

Asturias, a region in the north of Spain, has a large population of dairy cattle. The industrialization of cattle farming has led to surplus manure that cannot be used as fertilizer in certain areas with insufficient farming surface. Furthermore, the highest concentration of dairy farms (where cows are usually kept in stables) is found in the vicinity of the coast, where the removal of cattle manure by means of its use as a fertilizer may lead to environmental problems. The amount of surplus manure is estimated at 696400 t/year.

The authors of the present research had previously studied the anaerobic treatment of cattle manure in the mesophilic and thermophilic range using UASB reactors at the laboratory scale, obtaining high organic matter removal rates, although the amounts of biogas produced was not very high [1,2]. For a HRT of 16 days (Organic Loading Rate of 3.68 kg COD m^{-3} day^{-1}), for example, COD removal was 69.7% and the production of biogas was 0.20 m^3 kg^{-1} COD removed, with a methane percentage of 73.7%. It is a well known fact that biogas production from manure is usually low. For this reason, biogas plants are difficult to run with economically profitable results if the process is based solely on cattle manure. Co-digestion strategies are therefore widely applied in order to enhance methane production in biogas plants. In Denmark, the digestion of manure and organic waste is a well-established technological practice (Centralised Biogas Plants). For example, the Vester Hjermitslev Biogas Plant treats 54 t/day of animal manure and alternative biomass, under mesophilic conditions, obtaining a biogas production of 50.7 Nm^3/ton of waste; the Vegger Biogas Plant treats 59 t/day of animal manure and alternative biomass under thermophilic conditions obtaining a biogas production of 97.5 m^3/ton of waste.

Macias-Corral et al (2008) [3] studied the anaerobic co-digestion of dairy cow manure, the organic fraction of municipal waste and cotton gin waste. The maximum biogas production was obtained in this case for the co-digestion of cow manure and cotton gin waste (87 m^3 methane/ton of dry waste). Callaghan et al., 2002 [4], studying the co-digestion of cattle slurries with fruit and vegetable wastes (FVW) and with chicken manure, found that increasing the proportion of FVW from 20% to 50% improved the methane yield from 0.23 to 0.45 m^3 CH_4/kg VS added. Capela et al., 2008, [5] evaluated the technical feasibility of anaerobic co-digestion of three types of organic solid waste under mesophilic conditions: the organic fraction of municipal solid waste (OFMSW), industrial sludge and cattle manure. Different proportions of each substrate were used and the results showed that increasing the OFMSW in the mixture generally resulted in higher methane production and volatile solids reduction. The treatment of solid slaughterhouse waste, fruit-vegetable waste and manure in a co-digestion process was experimentally evaluated by Alvarez and Liden, 2008 [6]. The digestion of mixed substrates was in all cases better than that of the pure substrates, with the exception of the mixture of equal amounts of (VS/VS) solid cattle-swine slaughterhouse waste with fruit and vegetable waste. Methane yields were in the range 0.27 - 0.35 m^3/kg VS added, obtaining VS reductions between 50% and 67%.

As regards research on the effect of different pre-treatments used to increase the biodegradability of manure, González-Fernández et al (2008) [7] studied the effect of mechanical, chemical and thermal pre-treatment to improve methane production and anaerobic biodegradability of swine waste. The soluble COD was increased by 57% and 32% during the pre-treatment period with alkali and the thermal treatment, respectively. In addition, these two pre-treatments gave the highest enhancement in methane production with respect to the untreated sample. However, the addition of a flocculant improved methane production of the liquid fraction, but not that of the solid one. Mechanical pre-treatment did not result in any significant enhancement. With respect to ultrasound, it was shown that this treatment can improve the biodegradability of many types of waste, but it is necessary to find the optimal ultrasonic power level and treatment time. Xie B. et al, 2009 [8] studied the enhancement effect of low-intensity ultrasound on anaerobic sludge activity and the efficiency of anaerobic wastewater treatment. The chemical oxygen demand (COD) removal efficiency was increased by ultrasonic treatment, the COD in the effluent being 30% lower than that of the control (without exposure to ultrasound).

Directive 2003/30/CE requires that the use of biofuels must reach 5.75% of the total fuel used in vehicles in the European Union by 2010. At the present time, the most viable solution is the use of FAME (Fatty Acid Methyl Ester), conventionally known as biodiesel. There are two plants operating in Asturias that produce biodiesel from used vegetable oil. Glycerine is obtained as by-product in this process. To the best of our knowledge, little research has been carried out on the co-digestion of cow manure and glycerine. However a very interesting study was carried out by Amon et al., 2006 [9], in which glycerine was added in increasing amounts to a mixture of maize silage, pig manure and rapeseed meal at 38-40ºC. The addition of 6% glycerine to pig manure and maize silage resulted in a significant increase in CH_4 production from 0.57 to 0.68 m^3 CH_4/kg VS. The co-fermentation effect was especially high with glycerine additions of 3-6%.

The goal of the present research work was to study the effect on biogas production of the co-digestion of cattle manure with glycerine. A series of experiments were carried out in CSTR containing mixtures of cattle manure with different amounts of glycerine under mesophilic conditions. In addition, the effect of pre-treatment by means of the application of ultrasound was studied.

2. MATERIAL AND METHODS

2.1. Material

The glycerine was collected from a plant, located in Asturias, which produces biodiesel from used vegetable oil. The plant produces around 400 tons of glycerine per year as a by-product. The cattle manure used in the study came from a farm with 120 cows, which are kept in stables in a free stall barn. Samples were taken from the manure cesspit, always attempting to collect these after prior agitation of the cesspit. Samples were collected in 20-L plastic bottles, transported to the laboratory, stored at 4 °C and subsequently characterized.

2.2. Equipment employed

The reactors used were 2-L capacity jacketed batch reactors (CSTR) made of glass and provided with automatic temperature and pH control. The biogas was collected in TEDLAR bags and samples from the digestat were taken from an outlet located near the bottom of the reactors.

2.3. Analytical Methods

The parameters analysed in order to characterise both types of waste (manure and glycerine) and to monitor the performance of the reactors were: pH, total solids, total volatile solids, chemical oxygen demand (COD), total nitrogen and ammonium nitrogen, total phosphorus and volatile fatty acids. Samples from the reactors (digestat) and from the produced biogas were taken twice a week to monitor the biodegradation process. COD was determined in accordance with Method 5220 D (closed reflux, colorimetric method) of the Standard Methods for the Examination of Water and Wastewater [10] using a Visible–UV Perkin Elmer Lambda 35. Ammonium-nitrogen was determined by titration with boric acid after distillation using a FOSS TECATOR Kjeltec 2200 Auto Distillation System. Total nitrogen and total phosphorus were determined by ion chromatography (861 Advanced Compact IC 2.861.0010) after their transformation in nitrates and phosphates, respectively, by digestion under pressure with H_2O_2 and HNO_3 in a microwave oven (Milestone Ethos 1 Advanced Microwave Digestion Labstation). Volatile fatty acids were determined by gas chromatography using a Perkin Elmer AutoSystem XL system, equipped with a FID detector. Finally, the content in methane and carbon dioxide in the biogas was measured by gas chromatography using a TCD detector.

2.4 Methods

A series of experiments using CSTR containing cattle manure or mixtures of cattle manure with different glycerine proportions were carried out under mesophilic conditions. The cattle manure was strained through 2 mm sieve in order to remove straw.

To studying the influence of ultrasound, the cattle manure as well as mixtures of cattle manure and glycerine were treated in a cell-breaker (Bandelin SONOPLUS UW 3200, 20 kHz) for different periods of time (from 1 to 8 minutes) in order to find the most suitable sonication time to achieve maximum solubilization of the COD. Temperature and COD values were measured for the analysis of the results.

The experiments were carried out using the following as substrates: cattle manure, cattle manure + 4% glycerine, cattle manure (treated with ultrasound) + 4% glycerine, cattle manure + 4% glycerine (mixture treated with ultrasound) and cattle manure (treated with ultrasound) + 6% glycerine. No inoculum was needed for the start-up of the reactors as previous results had shown similar behaviour in the reactors regardless of whether an inoculum was added or not.

3. RESULTS AND DISCUSSION

3.1. Characterization of the cattle manure and glycerine

Table 1 shows the characteristics of the cattle manure and glycerine employed in this study. The cattle manure has a total solid content of around 42 g/L, volatile solids representing around 59%, and a COD of around 41 g/L. Nitrogen is found in both organic and ammonium forms, the average values being 2 g/L and 1.4 g/L, respectively. Total phosphorous values varied around 1.85 g/L. Glycerine has a high organic content, with a COD of 840 g/L. Nitrogen and phosphorous was not detected.

Table 1. Physico-chemical characteristics of the cattle manure and glycerine

Parameter	Cattle manure	Glycerine
pH	7.15 ± 0.15	7.65 ± 0.32
Moisture (%)	95.77 ± 0.23	2.07 ± 0.34
Methanol (%)		10.5 ± 0.15
Total Solids (g/L)	42.23 ± 2.38	
Volatile Solids (g/L)	25.23 ± 0.64	843.54 ± 12.34
Total COD (mg/L)	41314 ± 1115.57	837230 ± 1438
Soluble COD (mg/L)	35628 ± 834.25	
Total Nitrogen (g/kg)	3.55 ± 0.02	ND
Ammonium Nitrogen (mg/L)	1400 ± 0.01	ND
Total Phosphorus (g/kg)	1.85 ± 0.01	ND
Acetic acid (mg/L)	2015.31 ± 15.32	
Propionic acid (mg/L)	1106.07 ± 12.54	
Butyric acid (mg/L)	566.27 ± 34.81	
Valeric acid (mg/L)	157.49 ± 51.02	
Isobutyric acid (mg/L)	200.13 ± 32.47	
Isovaleric acid (mg/L)	1075.34 ± 2.71	

ND: Not Detected

3.2. Pre-treatment by sonication

Figure 1 shows the influence of ultrasound treatment on the total and soluble COD for a mixture of the liquid fraction of cattle manure plus 4% of glycerine. The most suitable sonication time to obtain a maximum soluble COD was 4 minutes. Longer sonication times did not lead to any further increase in soluble COD. Similar results were obtained for the other cases analyzed. Temperature increased with sonication time. After 4 minutes of sonication, the temperature varied around 38ºC.

3.3. Production of biogas

Figure 2 shows the production of biogas with time for the different substrates studied. The amount of biogas generated when adding only cattle manure to the reactor was 1.42 m^3 biogas/t, with a methane content of around 60%. When the cattle manure was pre-treated by ultrasound, the amount of biogas produced was twice that produced without pre-treatment (3.1 m^3 biogas/t).

On adding 4% of glycerine (in volume) as co-substrate, biogas production increased 400% (5.88 m^3 biogas/t). Pre-treatment of the mixture (manure + 4% glycerine) by ultrasound improved the results obtained, the production of biogas increasing to 11.6 m^3 biogas/t. This supposes an increase of 800% with respect to the untreated manure without the addition of glycerine.

The best results obtained under mesophilic conditions were found when adding 4% glycerine as co-substrate; biogas production decreased when adding 6% glycerine (Figure 2). Experiments are currently being carried out under thermophilic conditions. On the basis of preliminary results, it would appear that increasing the amount of added glycerine to 6% thus not produce an inhibitory effect, thus resulting in a higher production of biogas.

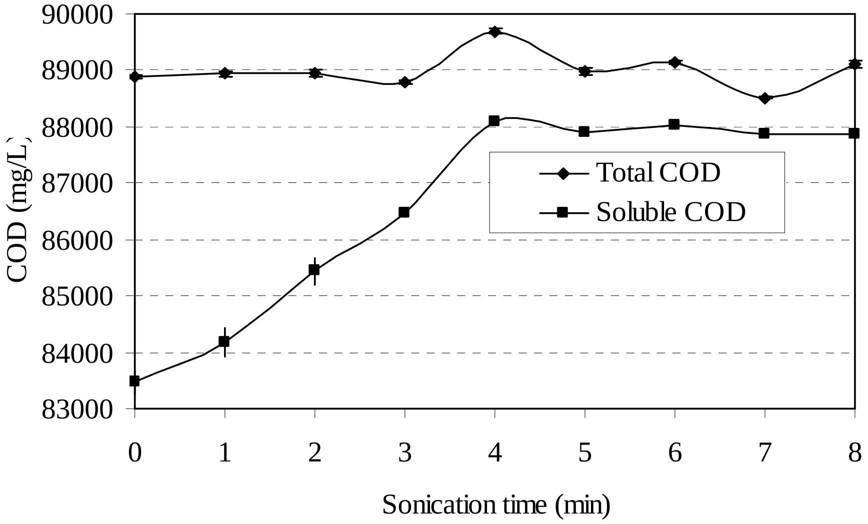

Figure 1. Influence of ultrasound on total and soluble COD for a mixture of cattle manure plus 4% glycerine

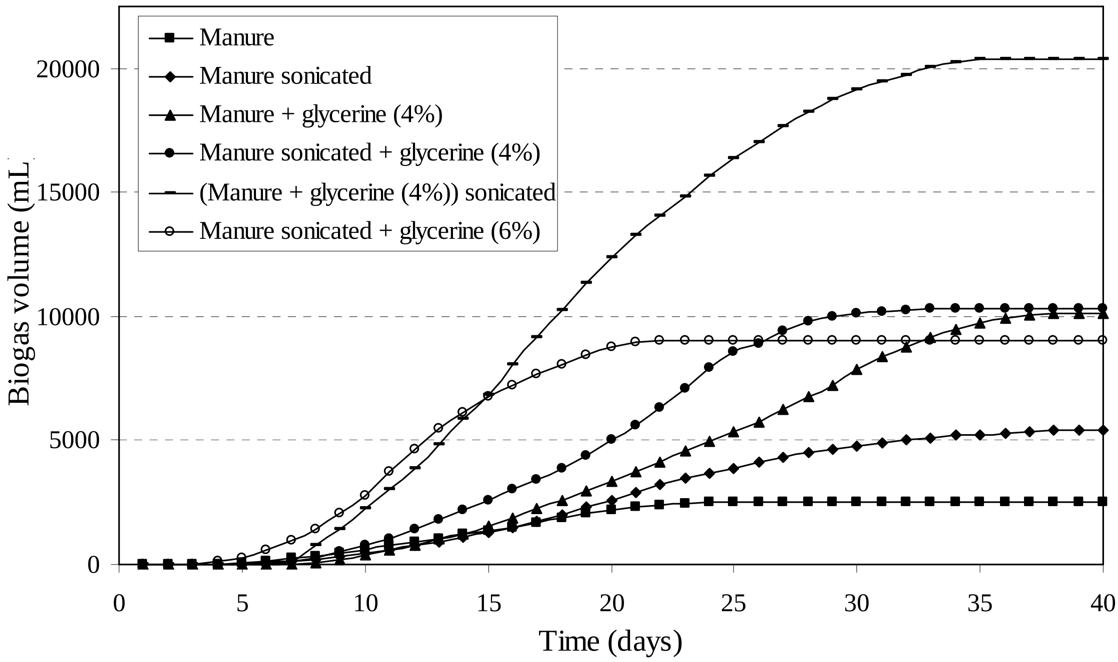

Figure 2. Production of biogas in different cases

4. CONCLUSIONS

The most suitable sonication time to obtain maximum solubilization of the COD for cattle manure and mixtures of cattle manure and glycerine was found to be 4 minutes. When applying ultrasound as a pre-treatment, the production of biogas in the anaerobic digestion of cattle manure or mixtures of cattle manure and glycerine as co-substrate under mesophilic conditions increased up to 200%.

The addition of small amounts of glycerine to cattle manure strongly increases biogas production. The best results obtained under mesophilic conditions were found when adding 4% glycerine as co-substrate. Co-digestion under thermophilic conditions is currently being studied. Preliminary results indicate that the amount of added glycerine can be increased to 6%.

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