Wat. Sci. Tech. Vol. 25, No. 7, pp. 311–318, 1992.
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0273–1223/92 $15·00

ANAEROBIC TREATMENT OF MANURE TOGETHER WITH INDUSTRIAL WASTE

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ABSTRACT

A joint large-scale biogas plant treats animal manure together with organic industrial and household solid waste and produces biogas and organic fertilizers. In the presentation we will discuss the importance of combined treatment of manure and organic waste. Furthermore, data will be shown on the effects of addition of lipid- and protein- containing wastes to thermophilic digesters treating cattle manure.

KEYWORDS

Biogas plant; manure; organic waste; thermophilic digestion.

INTRODUCTION

Under the Danish Action Program for Joint Large-Scale Biogas Plants starting in 1988, nine large biogas plants have been built. All the plants use single-phase digestion in fully agitated digesters and they treat from 40 tons to 400 tons of organic materials per day. Six plants use mesophilic digestion (35°C), while the remaining use thermophilic digestion (55°C). Four of the mesophilic plants include a special heat treatment (thermophilic pre-sanitation) between the pre-storage tank and the digesters to ensure a reduction of pathogens and also to increase the gas yield from the biomass.

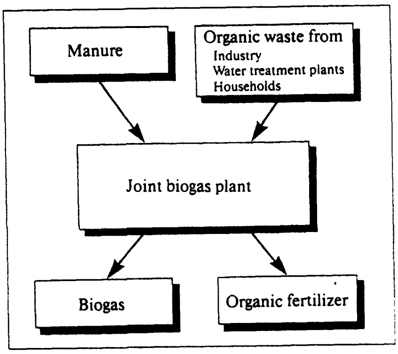

Fig. 1. Principle of Joint Biogas Plant

Tabel 1 Manure And Organic Waste Products That Are Realistically Usable In Biogas Plants In Denmark

	Dry content 1000 tons VS/year	Energy-potential TJ/year
Manure	1568	12383
Organic industrial waste	34	426
Source-sorted domestic waste	76	609
Sludge from water treatment plants	23	130
Total	1701	13548

Some of the plants have special devices for treatment of the degassed biomass, separating out the fibre fraction which is then converted into compost. A joint large-scale biogas plant converts animal waste and several kinds of organic waste from industries and households into biogas and organic fertilizer (Figure 1).

The animal waste comes from several farms and is transported to and from the biogas plant. Some plants have facilities for storage of the digested manure which then is returned to the farmers when needed as a fertilizer. The plant can treat all sorts of organic waste which do not contain toxic substances demanding a special care during handling and later deposit. The organic waste comes from slaughter-houses and food processing industries or will be source-sorted household solid waste. These materials normally contain a high concentration of easily degradable substrates, such as carbohydrates, lipids, and proteins having a high biogas potential which can increase the economical feasibility of the biogas plant. However, as the purpose of the joint large-scale biogas plants first of all is to treat animal manure and reuse the material as fertilizer, a maximum of 20% of organic industrial waste is allowed and this represents the approximate level of additional waste added to manure today in the existing biogas plants (Figure 2).

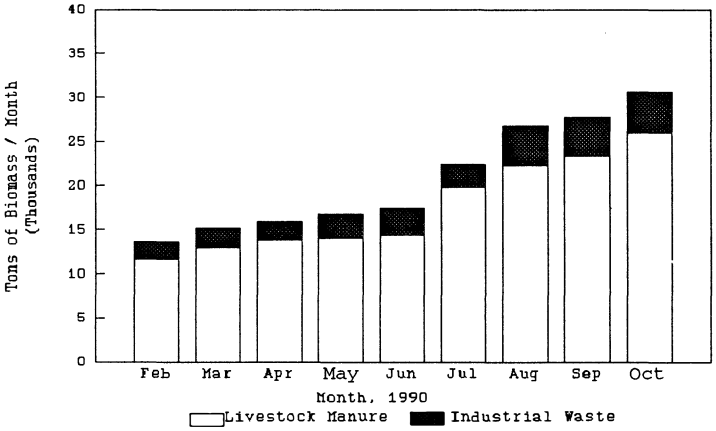

Fig. 2. Biomass treated in joint large-scale biogas plant, 1990

By the combined treatment of manure together with industrial and household solid waste, the joint large-scale biogas plants play an important role in decreasing the pollution from the materials treated. The plants offer a way for distributing manure between farmers as needed, and prevent landfilling of organic waste. At the same time, the plants will work for a recirculation of the nutients in the materials to the farmland and, thereby, decrease the need for additional fertilizers. Lastly, the biogas produced is a renewable energy source that can displace oil and coal, with all the environmental advantages this implies. Recently, the importance of biogas plants for reduction of the uncontrolled release of methane to the atmosphere from manure and organic waste has been emphasized.

Organic waste suitable for biogas production

As can be seen from Table 1, manure is by far the largest volume of biomass realistically usable for biogas production. If the future plants should receive approximately 20% organic waste it can be calculated that only approximately 15 new large-scale biogas plants can be built due to a shortage of organic waste. This means that the future biogas plants probably will have to be based on a much smaller supplement of easily degradable substrates and that a greater knowledge of the optimal "cocktail" is of importance.

A list of the different types of organic waste utilized today in joint large-scale biogas plants is shown in Table 2. Most of the different organic wastes added have a high volatile solids (VS) content and the theoretical methane yield is normally high, especially when the waste contains a high concentration of lipids.

TABLE 2 Characteristics Of Some Types Of Industrial Organic Waste.

Type of industrial organic waste and typical characteristics	Composition of the organic material	Organic content (%)	Methane yield (m^3/ton)
Stomach & intestine content	Carbohydrates, proteins and lipids	15-20	30-50
Floatation sludge	65-70% proteins and 30-35% lipids	13-18	80-100
Bentonite-bound oil (BBO)	30-35% lipids and 5-10% other organic material	40-45	300-350
Fish-oil sludge (FOS)	30-50% lipids and other organic material	80-85	450-500
Source-sorted household solid waste	Carbohydrates, proteins and lipids	20-25	40-60
Whey	75-80% lactose and 20-25% protein	8-12	30-40
Size water	70% proteins and 30% lipids	10-15	40-55

Due to the addition of organic waste, the daily gas production per m^3 reactor volume has increased remarkably in all the large biogas plants. The daily biogas production is today approximately 1.5 to 2 times the reactor volume in the mesophilic plants while the thermophilic plants on average produce more than 2.5 times their reactor volume. In the thermophilic plant in Vegger, a gas production of up to 7 times the reactor volume has been obtained for longer periods digesting cattle manure in combination with bentonite-bound oil and fatty sludge.

In the following we will discuss in more detail the experiences from laboratory and full-scale digestion of manure together with two particular types of waste: bentonite-bound oil (BBO) and size water.

Bentonite-Bound Oil

Bentonite-bound oil (BBO) is a waste from edible oil production which is produced during cleanup and decolorization of vegetable oils. The oil consists mainly of rape seed oil together with the clay mineral, bentonite (montmorillonite). Neutral lipids (fat and oil) are hydrolyzed in a biogas reactor by hydrolytic enzymes, produced by fermentative bacteria, to long-chain fatty acids (LCFA) and glycerol (Figure 3). The main part of the energy content of oil is conserved in the LCFA (Weng and Jeris, 1976; Hanaki *et al.*, 1981).

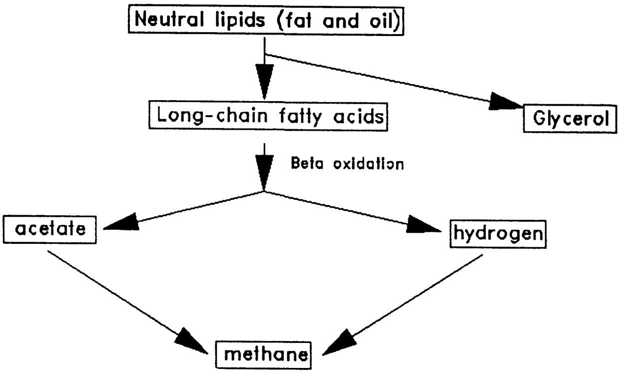

Fig. 3. Anaerobic degradation of oil

BBO was one of the first types of organic industrial waste introduced into the biogas plants. At a concentration of approximately 3%, it was shown in the thermophilic plant in Vegger to increase the gas production significantly and to stabilize the whole digestion process by decreasing the concentration of volatile fatty acids (VFA) in the effluent. Estimates over the gas production on the plant further indicated that more gas was produced than could be accounted for by the extra substrate added. To investigate the digestion of BBO and its influence on the digestion of manure in more details, a number of laboratory experiments were conducted.

<u>Digester experiments.</u> The effect of BBO was tested in six semi-continuous thermophilic (55°C) digesters fed with raw cattle manure (8.9% TS and 5.9% VS) and run with a retention time of 15 days. Two digesters were fed with manure alone and served as controls. The third digester was fed with manure with 1.65% bentonite added, corresponding to the amount of bentonite in 3% BBO. The fourth digester was fed with manure with 1% oil added, extracted from BBO and corresponding to the amount of oil in 3% BBO. The last two digesters were fed with manure with addition of 3% and 6% BBO, respectively. Figure 4 shows the biogas production from the digesters after a long adaptation period of 40 days.

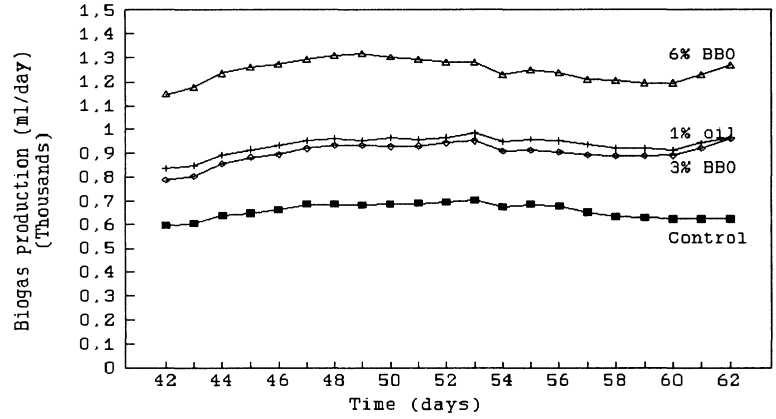

Fig. 4. Biogas production in the different digesters

The performance of the digesters fed with manure and bentonite was similar to the two control digesters, indicating no apparent effect of addition of bentonite alone. Addition of oil and 3% BBO results in the same increase in the gas production while 6% increased the gas production nearly 2 times the level with 3% BBO added. To evaluate the gas production from the reactors receiving oil or BBO, a relative oil utilization (%) was calculated by using this formula: measured methane production minus the methane production of the control digesters relative to the theoretical methane yield of the amount of oil added. Table 3 shows the relative oil utilization after different periods of operation of the digesters.

TABEL 3 Relative Oil Utilization Of Oil Added In Different Forms

Days of Operation	Oil Utilization (%) 1% Oil	3% BBO	6% BBO
10	-5	44	18
20	31	58	45
75	71	75	76

Addition of 1% oil to the digesters caused an immediate inhibition of the digestion process resulting in a negative oil utilization after 10 days operation. However, when the oil was added as 3% BBO, nearly half of the oil was metabolized during the same period. When the concentration of BBO was increased to 6%, the oil utilization was still reduced compared to the digesters with 3% BBO. After 75 days of operation all digesters exhibited nearly the same degree of oil utilization, approx. 75%. The results show that a large part of the oil will be utilized in addition to manure. However, an adaptation period is needed and bentonite helps to decrease this period.

Batch experiments with glyceride trioleate and oleate. The effect of oil on thermophilic digestion of manure was further studied in a number of batch experiments. Glyceride trioleate (GTO) was chosen because it accounts for approx. 55% of the oil in BBO. A concentration of 5 g/l GTO was found inhibitory and resulted in a negative oil utilization, indicating a general inhibition of the anaerobic digestion process, and with 2.5 g/l GTO added, a positive oil utilization was only observed in vials which also contained bentonite (4 g/l) (Ahring and Angelidaki, 1990). Addition of 0.5-1.5 g/l GTO resulted in approx. 80% oil utilization indicating that the inhibition is concentration dependent. This result shows that addition of oil has to be kept under a level of approx. 2 g/l GTO to prevent inhibition of the process.

Previous experiments with addition of GTO to manure have shown that oil is quickly hydrolyzed to oleate and glycerol (Angelidaki *et al.*, 1990). To further study the effect of neutralized and free fatty acids on the anaerobic digestion process, a second set of batch experiments was performed. When 6.2 g/l GTO (corresponding to 6 g/l oleate) and 6 g/l oleate were added to thermophilic digested manure adapted to 3% BBO originating from the biogas plant in Vegger, it can be seen that only the vials with GTO showed a positive oil utilization of about 15% after 20 days with no further increase (Figure 5). The vials with oleate were inhibited for the whole period.

These results indicate that the free long-chain fatty acids are the toxic component of lipids. In accordance with this, recent experiments in our laboratory have shown that only a very low concentration of oleate (0.1 and 0.5 g/l) is needed to cause initial and total inhibition of the anaerobic digestion process (Angelidaki and Ahring, submitted for publication). Furthermore, the inhibitory effect was solely dependent on the concentration of oleate and no adaptation to higher concentrations of oleate occurred. The reason for the low utilization of GTO could be that oleate accumulates to an inhibitory level during the hydrolysis of GTO due to a rapid hydrolysis of GTO to free oleate and relatively slower acetogenic degradation of oleate. Adaptation to oil, therefore, may be due to development of acetogenic bacterial populations that can degrade the free long-chain fatty acids, as they are released from the neutral oil by hydrolysis, at an adequate rate to prevent their accumulation to inhibitory concentrations.

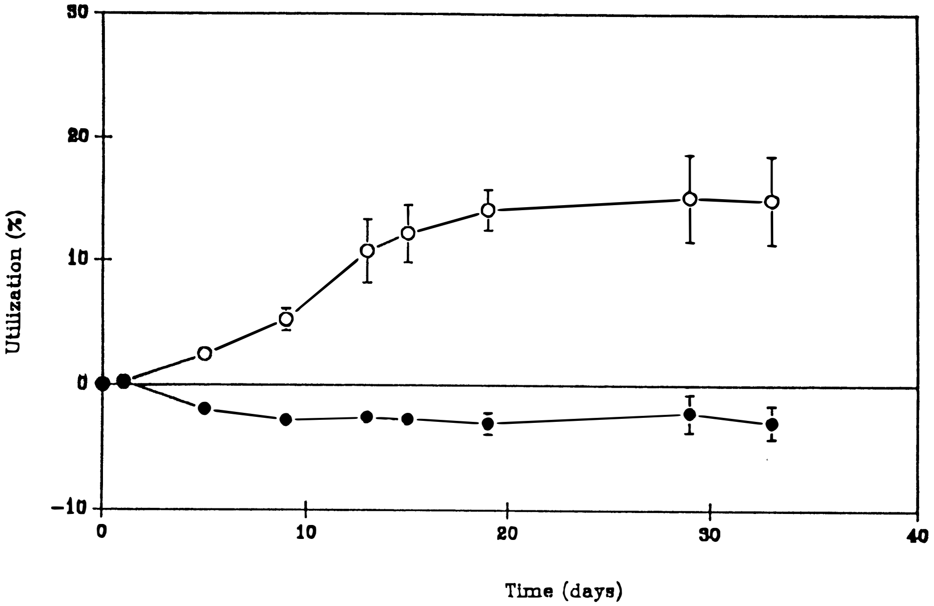

Fig. 5. Relative oil utilization with 6.2 g/l GTO, ● and 6 g/l oleate, o added

Effects of BBO on process stability. It has generally been observed at the thermophilic joint large-scale biogas plants that addition of BBO gives a more stable digestion process. However, due to the many factors normally varying at a full-scale plant, it is difficult to get reliable data in support of this observation. Recent experiments in our laboratory have shown that addition of BBO under some conditions can stabilize inhibited thermophilic reactors, leading to a lower effluent VFA concentration supporting the observations found from the biogas plants (data not shown).

Conclusions on addition of BBO. In conclusion, the experiences from full-scale treatment and the results from the laboratory experiments show that the lipid-containing waste, BBO, is suitable for addition to anaerobic reactors treating manure. Most of the extra carbon added will be converted, but we found no indications of a better conversion of the manure itself. Our results further show that the free long-chain acids formed during hydrolysis of oil can be inhibitory for the whole process. These results show the importance of a slow, gradual introduction of lipid-containing organic waste into biogas plants allowing the development of the microbial populations necessary for the removal of the free long-chain fatty acids.

Size Water

Size water is a waste originating from the extraction of protein from bones. The waste product has a high protein content and it also contains some lipids. Pure protein has been shown to be degraded at a high rate to volatile fatty acids (Beure and Van Andel, 1984; Beure *et al.*, 1985). However, experiments have shown that it can be difficult to degrade protein together with carbohydrates. The easily degradable substrates may repress the synthesis of exoproteases in the bacteria cultures tested (Glenn, 1976; Pansare *et al.*, 1985; Whooley *et al.*, 1983). As under aerobic conditions, deamination of amino acids under anaerobic conditions involves a coupled oxidation-reduction reaction (Stickland reaction) between two amino acids, one acting as hydrogen donor and the other as hydrogen acceptor (Nagase and Matsuo, 1982). Degradation of protein can also lead to increased levels of ammonia which can inhibit the process as a whole.

Full-scale experiences with addition of size water. Figure 6 shows the concentrations of VFA after addition of size water (approx. 5%) to a full-scale digester in Vegger converting manure together with BBO (3%). Shortly after size water was introduced into the reactor the VFA concentration increased from a level of approximately 300 mg/l, as acetic acids, to 4000 mg/l.

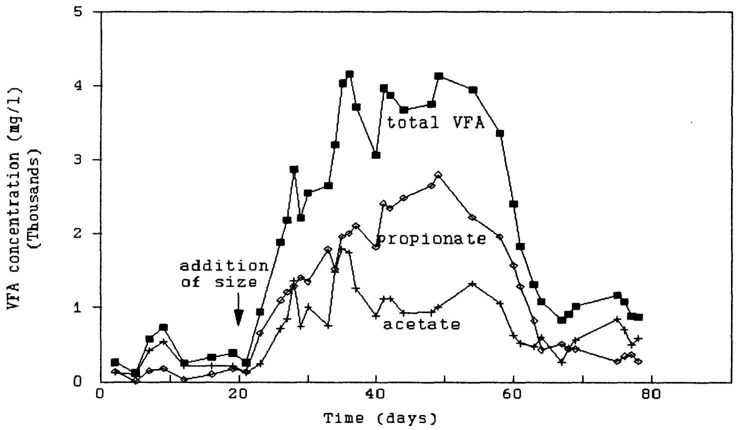

Fig. 6. Effect of addition of size water to Vegger biogas plant

Interestingly, the propionate concentration increased more rapidly than the acetate concentration, resulting in a P/A (propionate/acetate) ratio of ca. 2. This fact further indicated that the reactor was seriously inhibited (Hill *et al.*, 1987). At the same time the biogas production decreased (data not shown). The concentration of VFA was high for the following month, after which it suddenly dropped without any obvious reasons.

Conclusions on the addition of size. Addition of a waste with a high concentration of protein resulted in an immediate inhibition of the digestion process. However, the process was found to stabilize at an effluent concentration of 4000 mg/l VFA and a reduced biogas production for a period of 1 month with continuous addition of approx. 5 % size added. After this period, the process adapted to the waste, demonstrated by a decrease in the effluent VFA concentration to the same low level as before addition of the waste and by a high and constant gas production.

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