Codigestion of manure and organic waste at centralized biogas plants: process imbalances and limitations

H.B. Nielsen*,** and I. Angelidaki*

*Department of Environmental Engineering DTU, Technical University of Denmark, building 115, 2800 Lyngby, DK-Denmark, telephone +4545251429, email: ria@env.dtu.dk
**Biosystems Department, NRG-Group, Risø DTU, National Laboratory for Sustainable Energy, Technical University of Denmark, building 301, 4000 Roskilde, DK-Denmark, telephone: +4546774126, email: henrik.bangsoe.nielsen@risoe.dk

Abstract
The present study focuses on process inhibitions in Danish centralized biogas plants. Collection of data from the plants and a number of interviews showed that inhibitions occur frequently. High concentrations of ammonia, long chain fatty acids or other inhibitory compounds, and foaming in prestorage tanks are well known causes of inhibition. These problems mainly occurs due to: 1) inadequate knowledge about the waste composition and 2) its degradation characteristics, 3) inadequate process surveillance especially with regard to volatile fatty acids and 4) insufficient pre-storage capacity causing inexpedient mixing of the different waste products in the pre-storage tanks.

Keywords
Centralized biogas plants, process imbalances.

INTRODUCTION

Today, 20 centralized biogas plants and more than 60 farm-scale plants are in operation in Denmark. The main purpose of the centralized plants is to treat livestock manure and reuse the material as fertilizer (Ahring et al. 1992). The methane yield from manure is relatively small and in order to increase the biogas production, the plants co-digest manure together with other organic waste from food industries and municipalities (Angelidaki and Ellegaard 2003). The co-substrates – rich in lipids, proteins and carbohydrates - are essential for the plant's economy, but might lead to disturbances if not handled properly. Several of the Danish centralized biogas plants have been exposed to process imbalances that could be directly related to the composition of the substrate. However, the significance of the problem is unknown and in the present study we, therefore, focus on this topic. We present data obtained from several of the Danish centralized biogas plants and give examples of imbalances caused by the treatment of industrial waste. We propose reasons for the cause of the imbalances on a practical and microbial level and verify our theories with data from experimental results from our laboratory.

MATERIALS AND METHODS

Process data from the plants was obtained directly from the plants (daily to monthly average) or via the Danish magazine "Dansk Bioenergi" (monthly average). A number of interviews with plant managers were also carried out. The obtained data and information was analyzed and used for additional experiments (case studies) investigation relevant topics related to specific inhibition incidents at the plants:

Residual methane production estimation: Estimation of the residual methane production, left over in the effluent-biomass, was determined in digested biomass from the main digestion step as well as from down stream digestion/storage steps from a number of centralized biogas plants. Samples of 300 ml was transferred to 1 liter serum bottles flushed with 80%/20% N_2/CO_2 and incubated at the same temperature as the main reactor were operating under. The methane production was measured frequently over a period of approximately two months.

Effect of codigestion of manure together with blood: The effect of temperature on the process stability during codigestion of blood and cattle manure was investigated in a lab-scale experiment consisting of two 4.5 liter continuously stirred tank reactors (CSTR). One reactor was operated at mesophilic conditions (37^{o}C) with a HRT of 20 days and 4 liters working volume. The reactor was inoculated with digested material from a mesophilic full-scale biogas plant. The second reactor was operated at thermophilic conditions (53^{o}C) with a HRT of 15 days and a working volume of 3 liters. This reactor was inoculated with digested material from a thermophilic full-scale biogas plant. Both reactors were fed once a day with cattle manure (7.0% TS, 5.5% VS, pH 7.21) that was diluted with distilled water in a ratio of 10:7. During start up (approximately 4 weeks) the feed volume was slowly increased to 100 ml/d. From day 0-17 of the experiment the loading was 100 ml/d (period 1) and from day 16-39 full loading – 200 ml/d - was applied (period 2-4). From day 40 the reactors was fed 160 ml manure/d supplemented with 40 ml blood/d (19.1% TS, 18.0% VS, 16.0 g-N/l) (period 3). This procedure was continued until the end of the experiment with regard to the mesophilic reactor while blood was omitted from the feedstock of the thermophilic reactor from day 60 due to a low methane production and high volatile fatty acid levels (VFA). From day 60 to the end of the experiment this reactor was, therefore, only fed with 200 ml manure/d (period 4).

Toxicity of tall oil: The toxicity effect of tall oil on the anaerobic digestion of cattle manure was tested in batch experiments. Crude tall oil contains rosins, unsaponifable sterols (5-10%), resin acids (mainly abietic acid and its isomers), long chain fatty acids (mainly palmitic acid, oleic acid and linoleic acid, abbreviated LCFA), fatty alcohols, some sterols, and other alkyl hydrocarbon derivates. Tall oil, also called liquid rosin or tallol, is a viscous yellow-black odorous liquid obtained as a byproduct of the Kraft process of wood pulp manufacture (ref: http://en.wikipedia.org/wiki/Tall_oil). 1 liter serum bottles was added 150 ml cattle manure (7.0% TS, 5.5%) and 250 ml inoculum (3.6% TS, 2.8% VS) from a pilot-scale reactor treating cattle manure. The bottles were flushed with N_2, closed with rubber stoppers and aluminum crimps, and incubated at 55ºC. Eight days after when a steady methane production was obtained, the bottles were opened and different concentrations of tall oil were added: 0,1 g/l, 1,2 g/l, 3 g/l, 6 g/l, 10 g/L. Finally the bottles were flushed and closed as was explained before, vigorously agitated and incubated at 55^{o}C. Controls bottles were not added tall oil and blanks consisted of 150 ml water and 250 ml inoculum not added tall oil. The experiment was performed in triplicates. The methane production was measured frequently during the entire experiment.

pH and ammonia/total N content were determined using standard methods (Greenberg et al. 1998). CH_4 production in batch experiments was measured by GC using flame ionization detection. CH_4 and CO_2 production from lab-scale reactors were determined by GC using thermal conductivity detection. For VFA determination, 1 ml samples was acidified with 70 µl 17% phosphoric acid, centrifuged at 10500 rpm for 20 min, and analyzed on GC equipped with flame ionization detector.

RESULTS AND DISCUSSION

Examples of biogas output from centralized biogas plants and unknown process imbalances

As mentioned, the frequency of process imbalances is unknown but a typical example of the biogas output from three different plants is illustrated in figure 1. During a period of 3 years one plant (figure 1a) had 4 production failures all lasting 3-6 weeks while another plant (figure 1b) had one severe process imbalance lasting for several months. The third plant that is illustrated (figure 1c) was exposed to two severe imbalances during a period of 10 years. The cause of imbalance in all examples was unknown. However, according to the interviews inhibition with long chain fatty acids was suspected in figure 1b, while ammonia inhibition was suspected in figure 1c. Besides actual process failures, the biogas plants are often not operated optimally with a large unexploited methane potential in the residual. In table 1 it is seen that up to 30% of the potential can be unexploited. The reason for this is often due to suboptimal reactor conditions that especially are caused by high ammonia concentrations in the reactors (> 4 g-N/l) (Angelidaki et al. 2005). Additionally, short HRTs like (10-13 days) and high fractions of industrial waste in the feedstock were connected to large methane potential losses. Such long term sub-optimal process conditions are more difficult to recognize than actual process failures and require either correlation of the plant's methane production with the expected methane production based on the influent feedstock or estimation of the process stability as indicated by VFA levels or by estimation of the residual methane potential of effluent biomass. Estimation of ammonia might in some cases be useful (see later) and is also performed at a few plants. However one should not forget that ammonia concentration does not reflect the state of the process, but are a cause of imbalance. Furthermore, the high impact of ammonia adaptation on the inhibitory level (Angelidaki and Ahring 1993; Hansen et al. 1998) makes ammonia concentration somewhat difficult to use as an indicator of suboptimal reactor performance.

Table 1. Methane loss in (%) at the Centralized biogas plants. The loss was estimated as the amount of methane produced from the residuals compared to the methane production of the main reactor.

Lintrup	Filskov	Hashøj	Århus	Snertinge	Revninge	Blåhøj	Ribe	Studsgård
21,2	2,9	11,8	24,5	10,3	9,8	8,3	30,7	3,6
Fangel	Blåbjerg	Vegger	Sinding-Ørre	Vaarst-Fjellerad	Vester-Hjermitslev	Nysted	Thorsø	Lemvig
10,5	27,0	4,4	17,4	6,1	20,1	14,0	15,0	11,0

Examples of well defined process imbalances and case studies

Example 1 - ammonia inhibition caused by degradation of blood. Figure 2a shows the reactor performance of a full-scale plant during digestion of blood. The plant has a reactor capacity of 7600 m^3 and consists of three equal sized reactors that are operated at 53^{o}C with a HRT of approximately 17–18 days. The plant treats approximately 362 tons manure/d together with approximately 75 tons/d alternative waste (organic industrial waste). From the 1st of September 2005 the organic industrial waste consisted of blood from pigs. An increase in ammonia concentration and VFA was seen immediately and from the middle of October a decrease in biogas production of approximately 32% was observed. The blood was omitted from the feedstock from the 10th of November and approximately 2 weeks after the biogas production was back at the original level. The whole inhibition period of the methane production lasted for approximately 6 weeks. Not surprisingly the data from the plant shows that the process imbalance could have been avoided if the warning by the increasing VFA concentrations had been applied in the operation procedures. Besides this, the sudden sharp increase in ammonia concentration also gave an indication of a rather unrestricted reactor operation and an unbalanced process. The data also raises the question if the operation temperature of the plant was suitable for treatment of the blood and if blood should have been added to the reactors at all. It is well known that the inhibitory effect of ammonia increases with temperature (Anthonisen et al. 1976). In this context, the process at the full-scale plant was simulated in a lab-scale reactor experiment at mesophilic and thermophilic temperatures (figure 2b-

2d). The loading with blood was approximately the same as in the full-scale plant (18-20% w/w). As in the full-scale plant an immediate significant increase in VFA concentration in the thermophilic reactor was observed when blood was added, while a more moderate increase was seen in the mesophilic reactor. A clear increase in methane production was also seen (highest in the mesophilic reactor) due to an increase of the organic loading with easily degradable blood. This increase was not seen as clear in the full-scale plant since blood was added as a replacement of other organic industrial waste. The methane production in the thermophilic reactor started to decrease after only 6 days of feeding with blood and the production never fully recovered during the experimental period, despite the fact that the reactor was not added blood from day 60. An inhibition/decrease of the methanogenesis in the mesophilic reactor was also seen from approximately day 55. Interestingly, the free ammonia concentration (NH_3) in that reactor were not high and well below the inhibitory level of 0.7-1.0 g-N/l that previously has been suggested (Angelidaki and Ahring 1993; Hansen et al. 1998). This pattern illustrates that not only free ammonia but also other components in the blood might have affected the process stability of the reactors.
The results of this case study show that operation temperature has a high impact on process stability during codigestion of manure with blood. The results also show that it not possible to obtain a stable codigestion of manure with blood neither at thermophilic nor mesophilic temperatures when applying the same loading conditions as at the full-scale plant. Therefore, we conclude that blood should be added only at small amounts and under careful process monitoring in order to avoid process inhibition at the plant.

Example 2 - acute inhibition by tall oil. During spring 2006 two mesophilic centralized biogas plants was subject to severe process inhibitions. In one of the plants, the reactors needed to be emptied and re-inoculated with digested biomass in order to reestablish the production. Prior to the inhibition the plant had been added tall oil twice within a few days in an amount of 6 g/l. Apparently tall oil had an acute toxic effect to the process. The methane potential of tall oil was estimated by the supplier to be "high", but no practical evaluation of the degradability/toxicity of the product was performed before it was added to the plant. The inhibitory threshold level of tall oil was evaluated in our laboratory (batch tests) and found to be as low as between 0.1 to 1.2 g/l (figure 3). Although inhibitions caused by LCFA sometimes can be easily distinguish in batch experiments than in reactor systems (Nielsen and Ahring 2006), the results shows that the knowledge about the waste composition and degradation characteristic was inadequate.

Example 3 - foaming in pre-storage tanks and reactors
Foaming in the pre-storage is a problem repeatedly observed at the Danish biogas plants. A sudden lowering of pH due to inexpedient mixing of different waste types leading to a CO_2-stripping is normally considered as the main reason to foaming incidents. The practical reason for most of the foaming problems is a limited number of pre-storage tanks (1-3) forcing the plants to mix the different waste products before feeding to the reactors (figure 4). Construction of more pre-storage tanks would help on the foaming problems and at the same time ensure a more precise dosing of the individual waste product, which would help increasing the process stability. Finally, a more precise identification and removal of the complex/inhibiting waste types would be possible if more pre-storage tanks were build.
Sometimes foaming is not only observed in the pre-storage tanks but also occurs inside the reactors. This is illustrated in figure 5. In this plant the foaming also affected the biogas production. Foaming started in the beginning of April 2003 and happened frequently during a period of almost 2 years. As a consequence of the foaming a slow but long term decrease in methane production was observed. Thus from June 2004 to March 2005 the production was 32% lower than before the foaming problems started. According to an interview with the plant the foaming could not be related to a specific substrate and the problem ended just as suddenly as it had started.

CONCLUSIONS

From our interviews with various plant managers together with our data-collection and lab-results we conclude that the most frequent process imbalances that occurs at Danish centralized biogas plants are related to the composition and handling of the substrates. High concentrations of ammonia and long chain fatty acids is often a cause of inhibition but foaming might also affect the biogas output of the process. The high concentrations of inhibitory compounds are allowed to occur as a result of:

a) Inadequate knowledge about the substrate composition.

b) Inadequate knowledge about the degradation characteristics of the waste, with regard to inhibition level and biogas potential.

c) Inadequate process surveillance, especially with regard to volatile fatty acids.

d) Insufficient pre-storage capacity and inexpedient mixing of the different waste products in pre-storage tanks, hindering exact dosing of specific waste to the reactors.

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