Final report

Increased biogas production by removal of ammonia from biogas reactors

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Content

1. Introduction

1.1. Aim of the project

The purpose of the project is to study the role of NH_3 for the anaerobic digestion process and quantify the influence of the NH_3 concentration on gas yield. Furthermore the aim is to find ways to reduce the ammonia concentration by removing the inhibitory ammonia (NH_3) from the biomass. The project will develop, analyse, demonstrate and optimize the technology based on membrane units effective in removing NH_3 from biogas reactors by continuously depleting NH_3 from biogas reactor gas phase (headspace). This is accomplished by a circulation of the headspace through both the reactor liquid and membrane unit.

1.2. Dessimination

The result of the project has been published in a scientific journal and the national journal "Forskning i Bioenergi":

Møller HB. og Sutaryo S. 2011. Kvælstof kan kvæle produktionen af biogas. Forskning i Bioenergi nr 35. marts 2011

Sutaryo S., Møller HB., Ward A. J. 2011. Ammonia inhibition in anaerobic digestion of Dairy cattle manure. Submitted to Green Energy.

2. Results and discussion

2.1. Influence on ammonia on methane yield

The project has studied the effect of five different concentration levels of total ammonia nitrogen (TAN) and free ammonia (FA) on the methane yield and digester performance at thermophilic conditions (50°C). The different Ammonia levels were obtained by adding urea to obtain the target level of TAN and FA and subsequently maintained at the same concentration during experiment by daily additions. A strong negative correlation was found between both TAN and FA concentrations and methane yield (R^2 = 0,98 and R^2 = 0.96 respectively). The methane yield during the period of stable gas production was reduced by 24, 30, 52 and 66% in digesters that had 2.1, 2.9, 3.6, 4.4 and 5.1 g TAN L^{-1} respectively corresponding to 0.5, 0.7, 1.1, 1.5 and 1.8 g FA L^{-1} respectively. The recovery in digesters that were highly loaded with ammonia was faster than the ones with moderate ammonia load indicating that the microorganisms in these digesters were better adapted to high ammonia concentrations.

The average methane yield in R1 treating cattle manure during the experiment was 171.05 ± 15.45 ml g VS^{-1}. Methane gas yield from each digester is summarized in Figure 1. The day after urea addition, methane pro-

duction in R2, R3, R4 and R5 dropped sharply then increased slowly and stabilized. This phenomenon indicated that there was acclimation of microorganisms to higher ammonia levels.
Figure 1 shows that the methane gas yield in digester 2 during treatment (mean TAN concentration = 3,02 ± 0,11 g L^{-1}) drops approximately 29% compared to the reference digester (TAN concentration = 2,26 ± 0,12 L^{-1}).

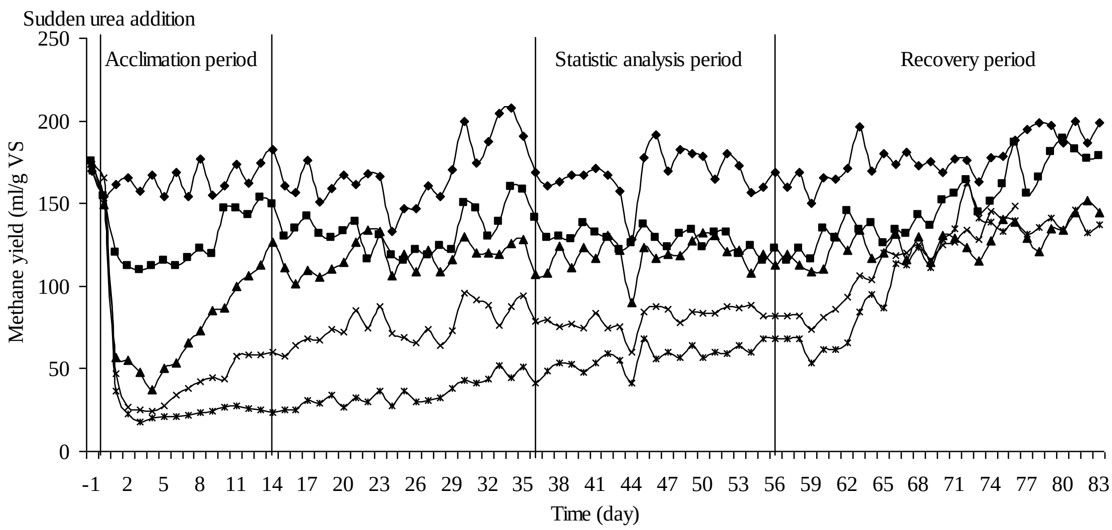

Figure 1. Methane gas productivity. (◆) R1/TAN 2.26 g L^{-1}; (■) R2/TAN 3.02 g L^{-1}; (▲) R3/TAN 3.75 g L^{-1}; (×) R4/TAN 4.54 g L^{-1} and (✱) R5/TAN 5.23 g L^{-1}.

The effect of ammonia inhibition on the methane yield during the last three weeks of treatment (day 37 to 56) was statistically analyzed. During this period the methane yield in R1-R4 was more stable than in other periods (Figure 1). Total ammonia nitrogen during this period was lower than the average TAN during days 15-35 due to the TAN concentration of the substrate during this period being lower. A regression analysis of days 37-56 data (determined using the Data Analysis Tool Pack available with the Microsoft EXCEL program) found a strong negative correlation (R^2 = 0.98) between TAN concentration and methane generation ratio (Figure 2). Methane yield during statistic period in R1, R2, R3, R4 and R5 were 168.31, 128.54, 118.33, 80.56 and 56.93 ml g VS^{-1} respectively. This study also found a strong negative correlation of R^2 = 0.96 between FA concentration and methane generation ratio (Figure 2). The addition of urea in R2 gave an increased FA concentration of 0.71 ± 0.03 g L^{-1} compared to the reference digester which had a FA concentration 0.48 ± 0.03 g L^{-1}. The methane yield in R2 was approximately 24% lower than in the reference digester.

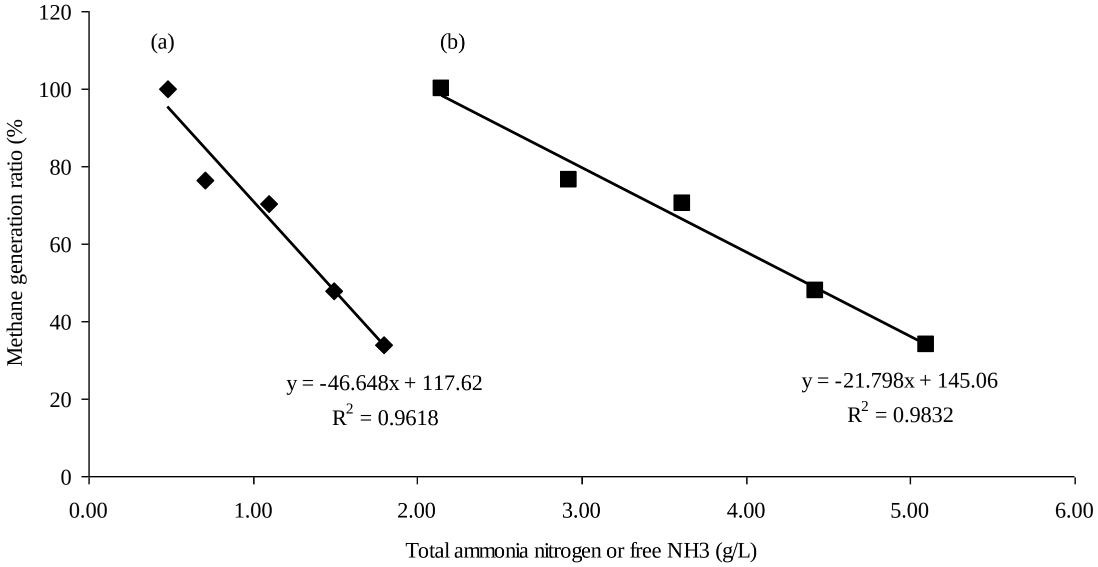

Figure 2. Methane generation ratio corresponding to the: a) free ammonia concentration and b) total ammonia nitrogen concentration

2.2. Development of NH_3 removal unit

In the project various technical solutions regarding.a gas bubble unit and a membrane modules to take out NH3 from the gas and bind it in sulphuric acid-have been tested and developed..

Gas bubble unit

In the project different gas bubble unit were considered and discussed various leading to test of different versions. The very first consideration and testing focused on the use of "plate"-aerators, which are known from aeration at sewage treatment plants. These plate-aerators were after internal tests scrapped for use in this project because they have a relatively large pressure drop.

After testing of plate-aerator was constructed and tested another version were tried built up as a rectangular box in which the top was equipped with a rubber membrane with holes..

This gas bubble unit with rubber coating gave problems associated with downtime, since it was blocked with biomass and finally this solution was given up. Given the challenges of preventing clogging and generate a maximum ammonia uptake with minimal pressure drop a third gas bubble units solution consisting of a cylinder without bottom and with grooves in the sides were constructed. This solution prevented clogging by stoppages but the bubble area and ammonia removal was still not satisfactory.

For the removal of ammonia from the gas different membrane solutions as listed below were tested.

Solution # 1:

The membrane module ran for approx. 2 to 3 weeks, after which we chose to stop. The reason was partly that the module after this period of operation showed signs of excessive leaks.

Another disadvantage of this module, it was relatively large pressure drop that would require a relatively high energy to continue with this. The resulting problems, especially the problem of sealing of the selected design, meant that we chose to concentrate on other possible solutions for membrane structure.

Solution # 2:

In an effort to solve sealing and pressure loss problems, we constructed and tested a second membrane solution. This solution was based on a cylindrical structure of membrane mats.

The membrane mats consisted of a multitude of small pipes, where the biogas was led around. Inside the tubes sulfuric acid were circulating.This cylindrical module was structured so that we could adjust the effective membrane area in order to determine the area the need for a given amount of ammonia uptake.

The principle of the cylindrical module showed good results in terms of removal of ammonia from biogas. This module also led to a lower pressure drop than the module from solution No. 1

Trial results:

Application of the above cylindrical membrane module combined with the above described gas bubble unit (cylinder with a hole in the bottom) gave the following test results for ammonia collection:

At a gas flow of approx. 300 m^3. hours through the bubble unit approx. 250 to 280 ppm NH3 in the gas was collected. The gas was then led through BIOSCENTs cylindrical membrane module where all the ammonia was captured (measured to 0 ppm at the end).

Unfortunately, it turned out after a period of operation of this module, that it was damaged by the operation, since some unwanted particles in the cylinder damaged the membrane material. It was not possible to determine exactly from where these particles originated.

Solution # 3:

In order to address problems of pressure drop, corrosion, etc., work was concentrated on producing flat sheet modules built of material which, in addition to satisfy the above conditions also should be temperature resistant up to thermophilic process. Work on this membrane modules built with flat sheet-frames has caused a number of challenges, among other things include:

- Membrane Material resistance during prolonged pressure and temperature loads.
- The durability of joints / glue adhesion to the special membrane material.

All the problems with the membranes and the bubble unit lead to the decision that other solutions should be developed. A stripping and scrubbing unit that treated a stream of liquid digestate was developed. This system was efficient for ammonia removal but there were several problems with clogging, condensate in gas pipes etc. After 1 month of initial tests an accident from one of the gas blowers set fire to the unit before the final tests could be initiated. Because of this further tests were not possible and there were not resources in the project to rebuild the unit.

3. Conclusion

The project has shown that NH_3 can reduce the gas yield in thermohilic digestes significantly. Several Danish biogas plant has NH_3 levels that is higher than the inhibitory level resulting in more than 20% reduction of the biogas yield. This means that ways to reduce the NH3 concentration in the future will be of high interest. In the present project a stripping system both inside the digester and outside the digester has been tested and has shown that it is possible to remove the NH_3. However because of problems in both the stripping and scrubbing unit a proper technical solution has not been developed in this project.