NH4+ acidification system
Biogas yield of fibres from acidified manure

Test Report
J.no.1002

Test no.1 Swine manure

Original version 2: 12.01.2010 Revised version 7 19. 04. 2010

1. Table of contents

2. Introduction

This test plan is the implementation of a test design developed for verification of the performance of an environmental technology following the ETV method.

2.1. Verification protocol reference

J.no 1002

2.2. Name and contact of vendor

Grundfos New Business A/S, Poul Due Jensens vej 7, 8850 Bjerringbro
Contact: Jesper Ravn Lorenzen, phone: +45 47501400, e-mail: jlorenzen@grundfos.com.

2.3. Name of centre/test responsible

Danish Technological Institute, Verification Centre, Life Science Division, Kongsvang Allé 29, DK-8000, Aarhus, Denmark.
Test responsible: B. Malmgren-Hansen (BMH), phone: +45 72201810, e-mail: bmh@teknologisk.dk.
Internal reviewer: Nils H.Nilsson (NHN), phone: +45 72201825, e-mail: nhn@teknologisk.dk,

2.4. Expert group

Thorkild Qvist Frandsen (TQF), Agrotech, phone: +45 87 43 84 68, e-mail. tqf@agrotech.dk
Lars Ditlev Mørck Ottosen (LDMO), Aarhus University, phone +45 8942 3306, e-mail: lars.ottosen@biology.au.dk.

3. Test design

The test design is based on a comparison of methane potential of untreated biomass fibres and biomass fibres treated with sulphuric acid in the NH4+ process on a farm. The slurry was collected from farms with pig production with comparable operations, housing design and manure handling. Fibres were obtained from separating the slurry in a mechanical separation process in the laboratory. After separation the fibres were diluted with degassed slurry from a bio gasification reactor and methane yield was measured in batch digestion experiments.

The target of the process is:

- Methane yield of separated treated (acidified) fibres in manure

The effects of the process were tested for:

- Change in methane yield from treated biomass compared to untreated biomass in the treatment period of interest in biogas plants (approx. 20 days for themophilic and-30 days for mesophilic in active growth)
  In the batch digestion experiments the methane yield of non acidified fibres were compared with 3 levels of concentrations of acidified fibres mixed into non acidified reference fibres.
- analysis of a number of parameters on the samples (TS,VS, Ntotal, N-NH_4+, P,K,S)

Measurements of Methane Potential

Fibre preparation

The following tests were made with a total of 25 g VS/l all in triple measurements

Test No	% non-acidified fibre	% Acidified fibre
1	100	
2	80	20
3	90	10
4	95	5

The methane potential was measured according to the method for measuring methane potential described in appendix 5.

The result is a calculation of (l CH_4 /VS of added biomass) for treated and non treated biomass as function of time for mesophilic biogasification.

Three different concentrations of acidified fibre were used in order to evaluate potential effects on biogas production originating from the acidification process.

The dry matter content (DM) and volatile solids content (VS) of the test samples were analyzed before performing biogas tests.

Biogastests were performed at Danish Technological Institute as described in appendix 5. A number of samples were tested in parallel at Aarhus University.

3.1. Test site

The sampling site for retrieval of acidified fibres was the selected NH_4+ acidification operation at farm 1.

The fibres were separated manually using a 1 mm sieve for sieving 50 l acidified manure in laboratory at Aarhus University, Department of agricultural engineering.

3.2. Type of site

The NH_4+ acidification system is installed at a farm with a pig production (fattening pigs, 30-100 kg) in 4 stables. The farm operates the 4 stables with the following conditions:

Pigs are produced in stables with 1/3 concrete floor, 1/3 so called “environment floor” with heating and 1/3 with slatted floor.

The pigs received wet feeding which is mixed on the farm. The ingredients are barley, wheat, soya +minerals and water.

Only a small amount of bedding material (cut straw) is used.

Sampling of non acidified reference fibres were first made from a nearby farm with comparable production and operation. However when manually sieving of 50 liter samples the amount of fibres obtained was to low for the required amount to the biogas test and nutrient analysis. Instead the reference fibres were obtained from a stable at farm 2, with comparable production and operation management. Farm 2 separates fibres from its pig slurry using a Mechanical separator (screw separator and shaking sieve from Staring Maskinfabrik).
Therefore the separation method for reference fibres deviates from the manual sieve method in laboratory used to separate acidified fibres.

3.3. Addresses

Test sites

The acidified manure was obtained from:
farm1 (acidified manure): Tage Lauritsen, Sandgårdvej 6, 7540 Haderup

The reference fibres are obtained from:
farm2: (normal manure) Niels Adelstorp/Henning Jørgensen, Krattetvej 77, 9740 Jerslev.

3.4. Descriptions

The INFARM NH_4+ acidification system acidifies slurry to reduce ammonia emissions from stables. In brief, the system pumps manure from the slurry pits below the slatted floors to an acidification tank at programmed intervals. In the tank sulphuric acid is added until a pH of 5.5 is reached. The acidified manure is pumped back into the stable ensuring a lowering of the pH in the slurry pits. This reduces the emission of ammonia by shifting the ammonia equilibrium from NH_3 towards NH_4^+ ($NH_3 + H_2O = NH_4^+ + OH^-$, PKa= 9.25 at 25 ˚C).

3.5. Tests

3.5.1. Test methods

The test methods, standards:
Methane potential were measured according to protocol in appendix 4

3.5.2. Test staff

The test staff is

B.Malmgren-Hansen	Sampling and reporting
Paul Lyck Hansen	Head of analysis lab (TI)
Eva Bak Jakobsen	Methane potential, GC analysis (TI)

3.5.3. Test schedule

Task	Timing
Application definition document	Sept. 2009
Verification protocol with test plan	Sept 2009
Test	Okt 2009
Test reporting	Nov 2009-april 2010
Verification	April 2010
Verification report	April 2010
Verification statement	April 2010

3.5.4. Test equipment

The test equipment includes:

- Sampling buckets
- 20 l Containers for samples

Type and number of samples

The types and number of samples are summarized in the table below.

Methane potential 1. Volume of biogas produced 2. Biogas composition (methane)	4 samples with 3 replicates all with 25 gVS/l where acidified fibres are added to reference fibres in VS concentrations 0, 5,10,20 %
Other analysis 1. Total solids 2. ash content 3. Total nitrogen 4. Ammonium nitrogen 5. Total phosphorus 6. K 7. S	3 samples for untreated and 3 samples for acidified fibres

3.5.5. Operation conditions

The operating conditions of the INFARM NH4+ system is a standard set up where all manure on the farm is treated to reach pH 5.5 (set point).

3.5.6. Operation measurements

- The pH was tested prior to sampling and compared with the pH stored in the data locker for 1 month
- Recorded management data from the INFARM system describing treatment frequency, alarms etc. was evaluated to check that the system was running as planned.

3.5.7. Sampling

To obtain homogeneous, representative samples the following sampling plan was followed

Sampling of acidified manure

Test of plant operation
Before sampling (14 days-1 month before the test) the operational stability of the acidification system was checked , using data from the acidification plants data logger. All deviations from normal operation was observed and reported in this test report. pH was measured on the acidified manure samples immediately after sampling and compared with internal pH measurement of the plant.

Sampling
Samples were taken by etc. 15 litre buckets lowered into the stirring tank of the NH_4+ plant
The content was transferred to 50 litre storage containers.

The sample was taken after the INFARM system had pumped manure into the treatment tank and acidified to the set point of pH=5.5.

The manure was stirred during sampling.

A subsample was taken for measurement of pH within one day

Sampling of untreated manure
Untreated manure was sampled from a separator installed on farm 2

Pretreatment and handling of samples
The acidified manure sample (40-50 liter) was taken to Aarhus University, Department of Agricultural Engineering where separation of particle matter was done using

1 mm sieves in the laboratory. The separation of the different samples was made in a reproducible way.

The sieving simulates the mechanical separation technique on farm2 meaning that the smallest particles are passing. No polymers for flocculation or other additives were used. The separated fibre material was refrigerated or frozen in cases where the analysis could not be performed within 2-3 days

3.5.8. Product maintenance
The INFARM NH4+ system is typically sold with a service contract.

3.5.9. Health, safety and wastes
The manual describes safety procedures for handling of sulphuric acid, correct operation of plant and handling of waste.
The Infarm system is a fully automated system and requires no physical contact with the suplhuric acid and it provides fully automated management of the slurry (including discharging into storage etc).

4. Reference analysis

4.1. Analytical laboratory

Analytical laboratories providing analysis of any kind as part of the verification tests, within or outside the test centre body has the responsibility for:

- Maintaining an ISO 17025 accreditation with the quality management system required herein.
- Application of accredited analytical methods, where available
- Application of other methods according to both international standard methods or in-house methods that are validated as required for accredited methods

The selected analytical laboratory subcontractors shall be listed by the test centre, test sub-body.

The used analytical laboratory are shown below

Analysis of total and ammonium nitrogen, total phosphorus, total and volatile solids are done by Eurofins Steins laboratory, Hjaltesvej 8, DK-7500 Holstebro, phone: +45 7022 4286, website: www.eurofins.dk

Determination of biogas volume and methane concentration at laboratory scale is done by: DTI Chemistry and Water Technology, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark phone +45 72201000. Contact: Paul Lyck Hansen.

Department of Agricultural Engineering, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark, phone +45 89 99 19 00. Contact: Henrik B. Møller

4.2. Analytical parameters

See 4.3

4.3. Analytical methods

Analytical parameters	Standard
Methane potential	Aarhus University method described in Appendix 5
Total solids	EØF 103°C
Total volatile solids (Loss on ignition)	DS 204
Total nitrogen	Kjeldahl
Ammonium nitrogen	71/393/EØF
Total phosphorus	ICP-OES: (ISO/DS 11885, 2009)
K	ICP-OES: (ISO/DS 11885, 2009)
S	ICP-OES: (ISO/DS 11885, 2009)

Optional measurement of levels of H_2S in headspace was performed by using Drägertubes/Kitagawa in combination with measurement on calibrated GC.

4.4. Analytical performance requirements

See 3.3.

4.5. Preservation and storage of samples

Samples to be analysed by Eurofins laboratory were stored in labelled 1 l PE bottles, freezed and sent directly to analysis after the tests (1 week)
Samples for batch testing of methane potential were freezed immediately after sampling until testing

5. Data management

5.1. Data storage, transfer and control

The data to be compiled and stored are summarized in table below. Analytical raw data were filed and archived according to the specifications of the laboratories quality management systems.

Data type	Data media	Data recorder	Data recording time	Data storage
Test plan and report	Protected pdf	Test responsible	When approved	DTI protected data storage
Test details at laboratory and full scale	Excel, word etc.	Test staff at test site	During Test	DTI protected data storage
Calculations	Excel	Test responsible	During calculation	DTI protected data storage
Analytical reports	Protected pdf, paper	Test responsible	When received	DTI protected data storage

6. Quality assurance

6.1. Test plan review

Internal review of the test plan was done by NHN.
External review of the test plan is described in 1.4.
Verification of this test report is performed by verification centre at DTI.

6.2. Performance control – reference analysis

Batch testing of methane potential
The incubation temperature was controlled by logging the temperature in the incubation chamber.

A test of possible leakage was performed by comparing the triplet measurements of methane potential. Further, the test system for measuring pressure produced volume of biogas and for measuring gas composition according to method in appendix 5 was thoroughly leak tested.

6.3. Test system control

Interlaboratory callibration was performed on selected samples between Aahus University and the DTI laboratory.

6.4. Data integrity check procedures

All transfer of data from printed media to digital form and between digital media were checked by spot check of not less than 5 % of the data.

6.5. Test system audits

Supervision of biogas tests by laboratory leader Paul Lyck Hansen.

6.6. Test report review

Internal review of the test report was done by NHN, phone + 45 7220 1825, email: nhn@teknologsik.dk
External review of the test report was done by the experts groups in 1.4.

7. Test results

The test report will be included as an appendix in the verification report according to the DANETV Centre Quality Manual

7.1. Test Performance summary

The purpose of the present verification was not a complete verification of an INFARM NH4+ system but a verification of the fibre quality regarding use as substrate in biogas production.

Operational data
The performance of the INFARM NH4+ acidification system regarding pH control was controlled by inspecting the data in log file from a period of 1 month before the test.

The data shows that all titrations exept 2 on stable 2 and one on stable3 reached the setpoint within +/- 0.2 pH units.

pH was measured in samples taken from acidified manure on 12. Oct. 2009.

The measured pH was in agreement with the set point of pH=5.5 within an acceptable difference of 0.2 pH units.

The average use of sulphuric acid per stable was 64 liter per day during one month treatment before the sampling of fibres according to logged data from weighing cells.

Data for Fibre Material
The analysis of acidified fibres and reference fibres showed 8.7 times higher concentration of sulphur per kg DM in the separated acidified fibres than in the separated reference fibres.

Biogas tests
Biogas tests with addition of different amounts of acidified fibres to reference fibres showed the same amount of produced methane at 5 and 10% addition of acidified fibres as the reference fibres after 30 days of biogasification at mesophilic conditions. The accumulated methane production was 200 ml/g VS after 30 days active growth of the methanogens. The start of the active growth period is defined as the point where the methane production increase dramatically (just after the lag phase) as shown in the figures in appendix 5.

7.2. Test measurement summary

Target and measured values of tested parameters.

Parameters	Target	Measured value	Method
Overall performance			
pH regulation	5.5	5.68	Calibrated pH meter
Chemicals			
Sulphuric acid liter/stable/day		64	Calculated from log file weighing cells
Fibre quality			
Sulphur content mg/kg DM		32333	Analysis
DM %		12.2	Analysis
Inhibition in Biogasification at 5 and 10% mixture with nonacidified fibers		No inhibition	Methane potential (mesophilic 35˚C)
Inhibition in Biogasification at 20% mixture with nonacidified fibers		Beginning inhibition	Methane potential (mesophilic 35˚C)
Operation			
User manual		Checked	Checked according to manual

It is concluded for the INFARM NH4+ system:

- there is no significant inhibition in biogas production with addition of 10% acidified separated fibres with a dry matter content(DM) of 12% to non acidified fibres
- there may be inhibition by addition of 20% acidified fibres (DM=12%) to non acidified fibres.
- From the results of tests with 100 % acidified fibres there is a significant risk of inhibition using acidified fibres only and a high H2S concentration in the gas phase must be expected.
- The hydrogen sulphide concentration in the gas phase is increased by approximately a factor of four with addition of 10% acidified fibres (DM=12%) to reference fibres
- When comparing conditions in test incubators and full scale plants and results from N_2 flushing of incubators it is likely that full scale biogasification plants will have less inhibition than the incubators used in this test (where pressure builds op between samplings and no stirring exist)

7.3. Test quality assurance

Selected tests of methane potentials were duplicated at DJF.

7.4. Deviations from test plan

The test plan was followed

In addition to the planned biogasification tests additional tests with 100% acidified fibres was performed at different concentrations (5,10,25 gVS/litre) and the effect of removing H_2S from the manure was tested by flushing with N_2

Appendix 1 Terms and definitions used in the test plan

Terms and definitions used in the protocol are explained in table below

Terms and definitions used by the DANETV test centres

Word	DANETV	Comments on the DANETV approach
Analytical laboratory	Independent analytical laboratory used to analyse test samples	The test centre may use an analytical laboratory as subcontractor
Application	The use of a product specified with respect to matrix, target, effect and limitations	The application must be defined with a precision that allows the user of a product verification to judge whether his needs are comparable to the verification conditions
DANETV	Danish centre for verification of environmental technologies	
(DANETV) test centre	Preliminary name for the verification bodies in DANETV with a verification and a test sub-body	Name will be changed, when the final nomenclature in the EU ETV has been set.
Effect	The way the target is affected	The effect could be concentration reduction, decrease in treatment period, pH increase etc
(Environmental) product	Ready to market or prototype stage product, process, system or service based upon an environmental technology	The product is the item produced and sold and thus the item that a vendor submit for verification
Environmental technology	The practical application of knowledge in the environmental area	The term technology is covering a variety of products, processes, systems and services.
Evaluation	Evaluation of test data for a technology product for performance and data quality	None
Experts	Independent persons qualified on a technology in verification	These experts may be technical experts, QA experts for other ETV systems or regulatory experts

Word	DANETV	Comments on the DANETV approach
Matrix	The type of material that the product is intended for	Matrices could be soil, drinking water, ground water etc.
Method	Generic document that provides rules, guidelines or characteristics for tests or analysis	An in-house method may be used in the absence of a standard, if prepared in compliance with the format and contents required for standards.
Performance claim	The effects foreseen by the vendor on the target (s) in the matrix of intended use	None
Performance parameters	Parameters that can be documented quantitatively in tests and that provide the relevant information on the performance of an environmental technology product	The performance parameters must be established considering the application(s) of the product, the requirements of society (regulations), customers (needs) and vendor claims
Procedure	Detailed description of the use of a standard or a method within one body	The procedure specifies implementing a standard or a method in terms of e.g.: equipment used
Producer	The party producing the product	None
Standard	Generic document established by consensus and approved by a recognized standardization body that provides rules, guidelines or characteristics for tests or analysis	None
Target	The property that is affected by the product	Targets could be *e.g.*. contaminant concentration
Test centre, test sub-body	Sub-body of the test centre that plans and performs test	None
Test centre, verification sub-body	Sub-body of the test centre that plans and performs the verification	None
Test/testing	Determination of the performance of a product for parameters defined for the application	None

Word	DANETV	Comments on the DANETV approach
Vendor	The party delivering the product to the customer	Can be the producer
Verification	Evaluation of product performance parameters for a specified application under defined conditions and adequate quality assurance	None

Appendix 2 References

1. DANETV. Centre Quality Manual, DTI 2009

Appendix 3 References methods

Appendix 4 In-house test methods

Separation of acidified fibres at Aarhus University, testcentre Department of agricultural engineering

The acidified fibres stored in 50 liter container wereseparated within a few days from sampling manually using a 1 mm sieve. A mild pressure was added by hand to dewater the fibres. Separated fibres were mixed in a bucket and divided into subsamples for testing.

Appendix 5 In-house analytical methods

Measurement protocol for methane potential measurements for ETV tests at DANETV:

Measurement protocol for biogas potential measurements for verification tests (ETV, CBMI)

First version:12-5-09 revision v5 22/12-09

B. Malmgren-Hansen and Lars Ditlev Mørck Ottosen, Danish Technological Institute
Revised by Thorkild Quist Frandsen/Kasper Stefanek, Agrotech Henrik B.Møller,DJF

The protocol is developed as part of the CBMI project subproject 05 Test, certification and declaration, www.cbmi.dk .

Purpose

The purpose is to make a common work protocol for performing batch biogasification on biomass used for mesophilic or thermophilic biogasification.

The protocol is based on methods used at DJF, Agrotech and DTI. DTU methods have also been evaluated.

Description test

The test is a modified version of ISO 11734 [1)]

The test is based on performing batch biogasification with degassed inoculum from a biogas plant and added media with recording of produced gas amounts and content of methane.

The biogasification is performed for

- test material
- inoculum (blank test)
- reference material
- varying concentrations of added test material (inhibition test)

The test on test material and blanks are performed as a triplicate test.

Conditioning of test material

Samples must be representative of the biomass to be tested and with a homogeneous structure allowing for taking representative subsamples. Procedures for correct conditioning of biomass (test material) and subsampling must be described elsewhere as it will depend on the structure of the biomass.

Handling and storing of samples

Test material (fibre samples/liquid) samples are taken in e.g. 1 litre PE bottles, filled only 80% allowing for freezing.

If testing cannot be performed immediately, the samples are frozen.

Materials

- Infusion bottles which can withstand a pressure of 2 bar (volume ½-1 litre)
- Butyl rubber stoppers+ Al Crimps
- Measurement device for measuring volume of produced gas (volume measurement or pressure measurement)
- Reference substrate

Conditions

Incubation at 35 +/- 1 ˚C (mesophilic) or 52 +/- 1˚ C (thermophilic)
The incubation temperature must be verified in the thermostating equipment within at least +/- 1˚C using calibrated temperature measurement devices.
When infusion bottles are removed for gas volume measurement, the period of storage outside the incubation chamber should be minimized (<1 hr).

Inoculum

Manure from biogas plant degassed 2 weeks at temperature of interest (mesophilic or thermophilic).
The NH4-N content shall be below 4 g/l unless a special test condition is chosen. pH must be between 6.5 and 8.5. For mesophilic biogasification, inoculum from thermophilic reactors may be used, as the mesophilic culture exists in such media, however, at a lower concentration.

Trial period

The test period may be up to 90 days.

However the test period may be shortened if the period of interest is lower. In normal operations of biogas plants the period of mesophilic operation is approx 30 days and thermophilic operation approx. 20 days. In this case 45 days of test is sufficient. See also figure 1 and 2 later.
Sufficient measurement points on the curve (10-15) should be made to calculate the biogas potential at least after 20 or 30 days and after the total number of days in the test.
If a lag phase in methane production is observed, the days in the lag phase should be added to the test period.

When running comparisons of products/process treatments etc. the same manure batch should be used as inoculum to decrease uncertainty from blank subtraction.

Biogas potential test in infusion bottles

Inoculum of known volume/weight and test samples are added to the infusion bottles.

There must be 40-60% free space in bottles allowing for accumulation of gas.

Addition of inoculum:
Preferred conditions:

- 500 ml infusion bottles : 200 ml inoculum (measured with 0.1% accuracy)
- 1000 ml infusion bottles : 400 ml inoculum (measured with 0.1% accuracy)

Addition of test material (biomass):

TS and VS shall be measured/known on test material before addition.

Test materials are added within a range that gives sufficient sensitivity and no inhibition.
The exact concentration must be estimated in an inhibition experiment.

Typical concentrations of test material are expected to be in the range
1 -30 g VS per liter inoculum.

The added amount is measured with 0.1% accuracy.

The test samples are flushed with N_2- 4 minutes before testing.

Tests are made in triplicate

Blanks
Tests are performed on inoculum (triplicate) for each new batch of inoculum.

The blanks are flushed with N2 for 4 minutes before testing.

Reference
A test compound (like sodium benzoate/cellulose powder) should be run in inoculum (double or triplicate) for each new batch of inoculum.

The reference samples are flushed with N2 for 4 minutes before testing.

Inhibition
Inhibition from different substances may occur.
For NH4-N, inhibition may occur at levels of approx. 4g/l in the inoculum/test material mixture.

If no inhibition occurs, the same amount of ml methane/g VS should be obtained for different added amounts of VS after complete fermentation.

To verify whether inhibition is present at test conditions, tests should be performed with at least two concentrations of added VS etc. 100% and 30-50% and followed for at least 45 days.

Produced gas
Volume can be calculated as pressure increase (ISO 11734) in headspace or measured directly with a volume collection tube (syringe or waterfilled gas collecting cylinder).
Efforts must be made to ensure no loss of process gas (ensuring gastight connections by pressure test).

CH4/CO2
Measured by GC for each measurement point during test (Method description in Biomass and Energy v26, 2004, p.487). GC must be calibrated using reference gas each day.

pH
pH is measured on inoculum batch before test.
pH is measured in test samples after finished biogasification as control of inhibitory acidification. (The measurement may be reduced to 1 pH measurement of triplicates showing same biogas production curves).

Result
For each measurement point, the ml methane amount is calculated.

Blank tests are subtracted.

A sum curve of produced (net) nml methane/gVS as function of time is calculated and plotted using correction for T,P.

All raw data on produced gas volume and methane should be available upon request.

Typical biogas production curves
In Figure 1 is shown a typical curve for accumulated methane production at mesophilic biogasification of fibres separated from the slurry. Figure 2 shows the production rate for methane. In this test there is a lag phase during the first 10 days with the major production of methane from day 15 to 30.

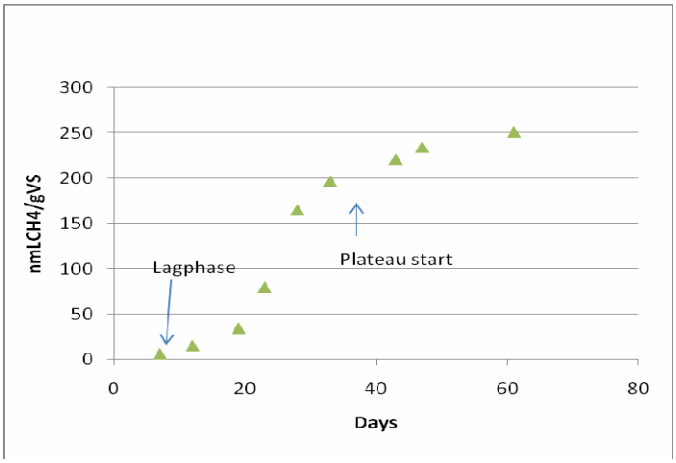

Figure 1. Accumulated methane production

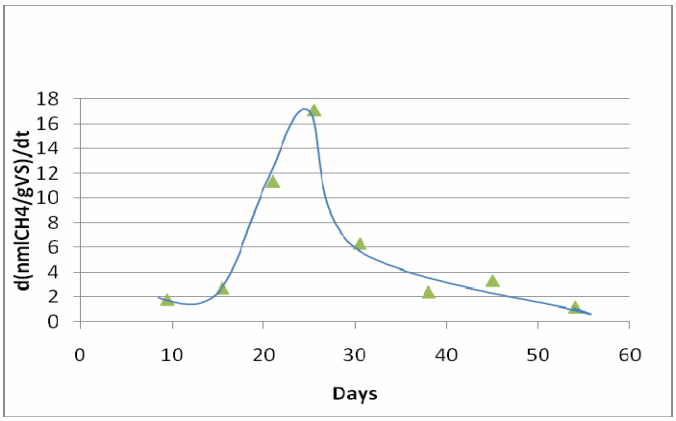

Figure 2. Methane production rate

1) The test is a modification of ISO 11734 including a simple inhibition test like required in Angelidaki Water sci. & Tech p.927, 2009. Additional nutrient medium is omitted – standard gasified manure is used as reference (including sufficient nutrients and bacteria adapted to biogasification at such circumstances).

Appendix 6 Data reporting forms

Data are reported in schemes given in appendix 7

Appendix 7 Test data report
Test

The test was performed as described in the test plan

Operational data
Data of operation is shown in fig. a7.1 and fig 7.2

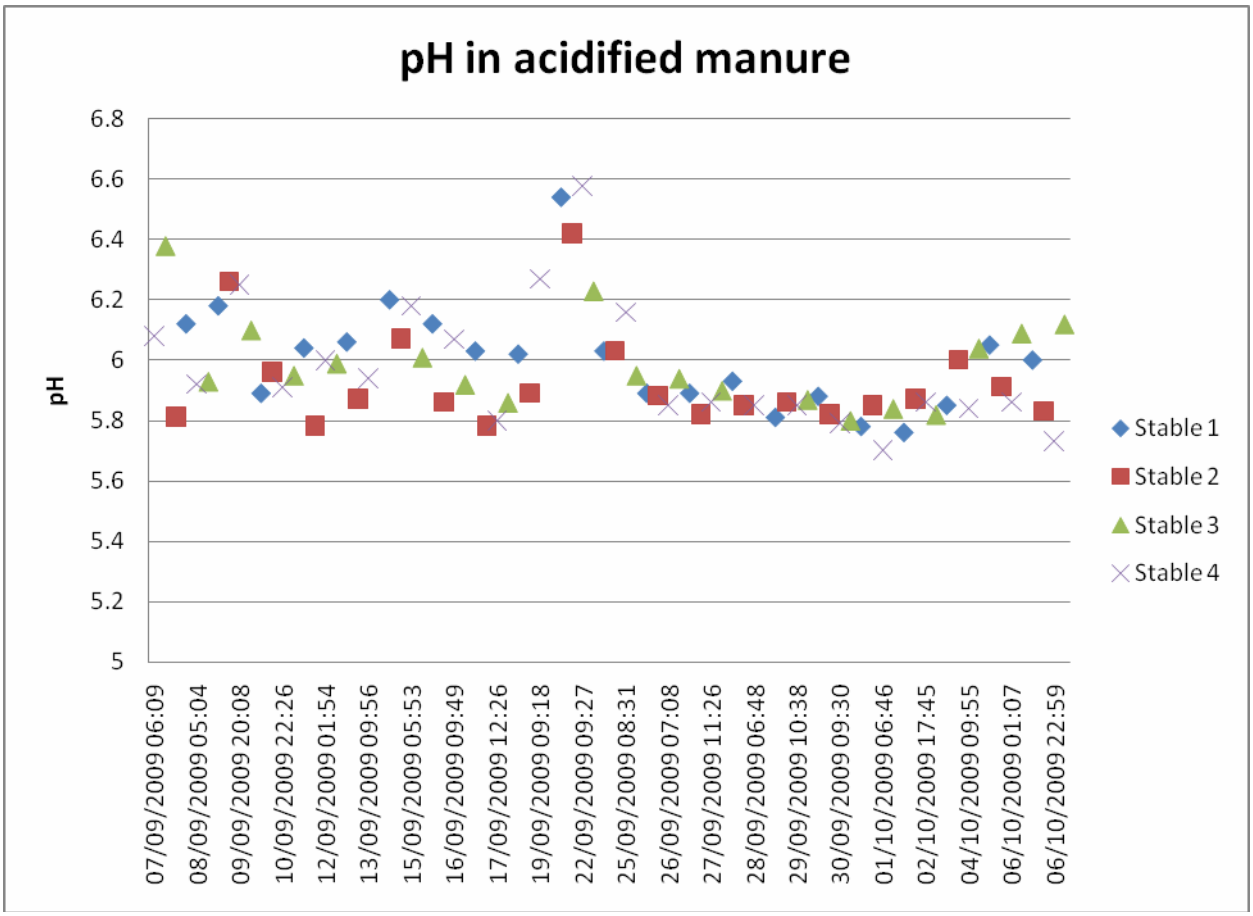

Figure a7.1 Operational data from NH_4+ acidification system. The curve shows pH after manure from the 4 stables have been pumped to the acidification tank for regulation of pH at Øster Sandgaard (farm1)

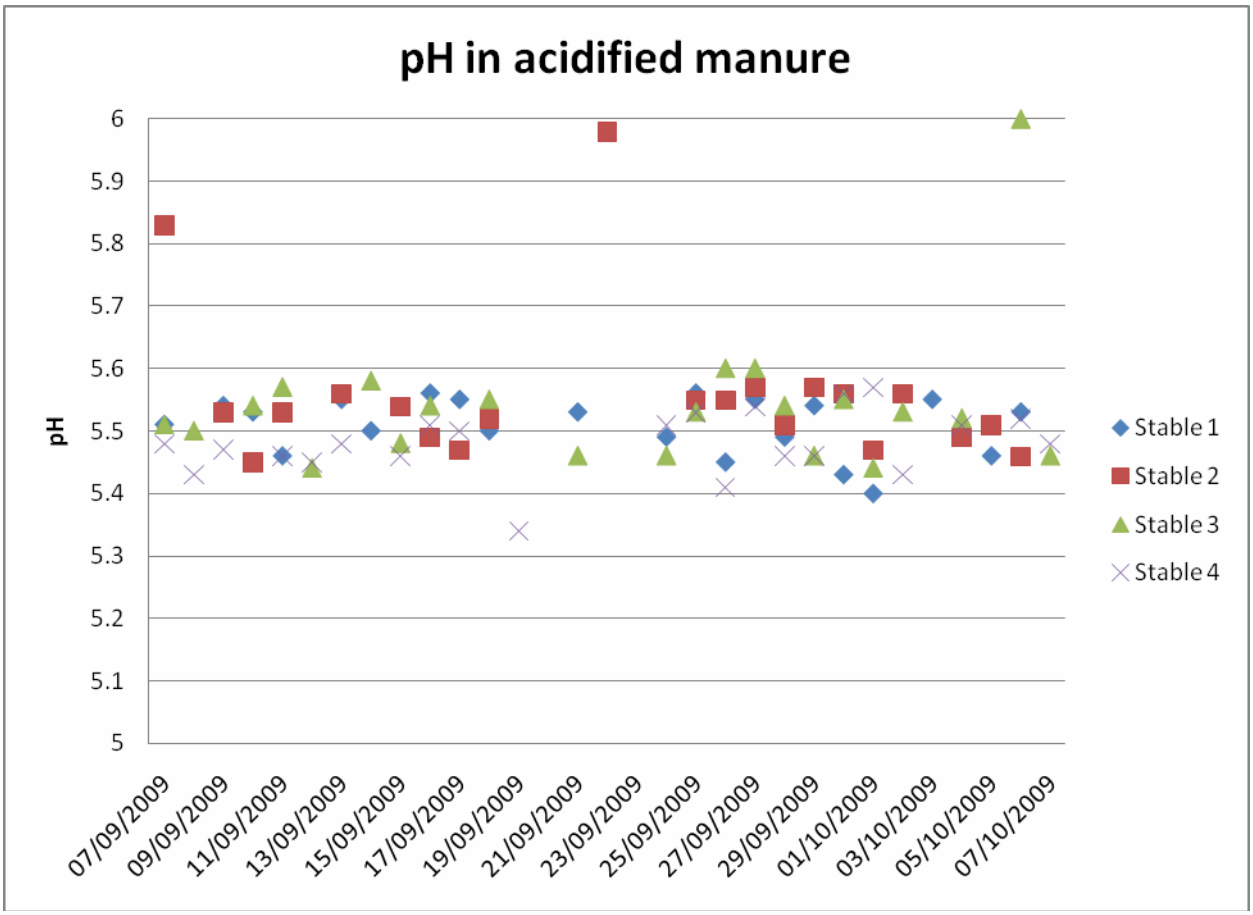

Figure a7.2 Operational data from NH_4+ acidification system, The curve shows pH of manure after regulation of pH has been performed in the acidification tank at , Øster Sandgaard, farm1

The figure shows that more than 95% (82 out of 86) of all pH regulation reached the set point within +/- 0.1 pH units.

pH was measured in samples taken of acidified manure on 12. Oct. 2009.
The pH was measured using a calibrated pH meter to : pH=5.68 which is in agreement with the set point of pH=5.5 within an acceptable difference of 0.2 pH units.

The dosage of acid during one month from 7-9-2009 to 7-9-2010 according to the log system was

Stable	Dosage liter sulphuric acid	Average dosage (l)/Standard deviation
1	1285	68+/-30
2	2329	129+/-79
3	2448	129+/-57
4	1653	87+/-56

Analysis results

Analysis of added and treated fibres

Table a7.1 shows analysis results for added fibres (input) and treated fibres (output).

Table a7.1 Analysis of input and (original data)

	Ref fibres	Ref fibres	Ref fibres	Acidified fibres	Acidified fibres	Acidified fibres
Parameter	**A**	**B**	**C**	**A**	**B**	**C**
Total N g/kg	5.41	5.44	5.44	5.59	5.32	5.46
NH4-N g/kg	2.62	2.57	2.77	3..64	3.65	3.61
P g/kg	1.6	1.6	1.6	0.74	0.72	0.71
K g/kg	2.1	2.1	2.1	2.2	2.2	2.2
DM %	29	29	29	12	11	10
S mg/kg DM	3600	3700	3900	33000	32000	32000
VS % [1]	90	90	90	89	89	87

1 VS :Volatile Solids

Table a7.2 Analysis of input and (Average and Standard Deviation)

	Ref fibres		Acidified fibres	
Parameter	**Average**	**STDEV**	**Average**	**STDEV**
Total N g/kg	5.43	0.02	5.46	0.14
NH4-N g/k	2.65	0.1	3.63	0.02
P g/kg	1.6	0	0.72	0.015
K g/kg	2.1	0	2.2	0
DM %	29.33	0.34	12.2	1.11
S mg/kg DM	3733	153	32333	577
VS %	90	0	88.3	1.2

From table a7.2 it is seen that the content of sulphur is 8.7 times higher per kg DM in the separated, acidified fibres than in the separated reference fibres.

Methane potential

The acidified fibres and the reference fibres were tested as described in 3 Testdesign.

The temperature of the climate chamber was 35 ˚C+/-0.5 ˚C except for small periods of approx 1 hour when bottles was removed for volume measurement as seen in figure.a7.3. However the data logger did not store 3 weeks of data from 28/11 to 21/12-09 but no deviation in operation of the climate chamber was observed whenever samples where taken.

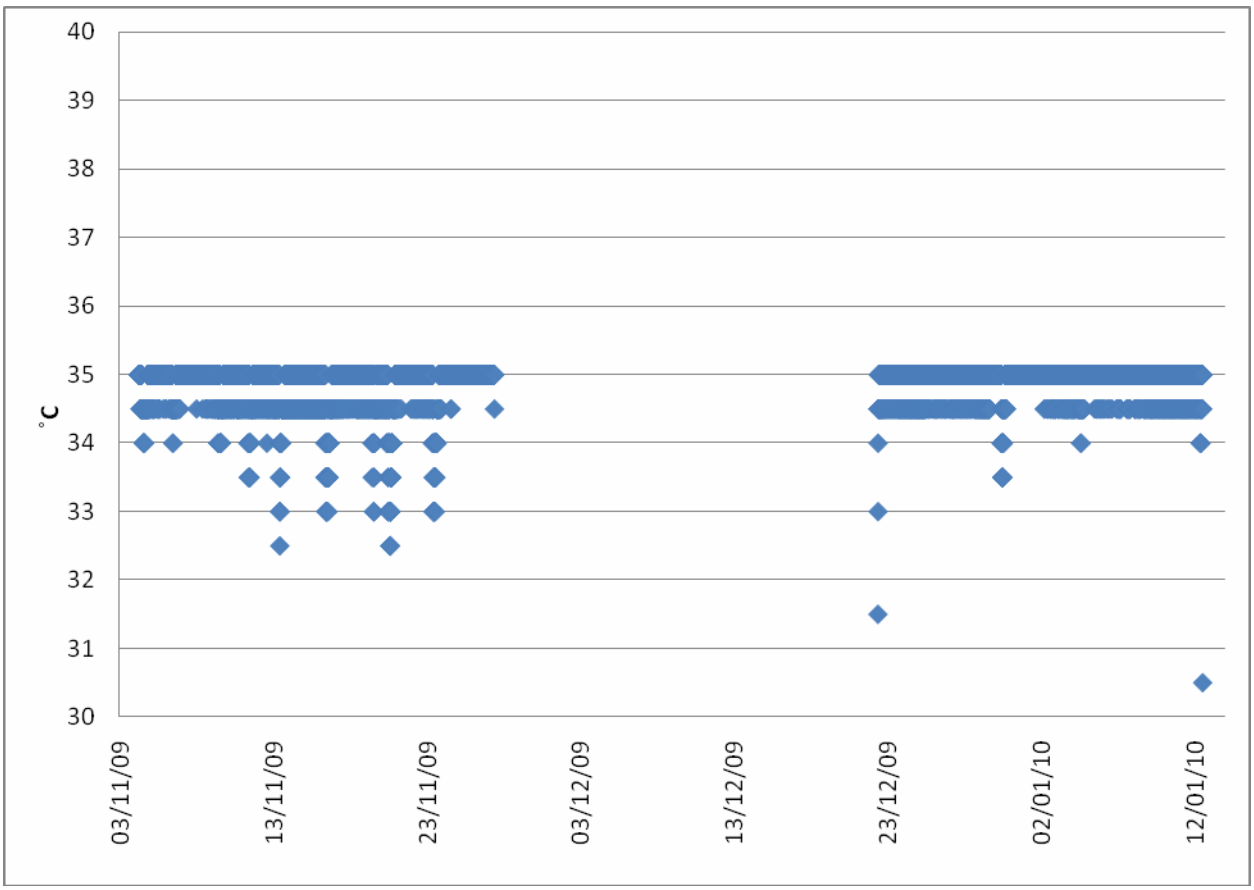

Figure a7.3 Temperature of biogasification

At regular intervals gas volume was measured and the gas composition was analysed.

The Methane content was measured with a gas chromatograph.
Calibration on a synthetic biogas with known amount of methane and carbon dioxide was performed each measurement day.

For H_2S concentrations the level was measured with the gas chromatograph and a rough calibration was regularly made with 2000 ppm dräger tubes on reference fibres with a reading accuracy of approx 50 ppm at a typical level of 1000 ppm H_2S. The accuracy at high H_2S

concentrations was tested by a high concentration tube which gave 23000 ppm where the GC gave 22300 ppm using the calibration from the 1000 ppm level. Therefore the error in calibration should within than 10-20%.

Tests with 100% fibres at different concentrations.

At first a test was performed with different concentrations of 100% acidified fibres (see fig a7.4a). The test was also performed at Aarhus University giving approximately same amount of accumulated methane after 60 days (150 ml CH_4/g VS, fig a7.4c). It is seen that the accumulated biogas produced is lower than from the reference fibres (150 ml CH_4 /gVS) compared with 250 ml CH_4 /gVS from reference fibres. This may be due to differences in the input and the separation method. Test at 25 gVS/liter inoculum showed an increased delay in methane production and the test was stopped after 60 days before the methane production had reached a plateau (fig 7.4b).

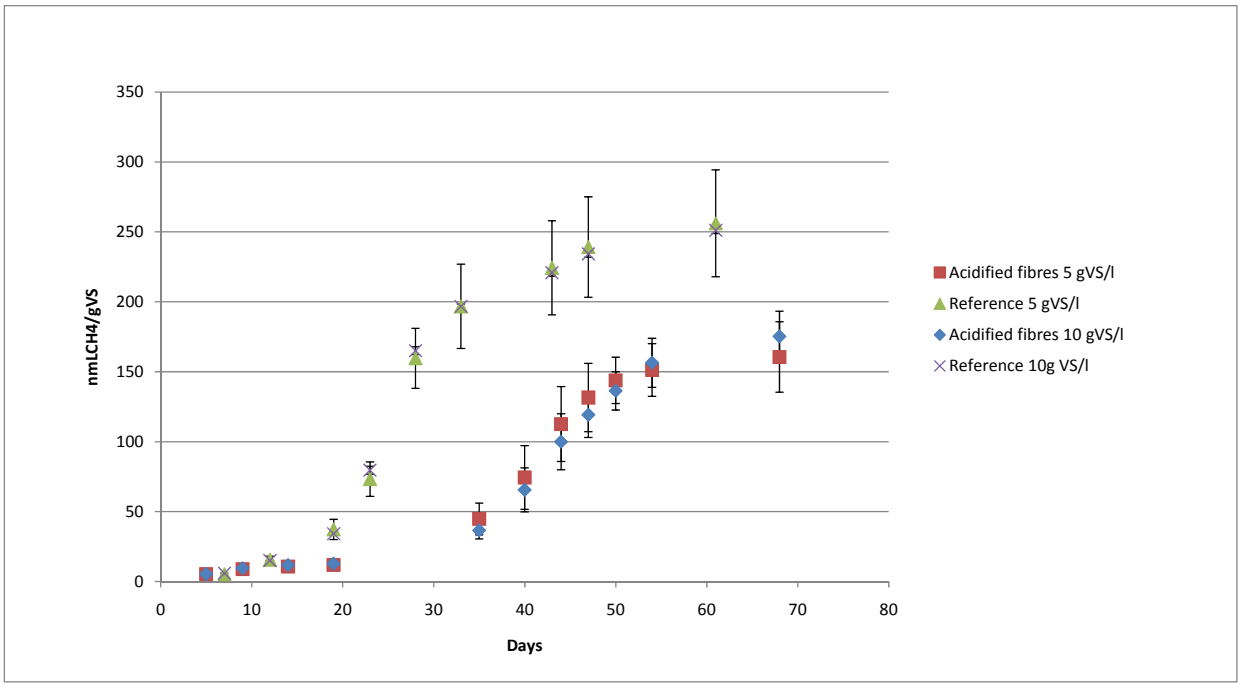

Fig a7.4a Accumulated production of CH_4 from 100% added reference fibres and 100% added acidified fibres 5,10 gVS/l (DTI). Standard deviations of the summarized methane production for each triple measurement are shown in the figure. The standard deviation at the measurement for acidified fibres after 54 days are 19 ml CH4/gVS for 10 gVS/l and 17ml CH4/gVS for 5 gVS/l.

In the test with 25 gVS/l one of the 3 samples where flushed with N_2 after 22 days which lead to a fast increase in methane production after 10 days delay. When comparing the conditions in the incubation flasks with a full scale biogasification plant the full scale plant has incorporated stirring and a continuous removal of H_2S with no pressure build up which is expected to ensure a lower H_2S concentration in the biogasification of manure. From this it may be concluded that

the inhibition from H_2S probably will have less effect in a full scale biogas plant than in the incubation flasks.

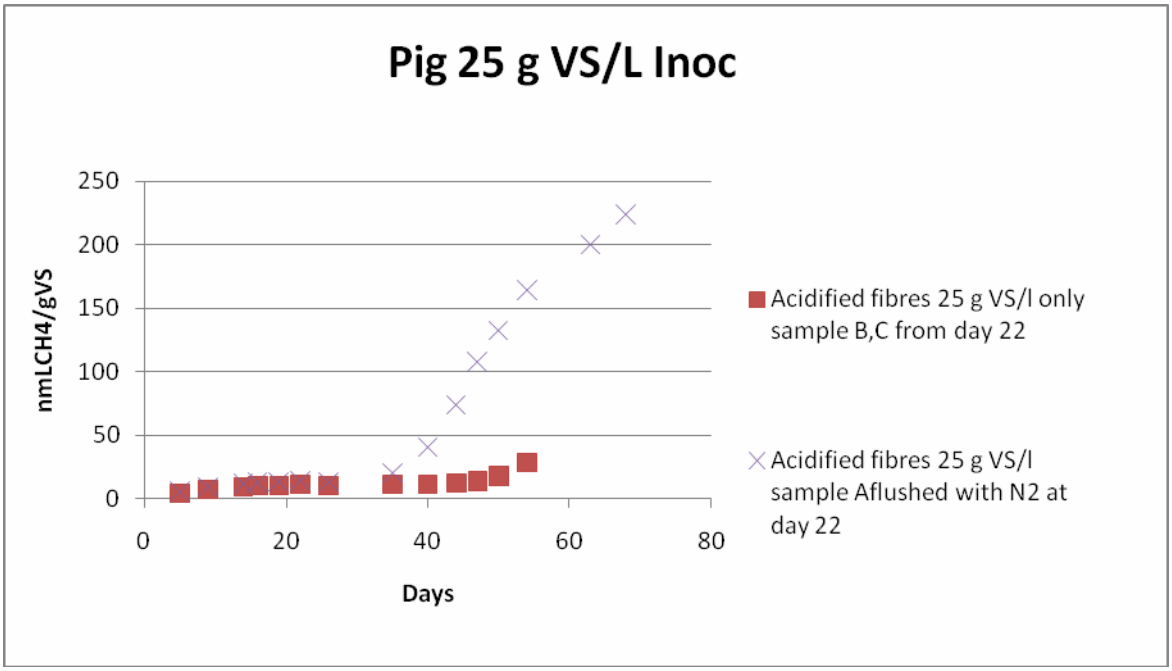

Fig a7.4b Accumulated production of CH_4 from 100% added Reference fibres and 100% added acidified fibres 25 gVS/l (DTI)

In fig. a7.4c the accumulated production of methane for acidified fibres is shown for the tests at Aarhus University

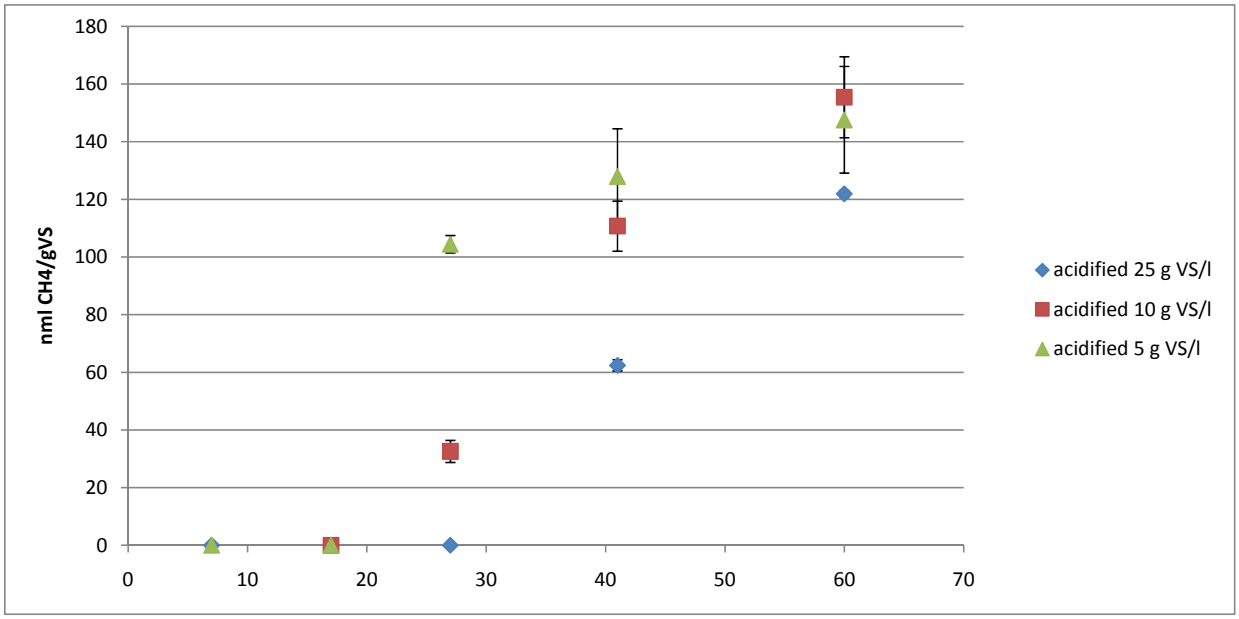

Fig a7.4c Accumulated production of CH_4 from 100% added acidified fibres 5,10,25 gVS/l (Aarhus University) Standard deviations of the summarized methane production for each triple measurement are shown in the figure.

The number of data points in the test at Aarhus University are much less than the test at DTI but the accumulated amount of methane is the same after 60 days for 5 and 10 g VS(l (approximately 160 nml CH_4/g VS)

The curve for 25 gVS/l from DJF increases somewhat earlier than the test at DTI. The reason may be the differences in inoculum (which was not the same) or the longer period between gas samplings.

The production from acidified fibres is delayed when compared to the reference fibres. Fig. a7.5 and a7.6 shows the H_2S concentration in the gas phase. The concentration reaches approximately the double value at the double fibre concentration (gVS/l). Methane production seems to be inhibited until most of the sulphate originating from the treatment with H_2SO_4 is reduced with approximately a 10 days delay.

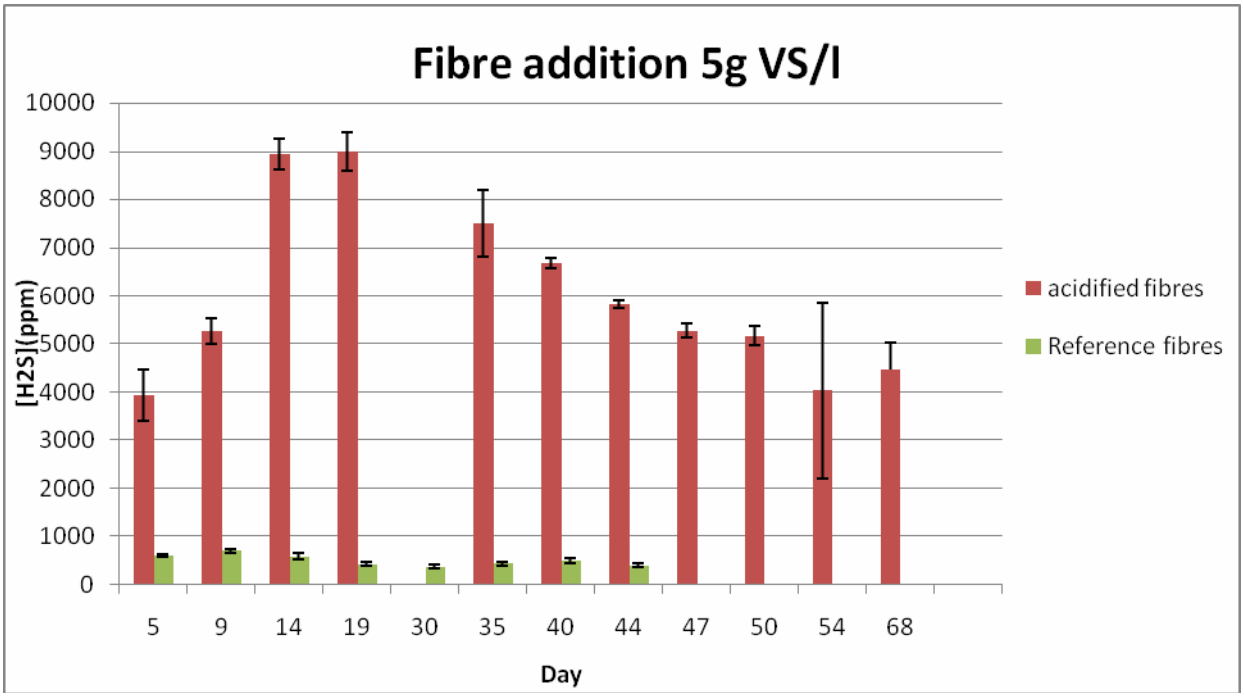

Fig a7.5 Concentration of H_2S in gas accumulated in headspace between two measurement points. From 100 % reference fibres and 100% acidified fibres added at 5 gVS/l

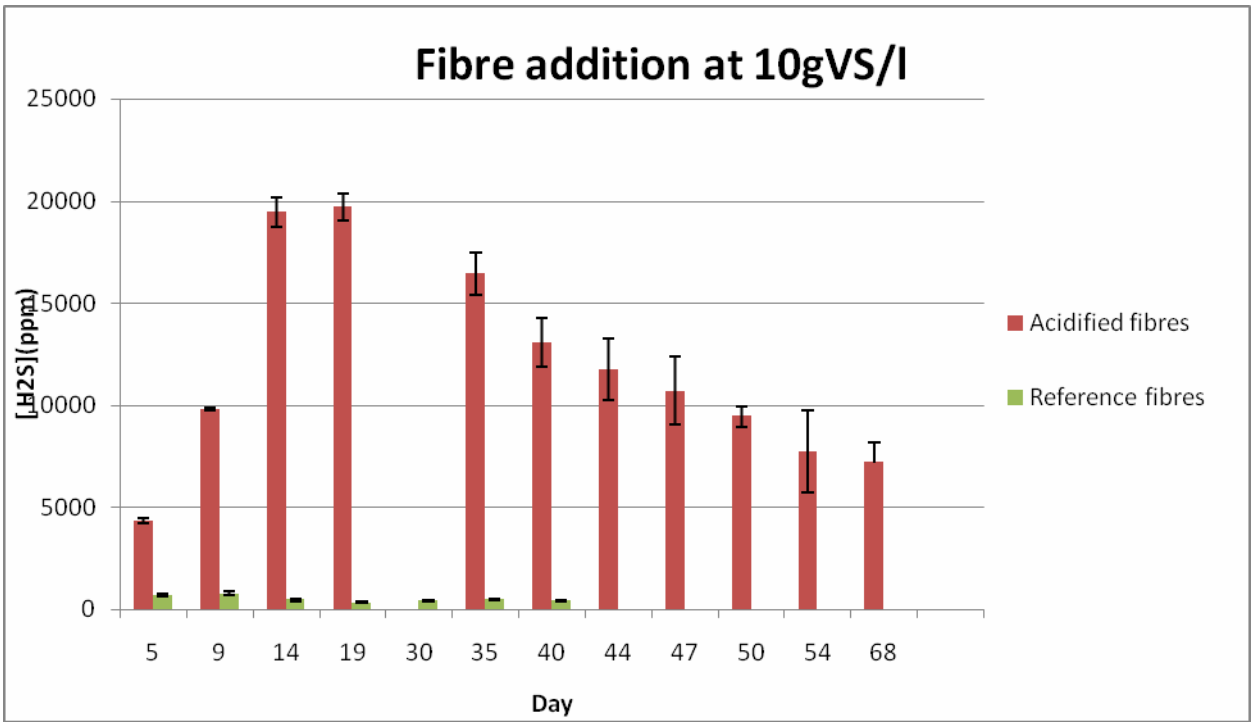

Fig a7.6 Concentration of H_2S in gas at times of measurements from 100 % added reference fibres and 100% added acidified fibres at 10 gVS/l

Tests with mixtures of reference fibres and acidified fibres.

Results are shown in fig. a7.7 for a total of 25 g VS/l and with a VS concentration of acidified fibres 0,5,10,20%. The wet weight of added acidified fibres and reference fibres were calculated from the measured values of TS, VS.

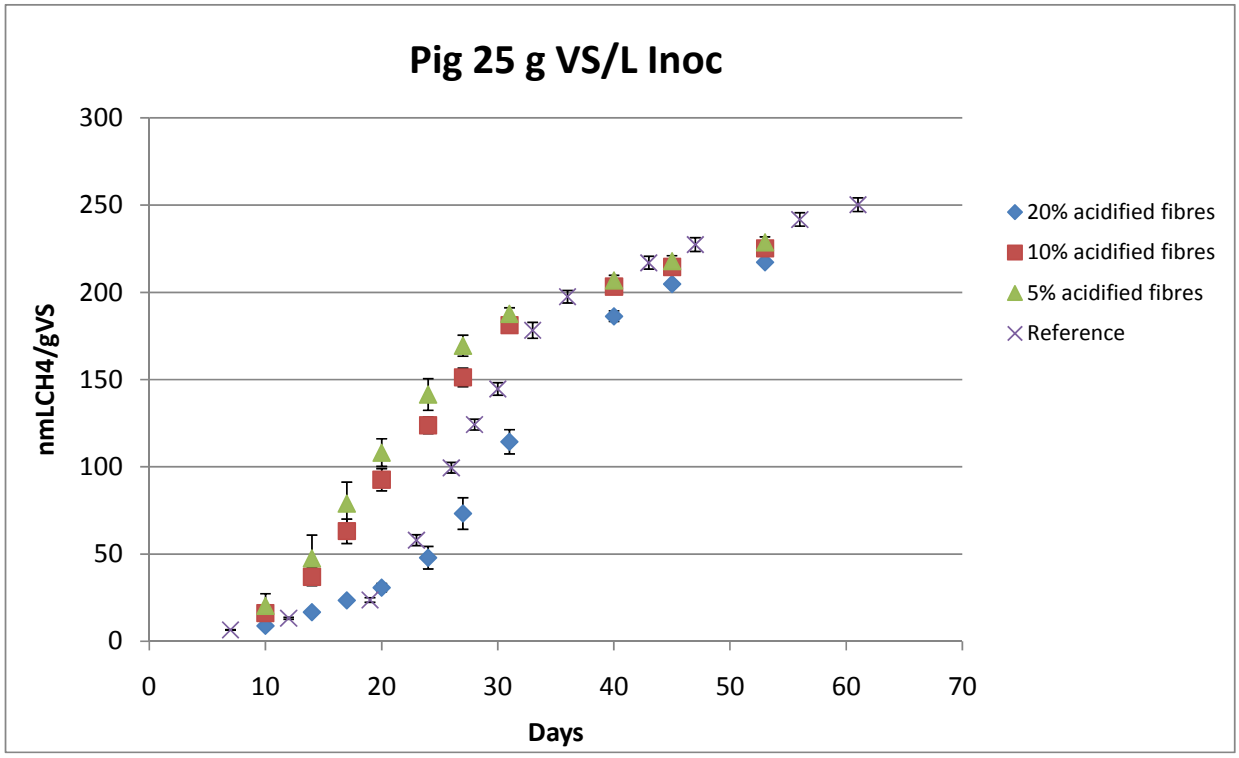

Fig a7.7 Accumulated methane production for 25 g VS/l (average of a triple analysis) 5,10,20% was measured from 20/11-2009 until 12/1-2010 whereas the reference (0%) was measured from 4/11-2009 to 4/1-2010. Standard deviations of the summarized methane production for each triple measurement are shown in the figure.

It is observed that there is no inhibition of the mixed methane production in the biogasification tests at 10% addition of acidified fibres. There is a inhibition (delay) at 20% addition of acidified fibres although the same accumulated methane production is obtained after 30-35 days of active growth (when correcting for 10 days initial lag phase).

On fig a7.8 the H2S measured in the gas phase is shown

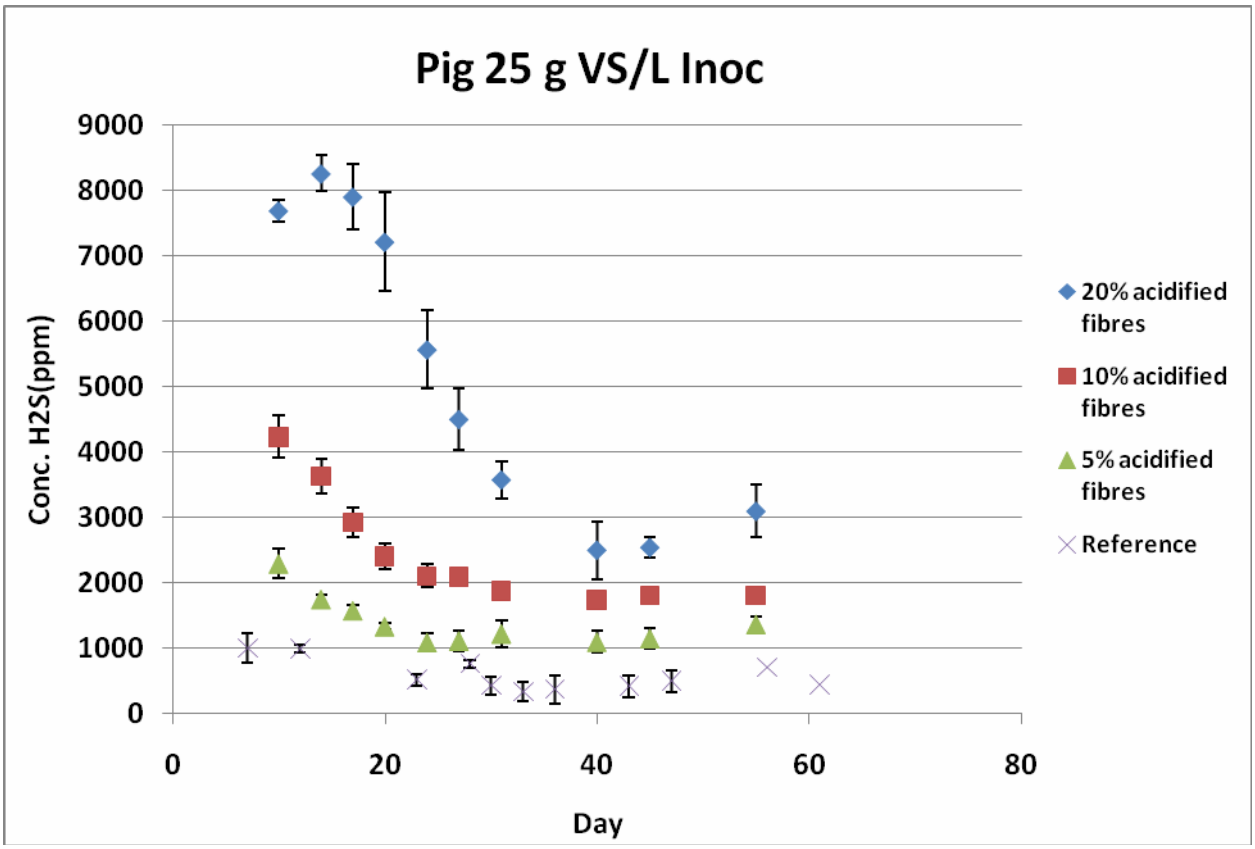

Fig a7.8 Concentration of H2S in gas at times of measurements

The high H_2S concentrations at 20% addition from day 10 to 30 seems to correlate well with the observed inhibition (delay in production) in Fig a7.7

Discussion and Conclusion

The method used for measuring biogas production deviates from the conditions in full scale on the following major points:

- The test is a batch test with a one time feeding and not a continuous feeding as in a full scale plant
- There is no stirring in the batch test incubators
- The produced gas is removed in intervals allowing for a pressure build up of 2 bars compared with a continuous removal of gas in full scale plants

Stirring and removal of gas at zero bars over pressure is expected to remove produced hydrogen sulphide faster and this may reduce inhibitive effects in a full scale reactor compared with a batch incubator.

Based on the above it is assumed that a batch incubator is a worst case test regarding inhibition and thus it is concluded for the INFARM NH4+ system:

- there is no significant inhibition in biogas production with addition of 10% acidified separated fibres with a dry matter content(DM) of 12% to non acidified fibres
- there may be inhibition by addition of 20% acidified fibres (DM=12%) to non acidified fibres.
- From the results of tests with 100 % acidified fibres there is a significant risk of inhibition using acidified fibres only and a high H2S concentration in the gas phase must be expected.
- The hydrogen sulphide concentration in the gas phase is increased by approximately a factor of four with addition of 10% acidified fibres (DM=12%) to reference fibres
- When comparing conditions in test incubators and full scale plants and results from N_2 flushing of incubators it is likely that full scale biogasification plants will have less inhibition than the incubators used in this test (where pressure builds op between samplings and no stirring exist)