GFE – pretreatment/NIX Concept

Pre-treatment of biomass for anaerobic digestion

Test Report

J.no 1001
Test no.1: Hen manure

Revised version 8: 18. may 2010 Original version 3: 22.dec.2009

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 DANETV method.

2.1. Verification protocol reference

J.no 1001

2.2. Name and contact of vendor

GFE Patent A/S, Løjstrupvej 12A, DK-8870 Langå.
Contacts: Lars Jørgen Pedersen (GFE), phone: +45 70252755, e-mail: ljp@greenfarmenergy.dk.
Anders Peter Jensen (Xergi A/S), phone: +45 99351600, e-mail: apje@xergi.com.

2.3. Name of centre/test responsible

Danish Technological Institute, Test Centre, Life Science Division, Kongsvang Allé 29, DK-8000, Aarhus C.
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 87438468, e-mail tqf@agrptech.dk.
Lars Ditlev Mørck Ottosen (LDMO), Aarhus University, phone: +45 89423306, e-mail: lars.ottosen@biology.au.dk.

3. Test design

The following effects of the GFE pressure cooker were tested:

- Increased methane yield
- Reduction of ammonia content

The GFE pressure cooker is operated in a way where liquids and vapours are added and removed during the treatment. Therefore a mass balance is used in order to calculate the conversion efficiency of the biomass and removal efficiency of ammonia with correct correction for added and removed amounts of substances during treatment.

The effects of the process were tested by:

- Analysis of a number of parameters on the samples
- Batch digestion experiments on the samples
- Weighing of all input and output streams

The test method is described in Appendix 4.

3.1. Test site

The pre-treatment of biomass by the GFE pressure cooker prior to anaerobic digestion was carried out at Green Farm Energy during the period 2-8. june, 2009.
The laboratory scale anaerobic digestion was carried out by the laboratories of Aarhus University, Department of Agricultural Engineering and DTI Chemistry and Water Technology
Analyses of chemical substances were performed by Eurofins.

3.2. Type of site

The tested GFE pretreatment /NIX concept (pressure cooker) is integrated into bio gasification plant at Green Farm Energy A/S Løjstrupvej 12A, 8870 Langå.

The fibres were obtained from the following farm:
Carsten Festersen Hokkerupgade 4a, Hokkerup, 6340 Kruså
The age of the hen fibres manure was 10 month. Manure was transported directly from farm house to biogas plant.

3.3. Address

The address of the test site is: Green Farm Energy A/S, Løjstrupvej 12A, 8870 Langå, Denmark

3.4. Description

The treatment equipment is a pressure cooker which can treat biomass at pressures up to 6 bar (160 ˚C). It is developed to treat and hygienise a number of biomasses incl. animal byproducts category 2 materials (according to EU regulation 1774/2002)
In the treatment CaO is added for increasing pH. The addition has two purposes. It helps degrading the biomass by alkaline hydrolysis and improves the removal efficiency of ammonia.

A simple PI diagram of the boiler and input/outputs is shown in Figure 1.

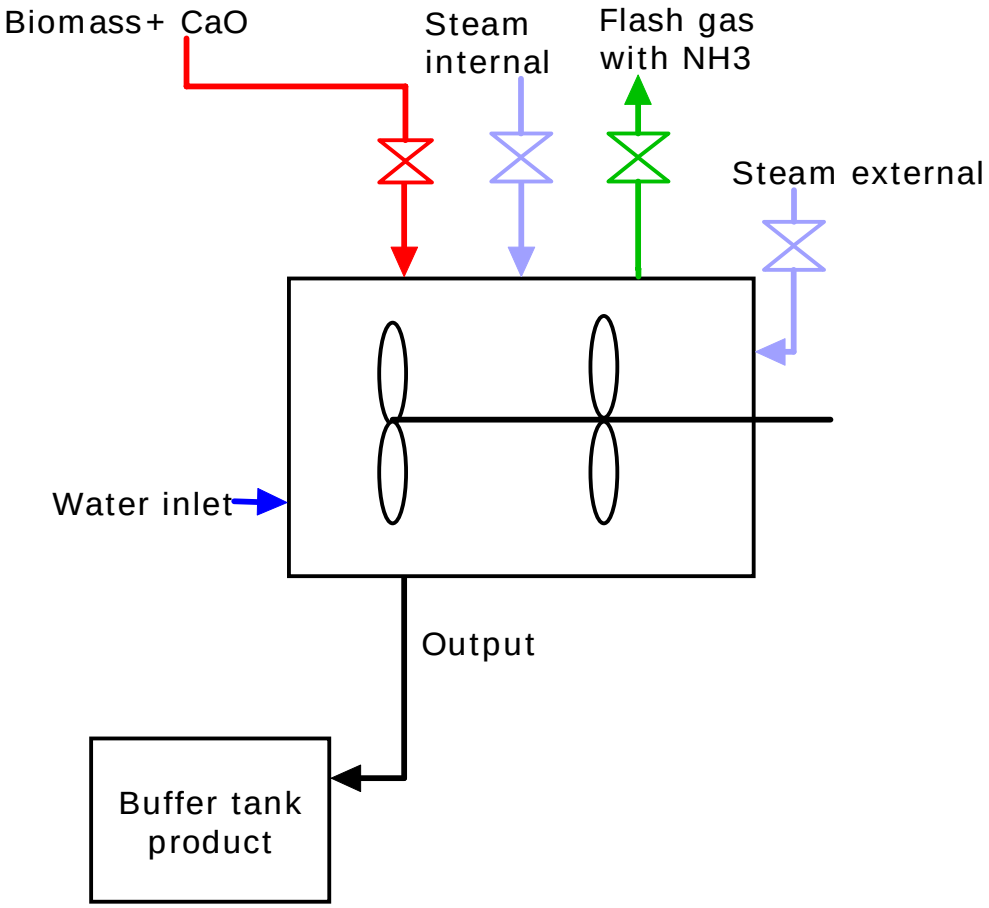

Figure 1 GFE pre-treatment Nix concept (pressure cooker)

The pressure cooker operates as a batch process. The cooker is mounted with weighing cells which makes it possible to register all added and removed masses within a given uncertainty. Added biomass is continuously mixed inside the cooker with a rotating mixer

A processing cycle is described below:

- Biomass is fed to the pressure cooker together with CaO.
- A given amount of water is added
- The pressure is increased by adding steam in the external chamber of the pressure cooker and by adding steam directly into the process.
- After a given treatment period (holding period) at selected temperature the pressure is released in a controlled way to a gas collection system which leads the gas to a scrubber.
- In this period the hot gas with a high content of ammonia and steam is removed from the process.
- When the temperature is below 100˚C, water is added for cooling.
- Finally the treated biomass water mixture is lead to a closed storage tank before being added to the biogas plant.

3.5. Tests

3.5.1. Test methods

The test method used is described 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	Biogas potential incl. GC analysis (TI)
Tenna Overgaard Pedersen	Other analysis (TI)

3.5.3. Test schedule

Task	Timing
Application definition document	May 2009
Verification protocol with test plan	May 2009
Test	June 2009
Test reporting	Oct 2009
Verification	march 2010
Verification report	April 2010
Verification statement	April 2010

3.5.4. Test equipment

The test equipment includes:

- Sampling device for taking samples from treated biomass. The sampling device is a long rod with a sampling cup in the end designed to take samples from outlet tube place >1 m below surface.
- 60 l Containers for mixing samples
- Equipment for supplementary sampling of flashed steam.

3.5.5. 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)	2 samples for input and 2 samples from output with 3 replicates
Removal efficiency of ammonia and data for mass balances 1. Total solids 2. ash content 3. Total nitrogen 4. Ammonium nitrogen 5. Total phosphorus 6. K	3 samples for input and 3 samples from output

3.5.6. Operation conditions

The operating conditions of the pressure cooker during verification of the product is expected to be approximately 139˚C (3.5 bars) with a treatment time of 30 minutes.
CaO is added to reach a high pH value in the treated biomass (preferably >10.5)
An estimate of the necessary amount to reach a high pH value is based on earlier used amounts in GFE/Xergi tests (ref. 2) supplemented with pre-experiments on the used biomass with addition of CaO at room temperature or in heated water. The pH value obtained in the pre-experiments are expected to deviate from the pH value measured on the treated biomass as the biomass reacts with OH- in the pressure cooking at a much higher temperature (140 ˚C).
Steam containing ammonia is normally flashed automatically to scrubber, but during the testperiod this was done manually, in order to allow sampling. This might have resulted in a decreased removal of ammonia than seen under normal operational conditions where the pressure in the cooker is decreased faster.

3.5.7. Operation measurements

- Temperature and pressure of cooker for a complete treatment
- All added and removed masses using weighing cells.
- Added CaO using calibrated weight
- pH of treated biomass (liquid of output)
- Added water using separate weighing of water tanks or the plants calibrated weighing cells when uncertainty is known

3.5.8. Sampling

Sampling was performed in a way to obtain representative subsamples. The sampling procedure was tested in a pre-sampling program and by calculating standard deviations on TS and VS for taken samples. The method used is described below:

Added biomass
During loading of biomass evenly distributed samples were taken from the loading grabs approximately 3-5 loadings - in total at least 10 litre material is taken in a sample.

Course material (larger dry agglomerated particles) was divided by hand. Fibres must be kept intact and therefore no grinding was used – only downsizing by hand and non cutting tools was used to avoid influencing the biogas potential measurement.

The samples were thoroughly mixed in a 60 l container and subsamples were taken by taking samples from different areas of the container transferring to 1 l PE bottles.

Treated biomass
During unloading of biomass liquid pulp in volume 10-20 l were taken from the outlet tube. The samples were thoroughly mixed in a 60 l container and subsamples were taken by taking spoonfuls from different areas of the container keeping it mixed during the whole subsampling. To test differences in concentration when unloading the biomass from the pressure cooker, the sampling was divided in two parts during onloading (first half and second half) using two 60 litre containers.

3.5.9. Product maintenance

The Pressure cooker is integrated into the bio gasification plant at GFE and is as such maintained regularly or when alarms arise in the plants SRO.

3.5.10. Health, safety and wastes

The pressure cooker system is a closed process with no possible contact to material inside the cooker or treated material during normal operation.

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 used analytical laboratory is shown below
Analysis of total and ammonium nitrogen, total phosphorus, total and volatile solids were performed by Eurofins Steins Laboratory A/S, Hjaltesvej 8, DK7500 Holstebro, Denmark. Tlf +45 7022 4286 website: www.eurofins.dk

Determination of biogas volume and methane concentration at laboratory scale was done by Danish Technological Institute, Chemistry and Water Technology, Kongsvang Allé 29, DK8000 Aarhus
Contact: Paul Lyck Hansen

or

Department of Agricultural Engineering, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark, phone +45 89991900.
Contact: Henrik B. Møller

Supplementary analysis on flashed steam was performed by:
Total Ammonia and NH4-N: Analytech
TOC (total organic carbon): Danish Technological Institute, Chemistry and Water Technology

4.2. Analytical parameters

See 4.3

4.3. Analytical methods

Analytical parameters	Standard
Methane potential	Measurement protocol for biogas potential measurements for verification tests (ETV, CBMI) ,Appendix 5
Total solids	EØF 103°C
Total volatile solids (Glødetab)	DS 204
Total nitrogen	Kjeldahl
Ammonium nitrogen	71/393/EØF
Total phosphorus	ICP-OES: (ISO/DS 11885, 2009 ICP: ISO/DS 11885, 1998
K	ICP-OES: (ISO/DS 11885, 2009)

Methane potential was measured according to in house protocol in Appendix 5.

4.4. Analytical performance requirements

See 3.3.

4.5. Preservation and storage of samples

Samples for Eurofins was 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 was freezed immediately after sampling until testing
Supplementary samples for analysis of flash gas were sent in cooling containers to analysis labs after labelling.

5. Data management

5.1. Data storage, transfer and control

The chosen data storage structure is summarized in the table below:

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 performed by NHN
External review of this test plan is described in 1.4

6.2. Performance control – reference analysis

Pressure cooker:

- The cookers weighing cells were calibrated by adding different known amounts of water from water tanks.
- Pressure/temperature sensors were checked using steam tables.

Batch testing of produced biogas:

- Temperature of fermentation was controlled by logging data during the complete measurement period by a temperature data logger.

Sampling:

- A supplementary sampling program was made with sampling of a number of samples of input and output measuring TS, VS and calculating mean and standard deviations to estimate errors of sampling. TI analysis laboratory measured TS (103˚C >=24 hours until constant weight loss) and VS (550˚C, 24 hours) on samples before obtaining final results from Eurofins in order to start batch testing earlier.

6.3. Test system control

The laboratory scale anaerobic digestion test design includes a sample with known Methane potential according to method in Appendix 5.
Further interlaboratory calibration was performed on selected samples between DJF, DTI.

6.4. Data integrity check procedures

All transfer of data from printed media to digital form and between digital media are checked by spot check of not less than 5% of the data. If errors are found in a spot check, all data from the transfer are checked.

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 will be done by NHN, phone: + 45 72201825, e-mail: nhn@teknologisk.dk.
External review of the test report was done by the experts groups in 1.4.

7. Test results

7.1. Test data summary

Operational data
In the test hen fibres was heated to 140˚C with a holding period of 30 minutes.

7.2. Test measurement summary

The summary of results is shown below. A detailed description is found in the test report in Appendix 7.

Table 1 Target and measured values of tested parameters

Parameters	Target	Measured value	Method/comment
Overall performance			
Capacity		9-10 ton fibres calculated as dry matter (DM) /day This corresponds to 15 batches pr. day Capacity for fibres separated from swine manure with 33% DM is calculated to: 30 ton/day The capacity for hen fibres with 52 %DM is calculated to approx. 18 ton/day	Calculation from Log files and tests The capacity depends on chosen treatment time and temperature.
Chemicals			
CaO		2.9%	Weighed amount out of added wet hen fibres
Water for wetting in test (kg)		1246	Weighed amount. In normal operation manure is added
Water addition normal operation		None	In normal operation manure is added for wetting and dilution of fibres
Steam (kg) for treatment of 890 kg hen fibres with DM 52-62%		383	Weighed amount. The used amount in test may be reduced. The amount of added steam depends on the added amount of water/manure for wetting of fibres.

Parameters	Target	Measured value	Method/comment
Energi			
Energy consumption as steam		Not calculated	The energy consumption was not calculated as it was not possible to measure the steam consumption in the external heater during the experiment
Electricity consumption		Estimate: 34 kW pr loading or 54 kW/ton Dry matter	Based on estimate for stirrer which consumes the major part of electricity
Treatment effects			
Removal of NH4-N %	50	60	Mass balance and measured NH4-N content in input and output
Increase in Methane production %	25	30	Methane potential (mesophilic 35˚C) after 30 days active methane production
Other demonstrated effects			
Loss of carbon in flashed steam		<0.35%	Analysis on sampled flashed steam

Conclusion

Demonstrated effects

It is concluded from the tests of the NIX Concept with Hen Manure that:

- The target of 50% NH_4-N removal is achieved
- The target of 25% increase in methane production is achieved

Other effects

It is further demonstrated that

- The carbon loss with flashed out steam is insignificant.
- The pressure cooker homogenizes the fibre material seen in smaller standard deviations for accumulated methane production after 40-55 days

Comments

it must be emphasized that:

- This verification is a result of a test of the pretreatment running under a certain pre-defined set of parameters (temperature, CaO dosis, treatment time and steam flashing). A potential for higher increase in methane production after optimization of these parameters is expected.
- The obtained ammonium removal might also be optimized further by changing the pre-defined set of parameters mentioned above and the result might have been affected by the manual flashing of steam during the test period.

7.3. Test quality assurance

Dry matter and Volatile solids where measured by 2 independent laboratories giving similar results within the uncertainty.

Bio gasification tests of other fibre materials (fibres from separated swine manure) where tested in parallel by DTI and DJF giving similar results.

7.4. Deviations from test plan

The test plan was followed.

In addition supplementary samplings on flashed steam were performed as described in Appendix 4, point 9.

Appendix 1Terms 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 center 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 center for verification of environmental technologies	
(DANETV) test center	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 center, test sub-body	Sub-body of the test center that plans and performs test	None
Test center, verification sub-body	Sub-body of the test center 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
2. Anders Peter Jensen Notat. Status over dokumentation af NIX-koncept 6.marts 2009

Appendix 3: References methods

Appendix 4: In-house test methods

Test of GFE pressure cooker

1 Pre-sampling program
A pre-sampling program was performed to evaluate the standard deviations of sampling and to select the best sampling strategy. A number of samples were taken from nontreated and treated fibres from separated swine manure with measurement of TS and volatile solids (from ash content).

2 Calibration programme
Before starting the tests the weighing cells were calibrated using added weighed amounts of water (etc. 200, 500, 1000 kg).
Further T and P sensors were tested when heating water to operational pressure by comparing with steam tables.

3 Preconditioning of pressure cooker
Before the biomass test the pressure cooker was fed with the biomass of the type used in the test to remove residues of earlier types of biomass from feeding and output system. Manure was used as liquid, but in the end at least 500 liter of water was added after emptying of cooker to flush out residues of manure.

The amount of CaO necessary to reach the preferred pH was estimated by performing a pre-titration experiment in the lab.

4 Test
During test added biomass, CaO was weighed.
CaO was added directly into the screw feeding system before starting addition of fibres.

All added masses of liquids were weighed using the weighing cells on which the pressure cooker is placed. Water is added from tanks in known amounts
It was necessary for stability of weighing cells to stop mixing a couple of minutes to obtain stable weighing results

5 Sampling
Based on the pre-treatment programme which showed small standard deviations on TS and ash content it has been decided that it is sufficient with the following sampling programme:

Sample	Samples input	Samples output
Methane potential	2	2
Combined TS, ash content, Ntotal, ammonia-N,K,P	3	3

Input samples
The samples were taken as 5-10 subsamples during feeding of biomass. The subsamles were thoroughly mixed in a container before taken the required sub samples in 1 liter PE bottles.

Output samples
The samples were taken as 5-10 subsamples during unloading of biomass. A special sampling device developed for the purpose was used

The subsamles were thoroughly mixed in a container before taken the required sub samples in 1 liter PE bottles.

pH was measured on an output sample.

During the test period the operational stability and deviations from normal operational functioning was observed and registered, and the observations reported.

Handling of samples
All samples were refrigerated immediately after sampling and freezed down the same day until later analysis of Methane potential and other analysis.

Measuring Methane potential
Methane potential was measured on added biomass and treated biomass from the pressure cooker

The Methane potential was measured according to the method for measuring biogas potential described in Appendix 5.

The result is a calculation of (l CH4 /VS of added biomass) for treated and non treated biomass as function of time for mesophilic bio gasification.

The dry matter TS and volatile solids content of the samples to be tested was analyzed before performing biogas tests.

6 Removal efficiency of Ammonia
Mass balance calculations were used to calculate removal efficiency of ammonia

7 Total mass balance
In the process the following inputs exist:
Biomass: m_b
CaO:m_{cao}
Water or other liquid for mixing m_{wm}
Process steam m_s
Water or other liquid added for cooling:m_{wc}

The outputs are:
Released gas: m_g
Treated biomass/water or other liquid mixture:m_t

The overall mass balance then is:

$$m_b+m_{cao}+m_{wm}+m_s+m_{wc}=m_g+m_t$$

8 Measuring removal efficiency of ammonia
Total nitrogen and NH4+ -N are measured in added biomass and treated biomass from the pressure cooker. From a mass balance the removed amount of ammonia is calculated.

The removal efficiency of N can be calculated as:

$$\text{Removal \% of N} = (m_b * cN_b - m_t * cN_t) / (m_b * cN_b) * 100$$

Where
Measured N in added biomass :cN_b
Measured N in treated fiber/water mixture cN_t
Added Biomass : m_b
Treated biomass/water mixture m_t

The calculation of the mass of treated biomass/water mixture m_t will be made by two methods for calculation comparison:

1: From registered weights by the weighing cells of the pressure cooker

m_t can be measured within the detection limits of the weighing cells. The detection limits are estimated in a separate calibration programme.

2: From a mass balance for potassium and phosphor:

It is expected that potassium and phosphorous do not evaporate in considerable amount at the used temperatures of the process. This can be verified by measuring concentrations in the condensed gas.

In the following calculation it is assumed that only water is added in liquids with no significant content of N,P,K

Measured N, P and K in input biomass: cN_b, cP_b, cK_b
Measured N, P and K in treated fiber/water mixture cN_t, cP_t,cK_t
This means that

$m_t=cP_b*m_b/cP_t$

and

$m_t=cK_b*m_b/cK_t$

9 Supplementary sampling and analysis of flash steam
It was decided as a supplement to sample the flashed steam to calculate the amount of removed ammonia.

The procedure is as follows:

Gas was transported from a by pass on the output tube to a rack of 3 gas washing bottles filled with a weighed solution of dilute sulphuric acid using a gas pump and by adjusting the bobble rate by a needle valve. The gas washers were placed in a bath with ice. Flash gas was lead through the wash bottles for approximately 10 minutes before changing to a second or third rack. The flow was adjusted to obtain a condensate in the first flask of approx. 100 ml in 10 minutes.

All bottles were closed immediately after sampling and the net content of solution was weighed by subtraction the weight of the empty bottles from the total weight.

Bottle 1,2 was mixed. Bottle 1+2 and 3 were transferred to glass flasks which were immediately closed. In the lab pH was measured. It was always acidic in flask 3. If pH was not acidic in flask 1+2 (pH<4) concentrated sulphuric acid was added until acidic. The amount added was recorded for later volume correction. The amount of condensed steam was calculated from the weighed amounts of solution before and after sampling.

The flasks were analysed for N total, NH4-N and TOC.

After analysis, the concentration of analysed substances was calculated per liter of condensed steam.

Appendix 5 In-house analytical methods

Measurement protocol for biogas potential measurements for verification tests (ETV, CBMI) revision v5 22/12-09.

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.

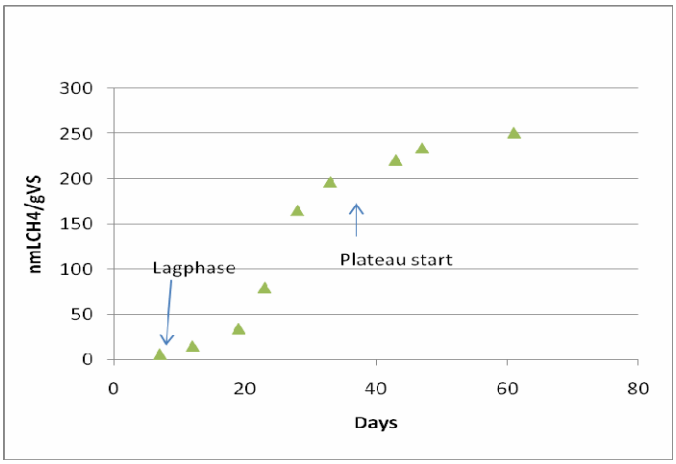

Figure 1. Accumulated methane production

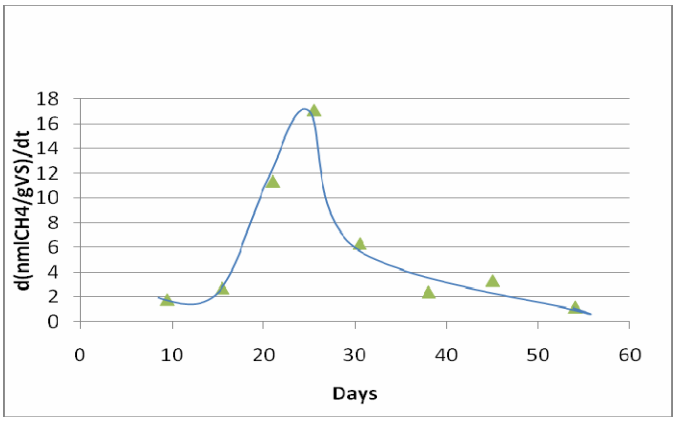

Figure 2. Methane production rate

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 6Data reporting forms

Data are reported in schemes given in Appendix 7.

Appendix 7 Test data report

Test
The test was performed as described in Appendix 4

Presampling and supplementary sampling
Presampling results are shown in Appendix 7a
Supplementary sampling results are shown in Appendix 7b

The pH of the fibres was measured in a 2.5 wt% CaO concentration at room temperature (0.5 g CaO+20 g fibres+50 g demin water). pH after 10 min was 11.96.

Earlier results on fibres from separated swine manure showed a similar pH after heating to 100 C and at room temperature (20 C, 10 min) within 0.1 pH at different CaO concentrations between pH 9.6 and pH=11.8. It was therefore concluded that any significant consumption of base due to degradation of biomass etc. exist at higher temperatures than 100 ˚C and at longer treatment periods than 10 minutes.

Calibration
Calibration results are shown in Appendix 7c.

Operational data for treatment in boiler
Data of operation is shown in fig.a7.1.

In order to obtain a high accuracy of the weighing cells the plant was driven manually during the test as it was shown during calibration test and pre-sampling program that this operation mode decreases the noise from the rotating mixer with a factor of approximately 10 (from approx +/- 30 kg to +/- 3 kg).

The figure shows a treatment temperature of approx. 140 ˚C a corresponding pressure of 3.4 bar and a holding period of approx 30 minutes. (At 12:18 a temperature of T=139 ˚C and a pressure of P = 3.4 bar was noted in the log book.)

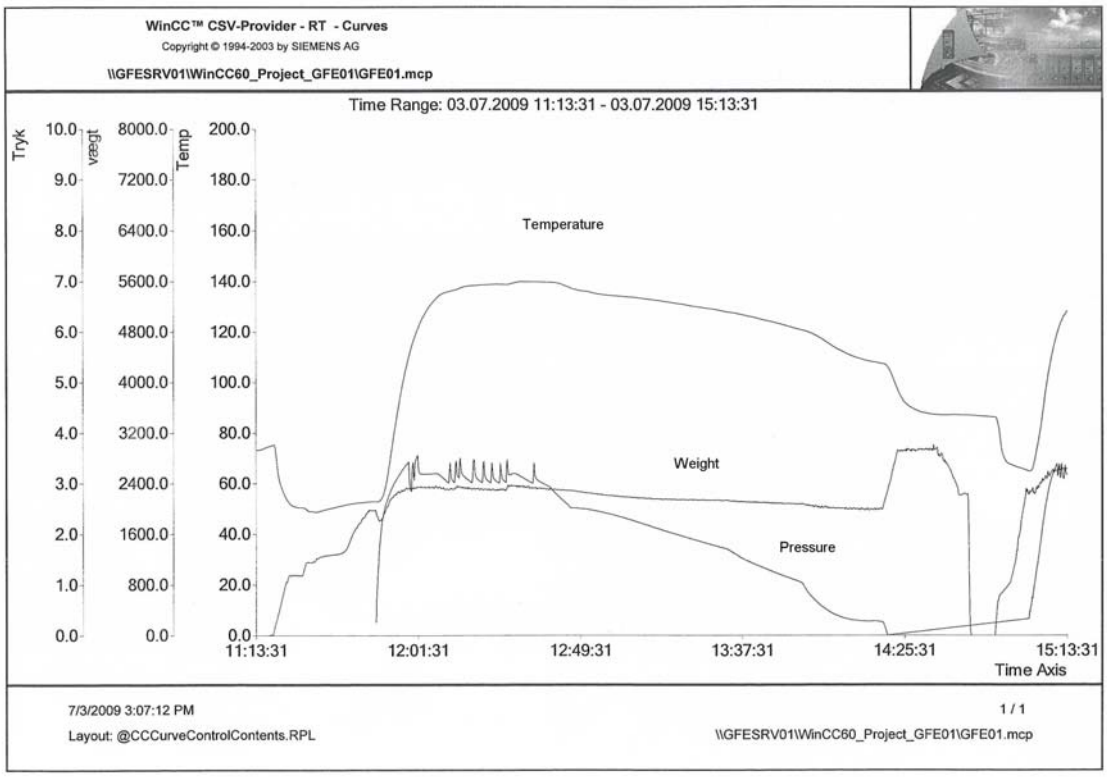

Figure a7.1 Operating data for the test

In fig a7.2 data are shown for automatic loading and control of the pressure cooker in the period 2/7-09 9:00 until 3/3 9:00. The curve shows a stable operation with similar loaded fibre amounts, temperature, pressure and holding period for each cycle.

Operational Data for Capacity
From the log data (fig a.7.2) other inspected log data and interview with operator the capacity of the plant is estimated below:

Minimum cyclus time is 85 min (20 min. holding time) corresponding to 17 cyclusses (loadings and treatment of fibres) pr. Day. At 30 min holding time 15 cyclusses can be performed.
The typical amount of fibres loaded is approximately 9-10 ton dry matter pr. Load corresponding to 150-170 ton dry matter fibres pr. Day. For swine fibres with 33% DM the load corresponds to 1700-1800 kg wet fibres pr. load.

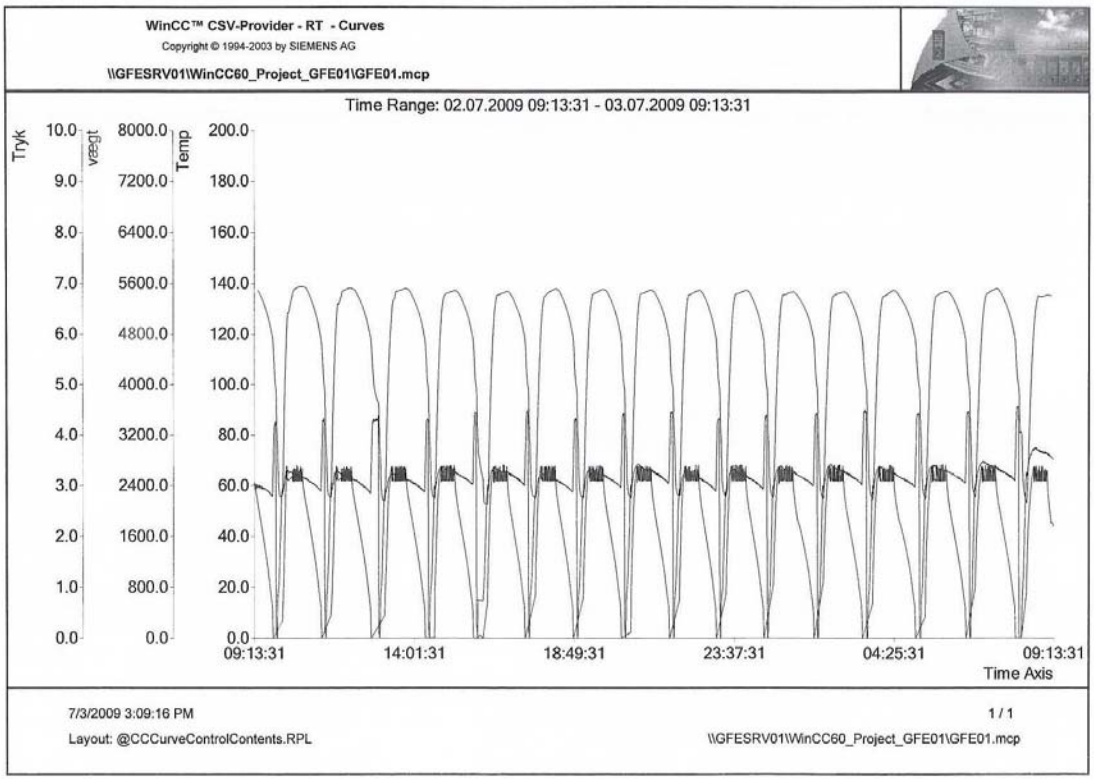

Figure a7.2 Added fibres from separated swine manure one from 2/7-09 9:13 till 3/7-09 9:13

Operational data for Electricity consumption

The major consumption of electricity is estimated to be used by the stirrer as it runs during the complete cycle. The feeding system also uses a comparable amount of power when it is operating, but the feeding system only runs for approximately 15 minutes out of 90 minutes and is thus neglegted in the estimate. From readouts on the SRO the stirrer power was estimated to around 20 A in average of the cyclus of approximately 90 minuttes. The stirrer use 3 fases of 380 V. The power consumption can then be calculated to 20*380*3*1.5=34 kW pr cyclus. This corresponds to 34*16 cyclusses/10 ton DM=54 kWh/ton or 0.2 GJ/ton DM. The dry matter fibres have a heat value approximately like wood (18GJ/ton) from which it can be calculated that the electricity consumption corresponds to approximately 1% of the heat value in the fibres and therefore is negligible.

Operational data for Consumption of steam

It was not possible to calculate a heat balance as it was not possible to measure the amount of added steam in the external heating loop of the boiler during the experiment. Further data for recovered energy was not available. However the heat from the treated biomass is recovered in the biogasification process and heat in returned condensated steam from the external heating loop of the boiler are recovered by heat exchange.

Mass flows
Calculated masses of inputs and outputs after correcting the weights of the weighing cells using the calibration results are shown in table.a7.1 and a7.2.

Table a7.1 Data from log book, added amounts, corrected weights

Time	Recorded weight - weighing cells (kg)	Corrected weight (kg)	Description
11:10	0	1.4	
	1152	1248.0	With added water
	1972.5	2135.8	With added fibres and CaO
12:43	2326.5	2518.8	With added steam (end holding period)
13:40	1990.5	2155.2	After steam flash
	2932.5	3174.5	With added cooling water

For the shown weights in the table, the mixer on the pressure cooker was stopped for approx. 2 minutes to reduce the noise on recorded weights.

Table a7.2 Calculation of mass flows

Amount	kg
water added	1246.5
fibres added incl. CaO	887.8
CaO	25
Fibres added	862.8
Steam added	383.0
Steam loss during flash	363.6
Cooling water added	1019.3

Sampling
Sampling was made as described in 3.5.8.

Input was sampled by taking a number of samples at different positions of each added grab and preparing two mixed average samples of approx. 10 litre named A and B.

Output from outlet tube was sampled in two separate halfs during unloading of treated biomass each with approx. 10 litre collected material named S1 and S2.

Supplementary sampling of flash gas was described in Appendix 4, point 9.

Analysis results

Analysis of added and treated fibres

Table a7.3 shows analysis results for added fibres (input) and treated fibres (output).

Table a7.3 Analysis of input and (original data)

	Added fibres	Added fibres	Added fibres	Treated fibres	Treated fibres	Treated fibres
Parameter	**A**	**B**	**A/B**	**S1**	**S2**	**S1/S2**
Total N g/kg	20.75	20.75	20.75	3.99	3.83	3.39
NH4-N g/k	8.2	8.01	7.85	0.69	0.72	0.73
P g/kg	12	12	13	2.8	2.4	2.3
K g/kg	20	20	20	4.4	4.3	4.3
DM %	63.18	61.9	62.36	15.28	13.44	13.34
S g/kg	4.8	5	4.8	1.1	1	0.99
VS %	59	60	60	59	60	60

A/B is a 1:1 mixture of the two separate input samples
S1/S2 is a 1:1 mixture of the two separate output samples

Table a7.4 shows average values of analysis data for input and output with absolute standard deviations and standard deviations in %

Table a7.4 Analysis of input and (Average and Standard Deviation)

	Added fibres			Treated fibres		
Parameter	**Average**	**STDEV**	**STDEV %**	**Average**	**STDEV**	**STDEV %**
Total N g/kg	20.75	0.00	0.00	3.74	0.31	8.31
NH4-N g/k	8.02	0.18	2.18	0.71	0.02	2.92
P g/kg	12.33	0.58	4.68	2.50	0.26	10.58
K g/kg	20.00	0.00	0.00	4.33	0.06	1.33
DM %	62.48	0.65	1.04	14.02	1.09	7.79
S g/kg	4.87	0.12	2.37	1.03	0.06	5.91
VS %	59.67	0.58	0.97	59.67	0.58	0.97

The pH of fibres in the pressure cooker before treatment should according to the pre-experiment at atmospheric pressure have been pH=11.96 which is much higher than the preferred value after treatment of pH=10.5. However pH dropped more than 2 units during the pressure cooking to pH=9.75 in the treated fibre liquid. This value is lower than the preferred value although not that far from it. It must be concluded that it is not possible to simulate the output value of treated fibres by addition of CaO at atmospheric pressure.

Regarding ammonia the equilibrium $NH_3 + H^+ = NH4^+$ the equilibrium will be shifted nearly completely towards NH_3 at 100 ˚C (>99%). The reason is that the pKa value decreases with temperature.

The pKa values are shown in the table below

pKa for ammonia equilibrium

Temperature ˚C	Calculated (1)	From ref.2	% NH3 at pH 9.75
25	9.26	9.245	75.5
50	8.52	8.539	94.4
100	7.17		99.7

1: Calculated from equilibrium data in Outokumpu HSC Chemistry 5.11
2: Ref.2 J.am.soc 1950 v72 p1393

This means that pH in the pressure cooker is theoretically sufficient to ensure that all ammonia are present as NH_3 which can be flashed out and not as NH_4^+ which is an ion and therefore not released with the flash steam.

Supplementary analysis on flash steam
Table a7.5 shows analysis results of contents of absorption flasks.

Table a7.5 Analysis on condensed flash steam

	NH4-N mg/l	**TOC (NVOC mg/l)**
absorption no. 2 (flask 1+2)	6000	360
Absorption no. 2 (flask 3)	1.1	
absorption no. 3 (flask 1+2)	5800	310
Absorption no. 3 (flask 3)	0.39	

In tests with treatment of other manure fibres (swine, cattle and chicken fibres) the following was observed:

- Ntotal equals NH4-N within the uncertainty of analysis. Therefore Ntotal was omitted here
- Analysis of VOC liq NVOC (l) and TOC (s) showed that NVOC was the major part of the total TOC content corresponding with more that 85%. Therefore Only NVOC (l) was analysed here.

The content of NH4-N in the control flask 3 was negligible showing that all NH4-N was captured in the absorption flasks.

Test results for ammonia removal
Based on the recorded mass flows of input and output a mass balance was calculated as described in Appendix 4.

Table a7.6 Mass balance using recorded masses, and analysis data (DM =62.5%)

Mass balance	Input	Output	%	diff kg
Fibre kg	862.81	3173.08		
Tot N kg	17.90	11.86	-33.77	6.05
NH4N	6.92	2.26	-67.29	4.66
P	10.64	7.93	-25.45	
K	17.26	13.75	-20.32	
S	4.20	3.27	-22.17	
Org N	10.98	9.59	-12.66	
VS	321.65	265.44	-17.48	
Removal NH4-N %		67.29		

A large error in P, K, S and VS is observed.

The supplementary sampling program in Appendix 7b showed that there was a large uncertainty in the dry matter estimation of the added fibre due to the heterogeneity of the material. The standard deviation of 11 samplings was 9% and a Dry Matter content from 51 to 71% was observed.

It is therefore assumed that the analysed DM average of 62.5 % is not representative of the true Dry Matter content of the added material.

In Tabel a7.7 the dry matter content has been adjusted to obtain a correct mass balance of VS (ie. VS of input= VS of output).

Table a7.7 Mass balance using recorded masses, and analysis data
But with analysis results corrected to DM=51.5 %

	INPUT	OUTPUT	%	diff kg
Fibre kg	862.81	3173.08		
Tot N kg	14.76	11.86	-19.65	2.90
NH4N	5.70	2.26	-60.32	3.44
P	8.77	7.93	-9.56	
K	14.22	13.75	-3.33	
S	3.46	3.27	-5.57	
Org N	9.05	9.59	5.96	-0.54
VS	265.13	265.44	0.12	

Example:
Tot N =862.81 kg*20.75 g N/kg/1000= 17.9 kg with DM =62.5%.

If the correct DM of the 863 kg is lower (51%) then the nutrients will be diluted i.e.
Tot N true= 20.75*51/62.5=17.23 g N/kg and then Tot N= 862.81 kg* 17.23/1000=14.76 kg.

Here mass balances for P, K, VS, S agrees within 10%.

Error analysis
Calculation of Standard deviation is based on the 3 analysis values.
The error on analysis at a 95% confidence limit (error on average) = 1.96 *sdev/sqrt(n) =1.13 *sdev.

To test the mass balance sensitivity to analysis error a calculation of the mass balance was performed with addition or subtraction of one standard error for each analysis value (N, P, K etc.).

The sensitivity test are shown in table a7.8 and a7.9.

Table a7.8 (test of analysis error on mass balance 1)

Change Input + rel stdev %	Change Output + rel stdev %		INPUT	OUTPUT	Difference %	Difference kg
		Fibre kg	862.81	3173.08		
0.00	-8.31	Tot N kg	14.76	10.87	-26.33	3.89
-2.18	-2.92	NH4N	5.58	2.20	-60.61	3.38
-4.68	10.58	P	8.36	8.77	4.92	
0.00	1.33	K	14.22	13.93	-2.04	
2.37	-5.91	S	3.54	3.08	-13.21	
0.00	0.00	Org N	9.18	8.67	-5.50	0.50
0.97	-0.97	VS	267.69	262.87	-1.80	

Table a7.9 (test of analysis error on mass balance 2)

Change Input + rel stdev %	Change Output + rel stdev %		INPUT	OUTPUT	Difference %	Difference kg
		Fibre kg	862.81	3173.08		
0.00	8.31	Tot N kg	14.76	12.84	-12.97	1.91
2.18	-2.92	NH4N	5.83	2.20	-62.30	3.63
4.68	10.58	P	9.18	8.77	-4.46	
0.00	1.33	K	14.22	13.93	-2.04	
1.04	7.79	0				
2.37	5.91	S	3.54	3.46	-2.31	
0.97	0.97	Org N	8.93	10.65	19.22	-1.72
0.00	0.00	VS	265.13	265.44	0.12	

Example total nitrogen table a7.9:
Total N input: 20.75 g/kg rel standard deviation 0%
Total N output: 3.74 g/kg rel standard deviation 8.31% Test + one rel standard error: =4.05 g/kg

Fibre output=3173.08 kg

Total N input corrected to dry matter 51% =14.76 kg (table a7.7)
Total N output at +one relative standard error =3173.08*4.05/1000=12.84 kg
Difference %= -12.97%

It is seen that the mass balance for P, K, S, VS is on slightly influenced by analysis error. Contrary the uncertainty in total nitrogen removal is very large (from 13 to 26 % removal) in table 7.8 and 7.9. Due to this it is not possible to calculate a useful value for the removal of organic N (Calculation of organic removal of N gives a removal from 5.5% to -19 %).

However, the removal of NH4-N is in all cases >60%.

Complementary tests on flash steam

Table a7.10 shows that the removed amount of NH4-N in the complete test period is approximately 7.4 kg NH4-N. This is a larger amount than calculated from the mass balance (3.44 kg) supporting the observed high removal efficiency of ammonia. The analysis data suggest that a considerable amount of the organic N content was converted in the pressure cooker and removed by the flash steam.

Table a7.10

	Absorption no. 2 (flask 1+2)	**Absorption no. 3 (flask 1+2)**
Flash steam total kg	363.60	363.60
Condensed water g	106.08	75.95
Solution total for analysis g	344.37	277.22
TOC mg/l solution	360.00	310.00
g TOC per l condensed steam	1.17	1.13
g TOC in all flash steam	424.94	411.42
NH4-N mg/l [1)]	6000	5800
g NH4-N per l condensed steam	19.48	21.17
g NH4-N in all flash steam	7082.27	7697.48

If a calculation is based on the total nitrogen in the output and the ammonia content of the flash steam the following removal efficiency of Total N can be calculated:

Total N in output =11.86 kg.
N in flash steam equals NH_3 in flash steam =7.4 kg
Then N total in input should have been =11.86 +7.4=19.26 kg and the removal efficiency of total nitrogen is estimated to =100- (19.26-7.4)/19.26*100 =38%.

In table a7.11 is shown an estimate of the carbon loss with the flash steam.

Table a7.11

Fibre weight wet kg	**862.8**	
TS %	62.5	
VS %	59.7	
VS kg	321.9	
% C of VS (C6H12O6)	40.0	
kg C	128.8	
	absorption no. 2 (flask 1+2)	absorption no. 3 (flask 1+2)
% C of input	0.33	0.32

The table shows that the loss of carbon with the flash steam is <0.5 wt % assuming that the volatile solids of the fibres has a composition is $C_6H_{12}O_6$ corresponding to 40% carbon content

Biogas (Methane) potential
The untreated fibres and the treated fibres were tested as described in the protocol of Appendix 4.

The temperature of the climate chamber was 35 ˚C+/-0.5 ˚C except for small periods of approx 1 hour when bottles were removed for volume measurement as seen in figure.a7.3

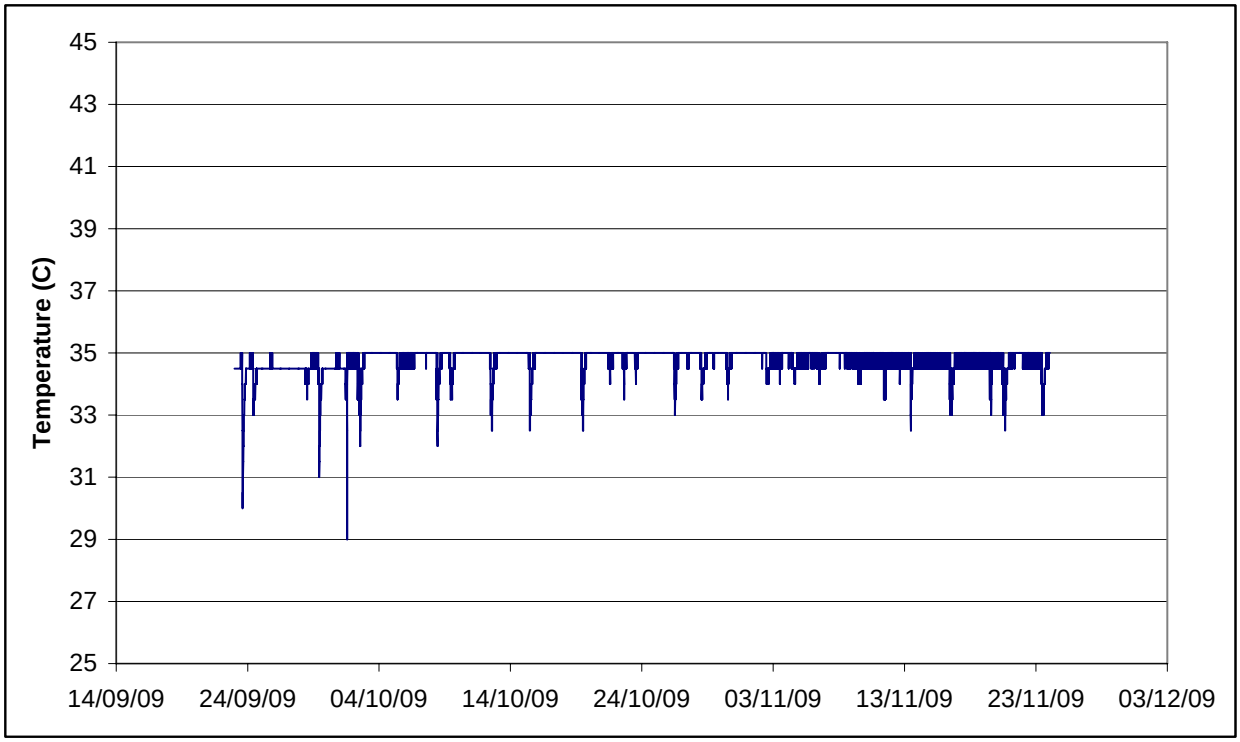

Figure a7.3 Temperature of biogasification

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

Results are shown below for 25 g VS/l and 10 g VS/l (a separate triplet test and a separate dublet test)

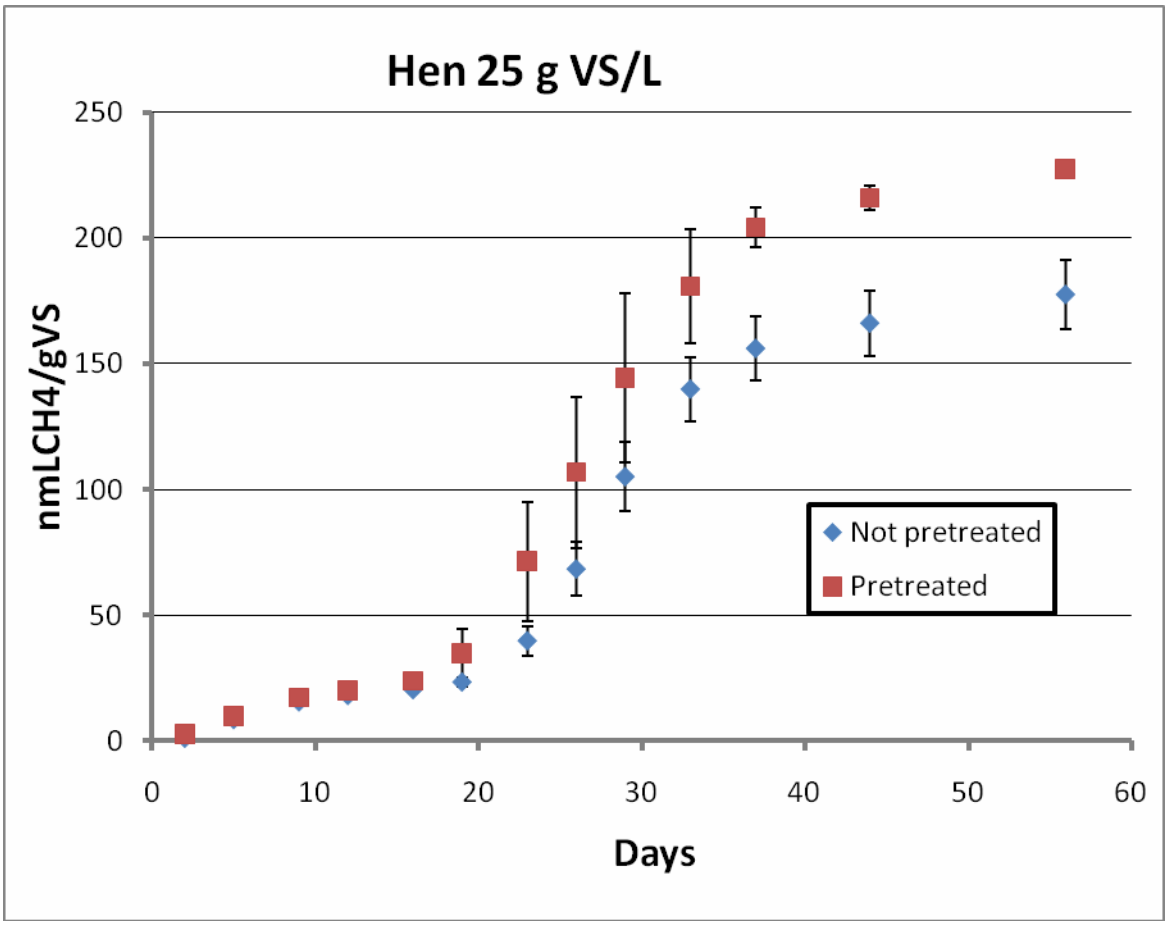

Fig a7.4 Accumulated methane production for 25 g VS/l (6-double) Standard deviations of the summarized methane production for each 6-double measurement point are shown in the figure.

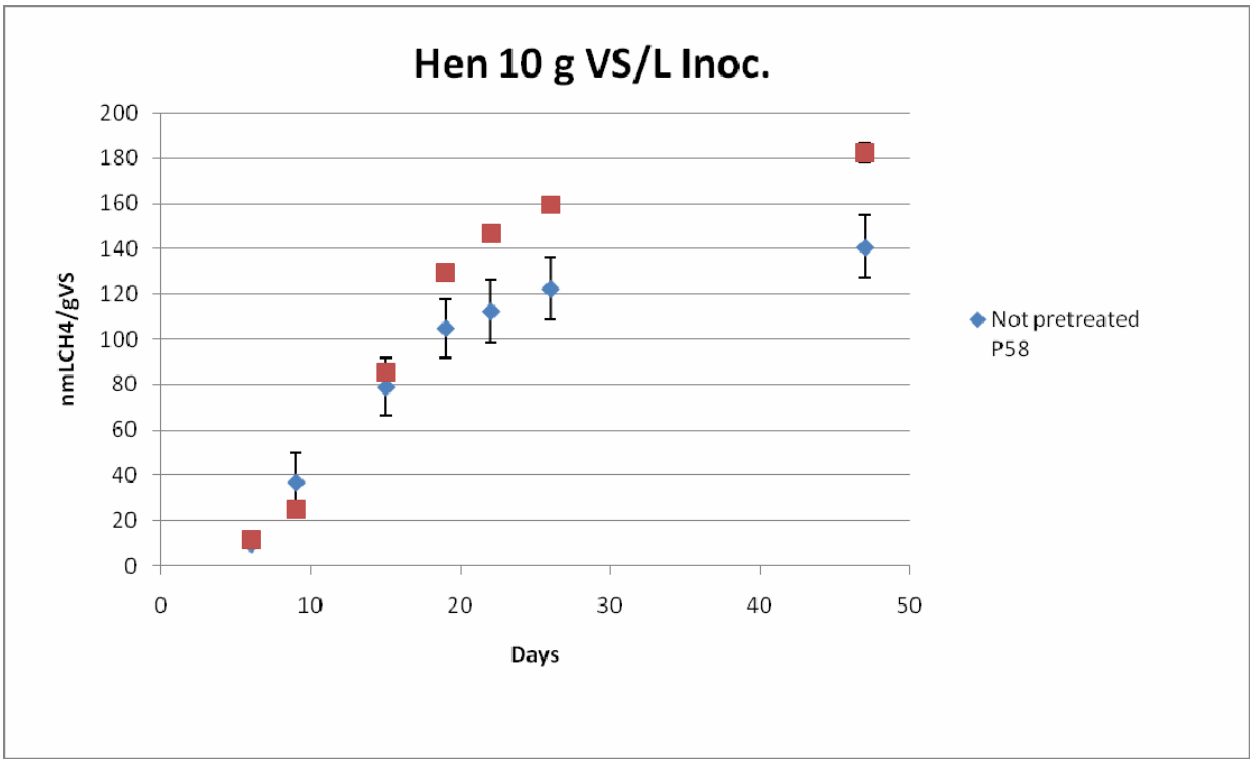

Fig a7.5 Accumulated methane production for 10 gVS/l (triplet test) Standard deviations of the summarized methane production for each triplet measurement point are shown in the figure.

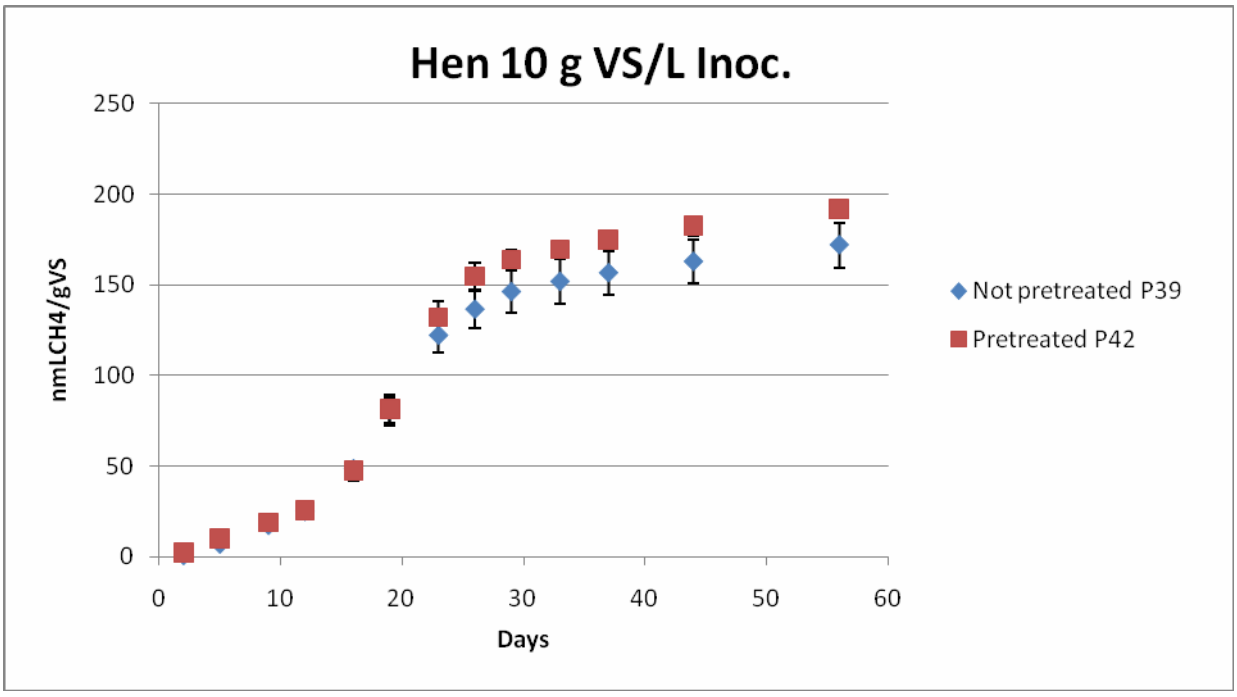

Fig a7.6 Accumulated methane production for 10 gVS/l (duplet test). Standard deviations of the summarized methane production for each duplet measurement point are shown in the figure.

In Fig.a7.4 to a7.6 it is observed that the standard deviations are much smaller for the pre-treated fibres than fibres which were not pre-treated. This observation is evaluated to be caused by the homogenization effect of treating the biomass fibres in the pressure cooker. In the interval 20-30 days the standard deviations are rather high. This can be explained by small differences in lag phases of the 6 tests in fig. a7.4 In contrast a commercial biogas plant is in steady state as loadings are continuously fed and will not show any lag phase.

The methane production rates are shown below:

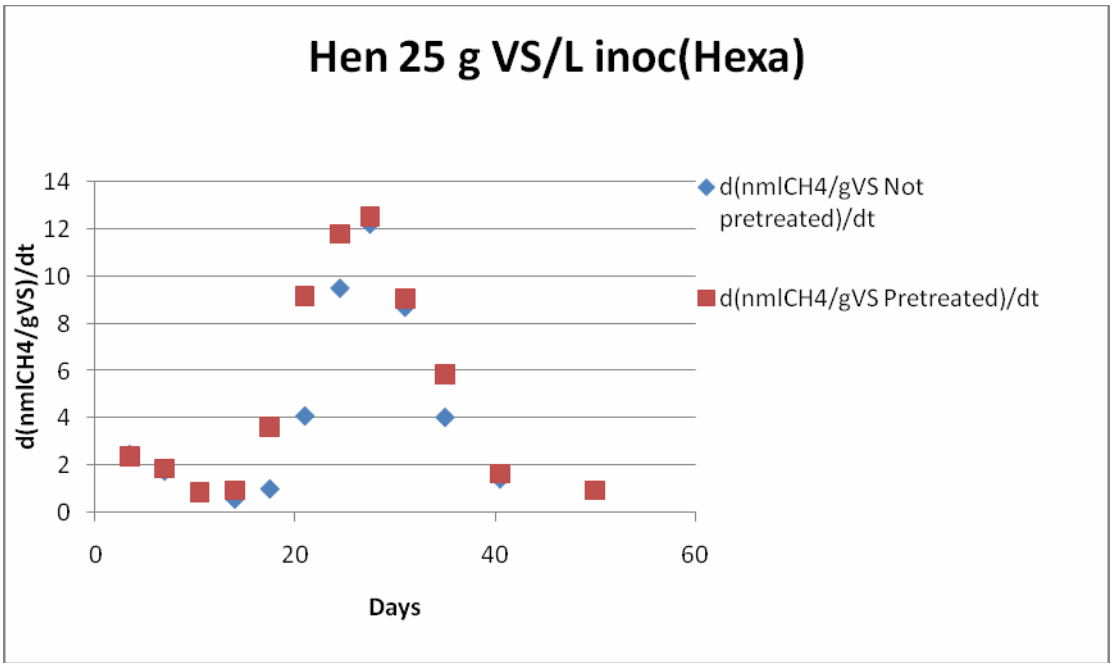

Fig a7.7 Methane production rate pr. day

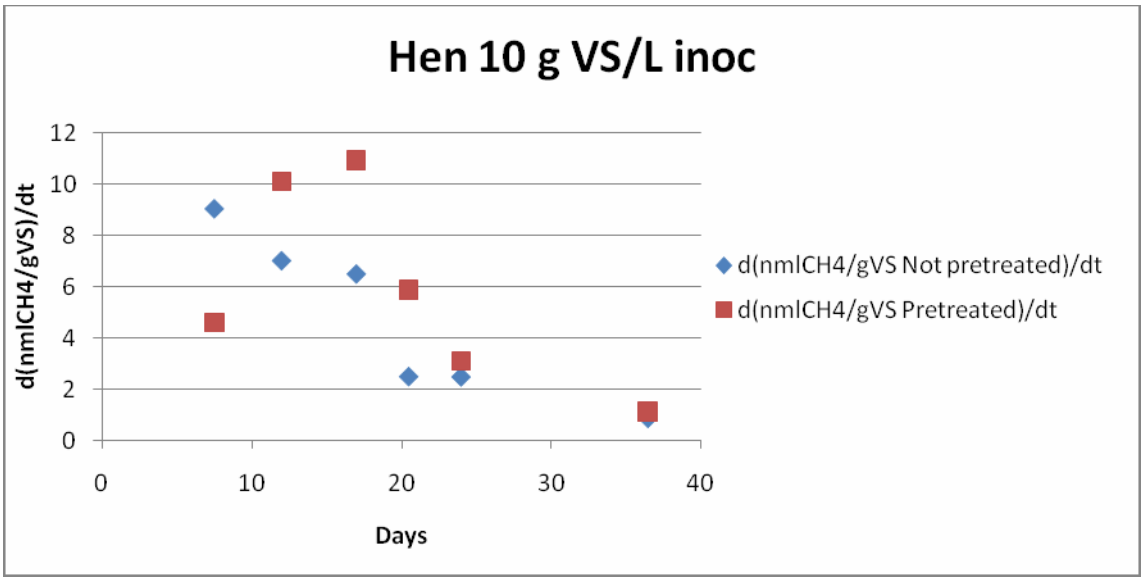

Fig a7.8 Methane production rate pr. Day (from triplet test)

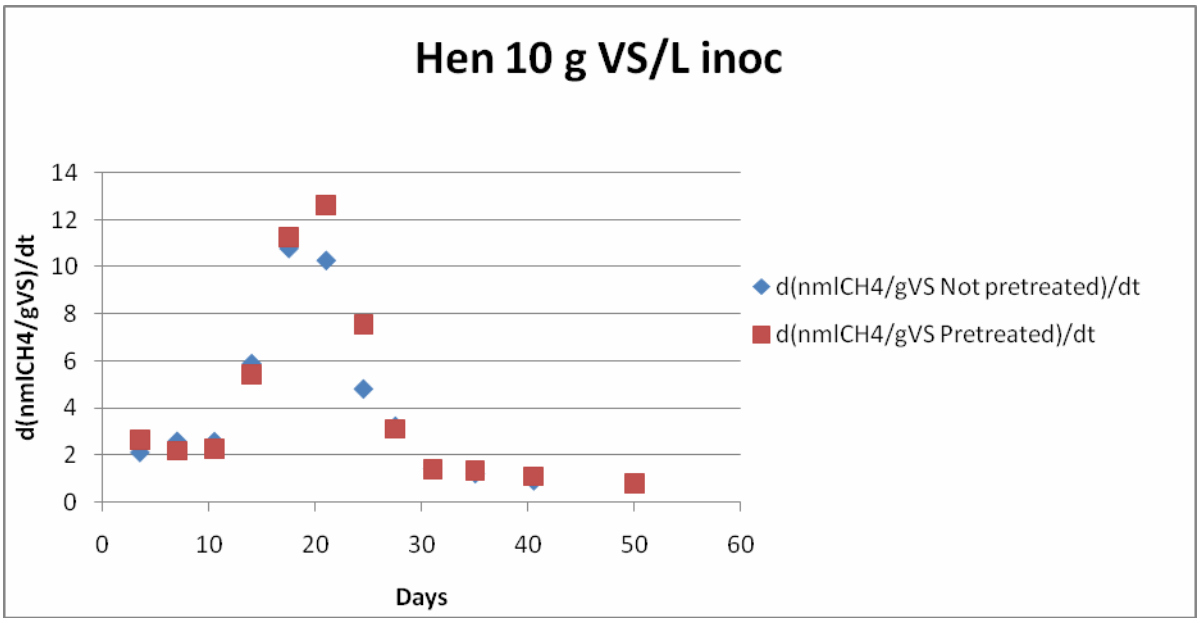

Fig a7.9 Methane production rate pr. Day (from dublet test)

As seen in fig a7.7 there is a lag phase of approximately 10-12 days in methane production for 25 g VS /l where the lag phase is approx 6 days for 10 g VS/l. The major production was finished after 40 days corresponding to 30 days production when correction for the lag phase.

Correcting for the lag phase the following results are obtained for increase in biogas

		Reading (corrected for lag phase)
Replicates	**gVS/l**	**day**
6	25	30
2	10	30
3	10	31

The methane production for all 6 measurements on input and output at 25 g VS/l are shown in the table below. The methane production /g VS was calculated after 40.5 days by taken the average of the methane production at day 37 and 44. The data corresponds to 30 days methane production when correcting for a lag phase of 10.5 days.

No.	**Input**	**Output**
1	167.45	201.10
2	155.44	203.59
3	181.89	202.37
4	158.08	208.31
5	147.96	215.53
6	148.84	214.40
Average	159.94	207.55

Taken the average of all 25 gVS/l after 40.5 days (30 days active methane production) gives:

Input: 159.94 ml CH4/g VS with STDEV = 12.9 and error at 95% confidence level= 10.3
Output: 207.55 ml CH4/g VS with STDEV =6.2 and error at 95% confidence level= 5.0

The increase in methane production at 25 gVS/l can be calculated to (207.55-159.94)/160 *100 = 30%.

Taken the average of all five 10 gVS/l tests after 40.5 days (30 days active methane production) gives

Input: 145.1 ml CH4/g VS with STDEV = 17.6 and error at 95% confidence level = 15.4
Output: 176.6 ml CH4/g VS with STDEV = 4.1 and error at 95% confidence level = 3.6

The average increase is 22%.

The error due to a non representative sampling is higher for the 10 g VS/l measurements than the 25 g VS/l measurements.

At biogas plants like Green Farm Energy loadings of >25 gVS/l are typically used. The test result shows that for hen manure an increased methane production of approximately 30% can be expected at VS concentrations in the range close to 25 g VS/l.

Appendix 7a

Presampling programme GFE pressure cooker

B. Malmgren-Hansen

Lars Ditlev Mørck Ottosen

27 May 09, revised 22 December 09

Introduction: Test, certification and declaration of environmental technology requires proper and documented sampling strategies. Improper sampling may obscure the test and lead to inconclusive results.

The presampling programme is part of the CBMI project subproject 05 Test, certification and declaration www.cbmi.dk . The purpose of the programme is to describe the best sampling strategies and methods for selected treatment processes for biomass and to test the proposed sampling methods. The final aim is to have a documented sampling programme for subsequent evaluation and verification of the pretreatment technology.

Slurry from intensive livestock production constitutes a major source of potential biomass for biogas production. However, the gas production is expected to benefit from pretreatment of the biomass which increases the anaerobic digestibility. The GFE pressure cooker is designed to treat the fibre fraction of separated slurry through controlled heating to approximately 139 degrees for 30 minutes with the aim of enhancing subsequent biogas yield from digestion in a thermo or mesophilic biogas reactor. The pressure cooker is automatically fed and emptied into the biogas reactor.

A presampling test was performed on 19 May 09 on added and treated fibres from a GFE pressure cooker to adjust the sampling strategy and evaluate the standard deviations of the samples, thus ensuring consistent and representative sampling (as a basis for subsequent testing of enhanced biogas yield potential following pressure cooking of the fibre fraction from separated slurry.)

Methods

Sampling of material feed to the pressure cooker (separated pig slurry fibres). A sample of input fibres was taken from the crane during feeding and was mixed in a 60 litre container. Following visual and mechanical inspection, it was estimated that 1000 ml samples would cover the in situ heterogeneity of the feeding material. 5 different samples of the feeding material (800 ml) were taken randomly and stored in 1000 ml PE bottles.
In the laboratory, the sample was subjected to further visual inspection for heterogeneity and a random subsample of approx 20 g was taken from each bottle for measurement of moisture content and loss of volatiles.

Sampling of treated fibres (after pressure cooking)

As part of the pressure cooking process, the feeding material is mixed with liquid slurry, which means that the product of the pressure cooking process is a highly viscous liquid, assumingly well mixed. In an operating pressure cooking system, the liquefied treated biomass is pumped directly to the anaerobic digester.

For the purpose of sampling treated biomass, access was given to the outlet of the pressure cooker and samples were taken with a specially constructed device from the 40 cm tube outlet from the pressure cooker.

Fig 1.: Sampling device

Fig. 2. Pipe for sampling (pressure cooker outlet)

Personal protection equipment with air supply through carbon filters was carried by the operator during sampling from the outlet pipe to avoid any risk of exposure to hazard gasses.

The output flow was manually controlled during sampling. Sampling was not initiated until the outlet pipe was thoroughly flushed with the actual batch of fibres, as to avoid mixing with remaining fibres from the previous cooking.

A sample of approximately 7 litres was taken and transferred to a 60 litre container, where it was thoroughly stirred by the operator. Seven 800 ml subsamples were transferred to 1000 ml plastic bottles.
In the laboratory, a subsample of approx 60 gram was taken of each 800 ml sample for measurement of moisture content and loss of volatiles after mixing the sample by stirring and rotating the bottles.

The moisture content was determined as weight loss following drying for 24 h and 72 h at105 °C. Dry Matter DM % defined as 100 – moisture content (%)

Loss of volatiles (VS) was determined as loss on ignition at 550 degrees for 24 hours.

Fig 3. Sampling of pressure-cooked biomass into a 60 l container

Results

Dry matter

Feeding material, untreated fibres

Sample	Tara (bottle)	Tara+Sample	Dried (24h)	Dried (72 h)	DM %
F1	67.642	85.368	73.631	73.613	33.685
F2	66.318	87.464	73.427	73.415	33.562
F3	70.295	94.642	78.138	78.120	32.139
F4	66.519	83.635	72.002	71.990	31.964
F5	70.565	88.440	76.285	76.272	31.927

Pressure cooked, treated fibres with added slurry

Sample	Tara (bottle)	Tara+Sample	Dried (24h)	Dried (72 h)	DM %
1	91.615	162.283	103.841	103.819	17.269
2	98.220	158.277	108.502	108.488	17.097
3	98.399	161.889	109.282	109.266	17.116
4	99.287	154.045	108.825	108.806	17.384
5	96.939	154.577	106.802	106.787	17.086
6	99.005	153.492	108.519	108.486	17.400
7	95.877	155.212	106.297	106.271	17.517

Untreated fibres: DM mean: 32.66% (SDEV: 0.89 % SDEV: 2.72)

Pressure-cooked fibres/slurry: DM mean: 17.27% (SDEV: 0.17 % SDEV: 1.00)

Volatiles = loss on ignition at 550 ˚C of dry matter

Feeding material, untreated fibres

Sample	Tara (bottle)	Tara+Sample	After 550 C 24 h	% loss (VS)
F1	26.8784	31.2024	27.5064	85.476
F2	25.9149	30.6993	26.5279	87.188
F3	30.2328	35.2685	30.8994	86.763
F4	29.1647	34.1119	29.8051	87.055
F5	26.5062	31.5648	27.1335	87.599

Pressure cooked, treated fibres with added slurry

Sample	Tara	Tara+Sample	After 550 C 24 h	% loss (VS)
1	21.0122	26.3096	22.3317	75.092
2	20.8501	25.8926	22.0670	75.867
3	17.6346	22.5625	18.8440	75.458
4	26.9163	32.0416	28.2121	74.718
5	27.7487	32.9086	28.9812	76.114
6	26.3549	31.2722	27.5169	76.369
7	23.5275	28.6342	24.7661	75.746

Untreated fibres: VS mean: 86.82% SDEV: 0.81 % SDEV: 0.93

Pressure cooked fibres/slurry: VS mean: 75.62% SDEV: 0.58 % SDEV: 0.76

Conclusion

The standard deviations for dry matter DM and volatile solids VS were low for the untreated feeding material, 2.7 % and 0.93 %, respectively. Standard deviations for the pressure-cooked samples were even lower, 1.0 % and 0.76 %, respectively, probably reflecting the higher level of mixing and hence, less heterogeneity following pressure cooking. Sampling of fibres was adequately reproducible and the tested sampling methods were appropriate for future technology verification of gas potentials.

Appendix 7b
Supplementary Sampling Programme - Hen Fibres

B. Malmgren-Hansen, Ulrik Toft Hansen and Lars Ditlev Mørck Ottosen
11 August 09

Introduction: Test, certification and declaration of environmental technology require proper and documented sampling strategies. Improper sampling may obscure the test and lead to inconclusive results.

The presampling programme is part of the CBMI project subproject 05 Test, certification and declaration www.cbmi.dk . The purpose of the programme is to describe the best sampling strategies and methods for selected treatment processes for biomass and further to test the proposed sampling methods. The final aim is to have a documented sampling programme for subsequent evaluation and verification of the pretreatment technology.

Slurry from intensive livestock production constitutes a major source of potential biomass for biogas production. However, the gas production is expected to benefit from the pretreatment of the biomass, which increases the anaerobic digestibility. The GFE pressure cooker is designed to treat the fibre fraction of separated slurry through controlled heating to approximately 139 degrees for 30 minutes, with the aim of enhancing subsequent biogas yield from digestion in a thermo or mesophilic biogas reactor. The pressure cooker is automatically fed and emptied into the biogas reactor.
A supplementary sampling of input was made on 3 July 09 during tests with hen fibres in order to evaluate the possible sampling error.

Sampling during test
During feeding, 4 subsamples were taken from grab 1, 3 from grab 2, and 4 from grab 4. The samples were filled in 1 l PE bottles with approx. 800 ml. The samples were all taken from random chosen places in the grabs.

Taking subsamples in the laboratory

All 11 subsamples were treated the following way:

The content of each bottle was emptied into a larger container and all larger particles were manually broken into pieces of less than 5 mm. The material was mixed thoroughly and a subsample of approx. 10 g fibres was taken for measurement of DM (dry matter) and VS (volatile solids) using a weighed crucible.

The moisture content was determined as weight loss following drying for 24 h and 72 h at 105 °C. Dry Matter DM % defined as 100 – moisture content (%)
Loss of volatiles (VS) was determined as loss on ignition at 550 ˚C for 24 hours

Results

The results are shown below

Dry matter

Samples	Tara	tara+sample	dryed for 24 h	DM %
Chicken F5 3/7				
Grab1 a	23.2245	32.3301	29.469	68.58
Grab1 b	25.304	35.4181	32.195	68.13
Grab1 c	19.0322	26.68	24.489	71.35
Grab1 d	24.584	35.8675	32.0298	65.99
Grab2 a	25.3633	35.902	32.6639	69.27
Grab2 b	25.4185	38.8504	34.4077	66.92
Grab2 c	20.8515	28.7162	25.8636	63.73
Grab3 a	19.8078	26.7975	24.1289	61.82
Grab3 b	24.3076	33.4238	28.9717	51.16
Grab3 c	21.0113	29.2807	25.8777	58.85
Grab3 d	20.1642	26.434	24.1287	63.23

Grab1	DM% mean: 68.50; SDEV: 2.20; % SDEV: 3.22
Grab2	DM% mean: 66.64; SDEV: 2.78; % SDEV: 4.18
Grab3	DM% mean: 58.77; SDEV: 5.39; % SDEV: 9.17
All measurements	DM% mean: 64.46; SDEV: 5.72; % SDEV: 8.87

Volatiles = loss on ignition at 550 ˚C of dry matter

Samples	Tara	Tara+sample	550˚ C 24 h	% loss (VS)
Grab1 a	23.2245	29.469	25.5971	62.01
Grab1 b	25.304	32.195	27.8746	62.70
Grab1 c	19.0322	24.489	21.0506	63.01
Grab1 d	24.584	32.0298	27.4502	61.51
Grab2 a	25.3633	32.6639	28.0139	63.69
Grab2 b	25.4185	34.4077	28.7775	62.63
Grab2 c	20.8515	25.8636	22.7532	62.06
Grab3 a	19.8078	24.1289	21.3163	65.09
Grab3 b	24.3076	28.9717	25.8814	66.26
Grab3 c	21.0113	25.8777	22.8305	62.62
Grab3 d	20.1642	24.1287	21.5865	64.12

Grab1	VS% mean: 62.31 ,SDEV: 0.68 % SDEV : 1.09
Grab2	VS% mean: 62.80 ,SDEV: 0.83 % SDEV : 1.32
Grab3	VS% mean: 64.52 ,SDEV: 1.54 % SDEV : 2.39
All measurements	VS% mean: 63.25 ,SDEV: 1.43 % SDEV : 2.27

Conclusion

It matters a great deal from which grab the sample is taken. The standard deviations of DM measurements are high and the mean values are remarkably different. Mean values beween 51.2% and 71.4% were registered. The standard deviations of VS measurements are lower and the mean values are between 61.5% and 66.3%.

It can be concluded that significant errors may be expected in the DM measurement of the experiment.

It shall be mentioned that it was not possible to obtain a correct representative sampling from the added fibres in the loading grab, as a proper sampling from the three-dimensional space in the grab is very difficult. A correct sampling can be made if a one-dimensional sampling can be performed. An example of a one-dimensional sampling is if all fibres are transported on a belt and subsamples are taken at evenly spaced intervals.

Alternatively, an improvement in sampling can be made if the entire amount of the very inhomogeneous material is premixed and, if possible, downsized moderately to etc. 10 mm particle size.

Appendix 7c
Calibration of weighing cells used in connection with GFE pressure cooker (ETV)
11.sept. 09

B.Malmgren-Hansen

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

Purpose
To calibrate weighing cells of GFE pressure cooker.

Method for calibration of weighing cells.

The GFE pressure cooker is mounted on weighing cells.

To calibrate the weighing cells tanks with water was weighed on a calibrated weight and added to the pressure cooker using a pump as seen on figure 1.

Figure 1 adding water for calibration

The result is shown in figure 2.

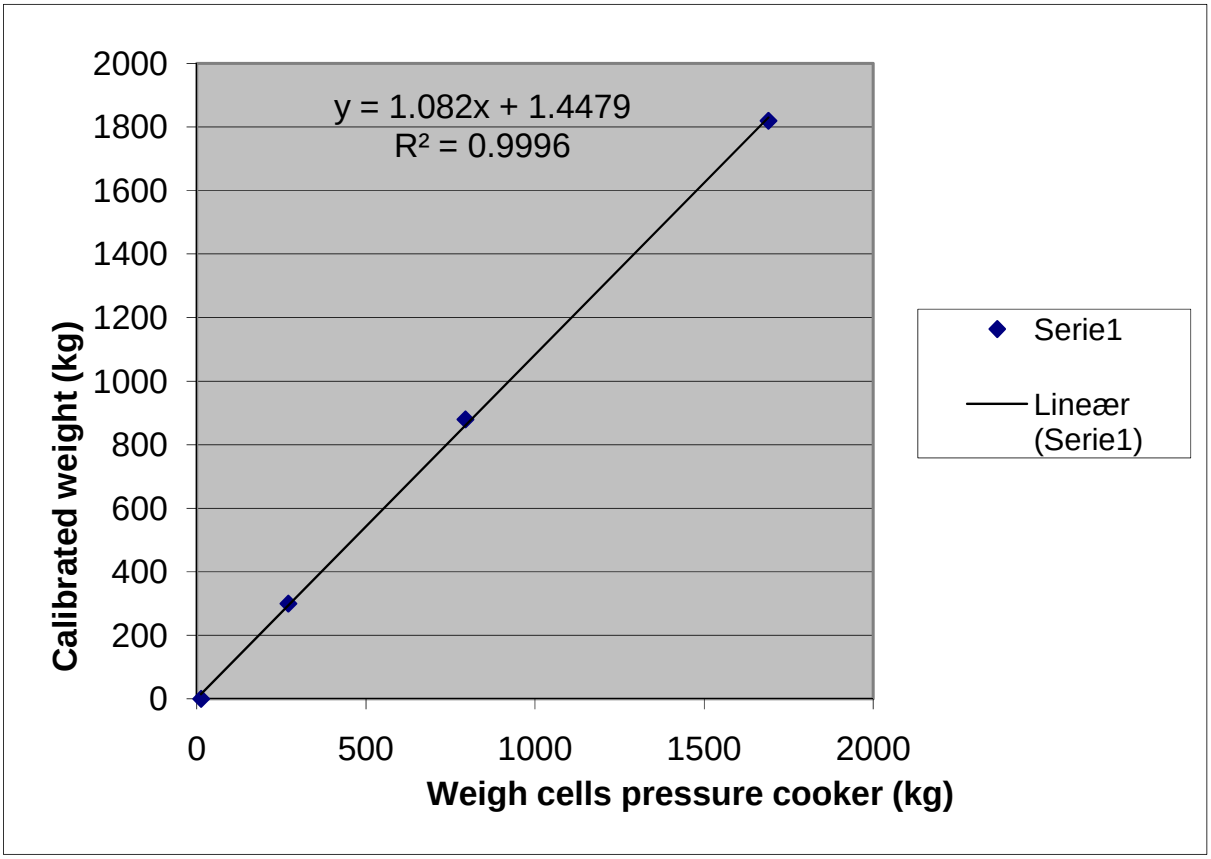

Figure 2 calibration of weighing cells.

The result shows that the weighing cells are linear but most be corrected by 8.2 %