GFE – pretreatment/NIX Concept

Pre-treatment of biomass for anaerobic digestion

Verification Report

J.no. 1001
Test no.1: Hen manure

Revision version 4: 18.may 2010 Original 29.april 2010

1. Table of Contents

2. Introduction

Environmental technology verification (ETV) is an independent (third party) assessment of the performance of a technology or a product for a specified application, under defined conditions and quality assurance.

DANETV is a Danish centre for verification of environmental technology.

This protocol describes the framework for the verification of the technology product and provides information required for the Test plan.

2.1. Name of product

The product is the GFE – pretreatment /NIX concept

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/verification responsible

Danish Technological Institute, Verification Centre, Life Science Division, Kongsvang Allé 29, DK-8000, Aarhus C.
Verification responsible: Arne Grønkjær Hansen, phone: +45 72202142; e-mail: agha@teknologisk.dk.
Internal reviewer: Nils H. Nilsson (NHN), phone: + 45 72201825, e-mail: nhn@teknologisk.dk.

2.4. Verification and test organization

The verification will be conducted by Danish Technological Institute.

The test organization is shown in Figure 1.

The verification is planned and conducted to satisfy the requirements of the ETV scheme currently being established by the European Union (EU ETV).

Verification and tests will be performed by Danish Technological Institute under DANETV under contract with GFE Patent A/S.

The day to day operations of the verification and tests will be coordinated and supervised by TI personnel, with the participation of the vendor, GFE Patent A/S.

The testing will be conducted at Green Farm Energy, Løjstrupvej 12A, 8870 Langå.

TI testcentre Test subbody will perform all samplings during the verification.

Green farm energy personnel will operate the pressure cooker which is installed on the biogas plant in normal operation and assist with all necessary tasks as described necessary for verification as described in the contract.

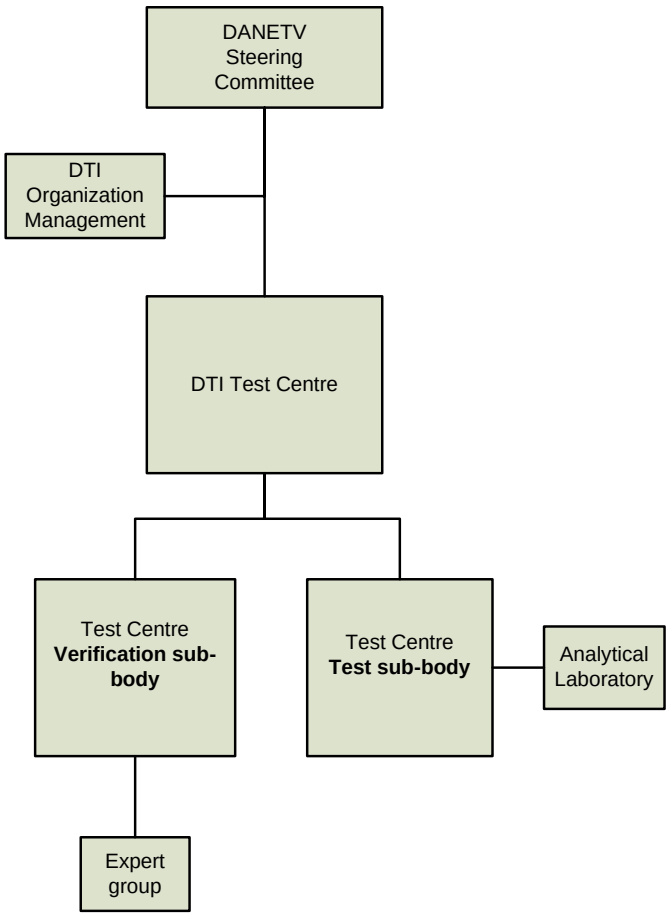

Figure 1 Verification organization

Table 1 Responsible personnel in test organization

Unit in test organization	Responsible
DTI Dan ETV steering committee member	Lars Jøker
DTI organization management Life science division	Bo Frølund
DTI Life science division Test Centre, Verification subbody	Arne Grønkjær Hansen
DTI Life science division Test Centre, Test subbody	Bjørn Malmgren-Hansen

2.5. Expert group

The expert group assigned to this verification and responsible for review of the verification plan and report documents includes:

Thorkild Qvist Frandsen (TQF), Agrotech, phone: +45 87438468, e-mail: tqf@agrotech.dk.
Lars Ditlev Mørck Ottosen (LDMO), Mikrobiologi, Biologisk Institut, Aarhus Universitet, Bygning 1540, Ny Munkegade 114, 8000 Århus C, phone: +45 89423306, e-mail: lars.ottosen@biology.au.dk.

2.6. Verification process

Verification and tests are conducted in two separate steps, by the Verification sub body and the Test sub-body respectively.

The verification sub-body is responsible for preparation and compilation of the Verification protocol and the Verification report.

The Test sub-body is responsible for the test plan and the test report.

The steps in the verification are shown in Figure 2.

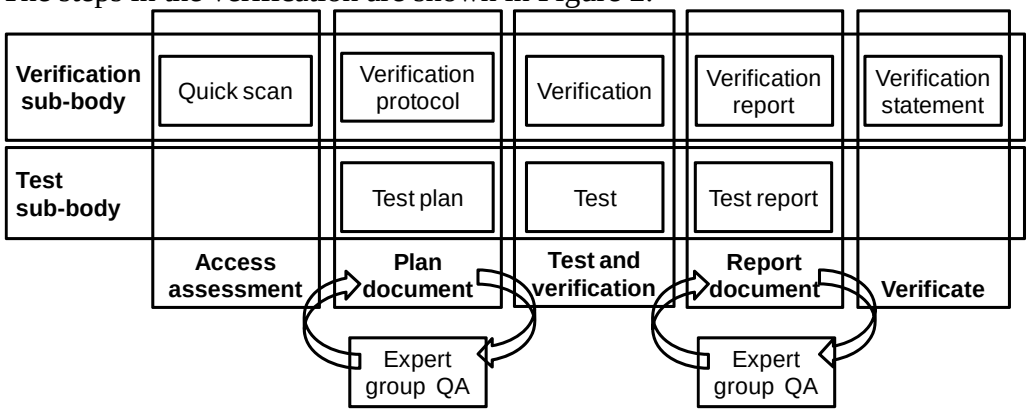

Figure 2 ***Verification steps***

A DANETV verification statement will be issued after completion of the verification

3. Description of the technology

The process is a thermal/chemical conversion process for pre-treatment of biomass to increase production of methane in bio gasification.

This is accomplished by a combined effect of temperature and alkaline hydrolysis at pH around pH=10.

The purpose of the process is to increase the surface area of particles in the biomass and degrade the organic material into smaller more easily digestible compounds.

In addition the process also liberates ammonia from the biomass. Organic nitrogen in proteins etc. is partly converted to ammonia in the water phase. The ammonia is removed from the water phase in the process in a flashing step where pressure is reduced and steam with ammonia is removed through a valve. A high pH in the process of pH>10 is obtained by adding CaO.

pKa for NH_4^+ =NH_3+H^+ is 9.25 at 25˚C and decreases with temperature. Therefore the ammonia equilibrium is shifted towards NH_3 ensuring that a large amount of ammonia will leave the pressure cooker when the vapour is flashed out. This makes it possible to use nitrogen rich biomasses for bio gasification without reaching inhibitory limits of NH4-N in the bioreactor.

4. Description of the product

The product verified 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 additives can be added such as lime (CaO) 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 3.

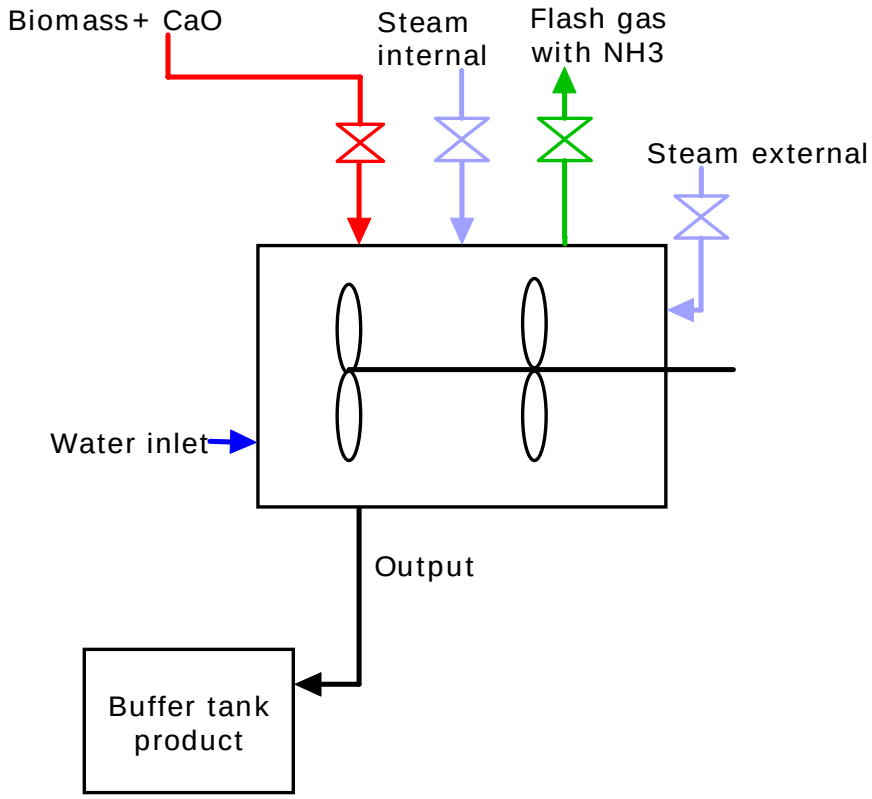

Figure 3 GFE pre-treatment NIX concept (pressure cooker **).**

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 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.

5. Application and performance parameter definitions

5.1. Matrix/matrices

Matrix: Biomass for anaerobic digestion
Application:Thermal/chemical pre-treatment of biomass

5.2. Target(s)

The targets of the product are:

- Methane yield per kg VS
- Concentration of ammonia (NH4-N)

5.3. Effects

The effects of this application are

- Increased methane yield for treated biomass compared to untreated biomass in the treatment period of interest in biogas plants (15-30 days)
- Reduction of ammonia (NH4-N) content in treated biomass

5.4. Performance parameters for verification

The ranges of performance relevant for the application, as derived in Appendix 3, are presented in Table 2. These ranges are used for planning the verification and testing only.

The performance parameters relevant for this protocol are:
For added biomass and treated biomass the following parameters must be measured:

- Biogas potential
- Total nitrogen content
- Ammonia content
- Total phosphor and potassium
- Dry matter
- Volatile solids

Other performance parameters which must be measured includes:

- The amount of added biomass for a complete batch
- The amount of added additives for a complete batch

- All other added amounts or removed amounts either through weighing or from calculation

5.5. Additional parameters

No additional parameters have been evaluated see comments on user manual below (8.3).

6. Existing data

6.1. Summary of existing data

A number of experiments have been performed on the plant so far.
The experiments show a good effect on removal of ammonia and an increase in biogas potential for a number of biomasses.

6.2. Quality of existing data

A thorough documentation of used methods is lacking in the received material and there are no repeated measurements on different samplings for treated and added biomass for each run. In addition the previous experiments have not been performed by an independent third party.

6.3. Accepted existing data

It has been decided that the existing data are not sufficient for verification of the GFE pressure cooker. To obtain verification new test runs with the types of biomass of interest must be performed according to the guidelines in this protocol.

The experiments performed by the company shows the following improvements (Ref.6):

Table 2 Results of experiments

Type	CaO added wet %	% improval CH4 35 days mesophile biogasification	% reduction NH4-N
Fibres from separated swine manure without polymer	1.5	Approx. 100	92
Cattle manure polymer separated	2.5	(30 days thermophile: 23%)	68
Poultry manure	1.9	(0)	37
Hen manure		No data	No data

7. Test plan requirements

7.1. Test design

The test design is based on taking representative samples of untreated biomass that is fed to the pressure cooker and samples of treated biomass. In addition all mass flows are registered.

The effects of the process are tested by:

- analysis of a number of parameters on the samples
- laboratory batch digestion experiments on the samples
- weighing of all input and output streams

The detailed test design is given in the test plan.

The GFE pressure cooker was 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 correction for added and removed amounts of substances during treatment.
During treatment some of the organic content (cellulose and hemicellulose) in the biomass is expected to be converted to soluble substances. Further a large amount of the nitrogen content will be converted to soluble ammonia which is partly removed in the process.

This means that the dry matter and volatile solids content of the treated biomass can be somewhat different from the added biomass.

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

The biogas potential was measured according to the method for measuring biogas potential described in ref.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 were analyzed before performing biogas tests.

Ammonia
Mass balance calculations are used to calculate removal efficiency of ammonia

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:

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

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:

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

$m_t = cK_b * m_b / cK_t$

Sampling
At least two independent samples must be taken of input and output streams in order to calculate standard deviations.

The actual number of samples and the technique for sampling will depend on plant design and the used biomasses. The samples necessary for performing the test is given in the test plan.

To reduce sampling error a number of representative samples should be taken during feeding and unloading of treated biomass. Subsamples can then be taken and mixed to representative samples.

Presampling was performed prior to testing in order to evaluate the standard deviations of parameters which depend on fibre composition, moisture content, ash content, volatiles etc.This was done because hen fibers had not been tested before. The pre sampling is described in detail in test plan and test report.
During the test period the operational stability and deviations from normal operational functioning was observed and registered, and the observations reported in the test report (test personnel is responsible for this see-test plan).

Normal operation of plant outside the test periods with automatic loading of biomass was inspected by looking at 2 selected logs (with 10-20 automatic cycles each). The logged data was available for test personnel. The parameters in logs included weight, temperature and pressure of pressure cooker. From inspection of the logs it can be verified that the plant is able to operate automatically with reproducible result.

7.2. Reference analysis

For batch tests of biogas potential a reference component in the medium will be tested as described in ref.5.

7.3. Data management

Data storage, transfer and control was done in accordance with the requirements of the “ETV centre quality manual for DTI “Water and Chemistry Technology” enabling full control and retrieval of documents and records.

7.4. Quality assurance

The quality assurance of the tests included control of the reference system, control of the test system and control of the data quality and integrity.
The test plan, test report and verification protocol was reviewed by the expert group prior to verification. see Figure 2.

7.5. Test report

The test report followed the template of the TI verification centre quality manual /2/ with data and records from the tests presented.

8. Evaluation

8.1. Performance parameter summary

The average figures of performance parameters are shown below:

Table 3 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.
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

Figure 1 shows the accumulated methane production in laboratory test at mesophillic conditions during the test period of 55 days. There is a lag phase of approximately 10-12 days in methane production The major production was finished after 40 days corresponding to 30 days production when correcting for the lag phase.

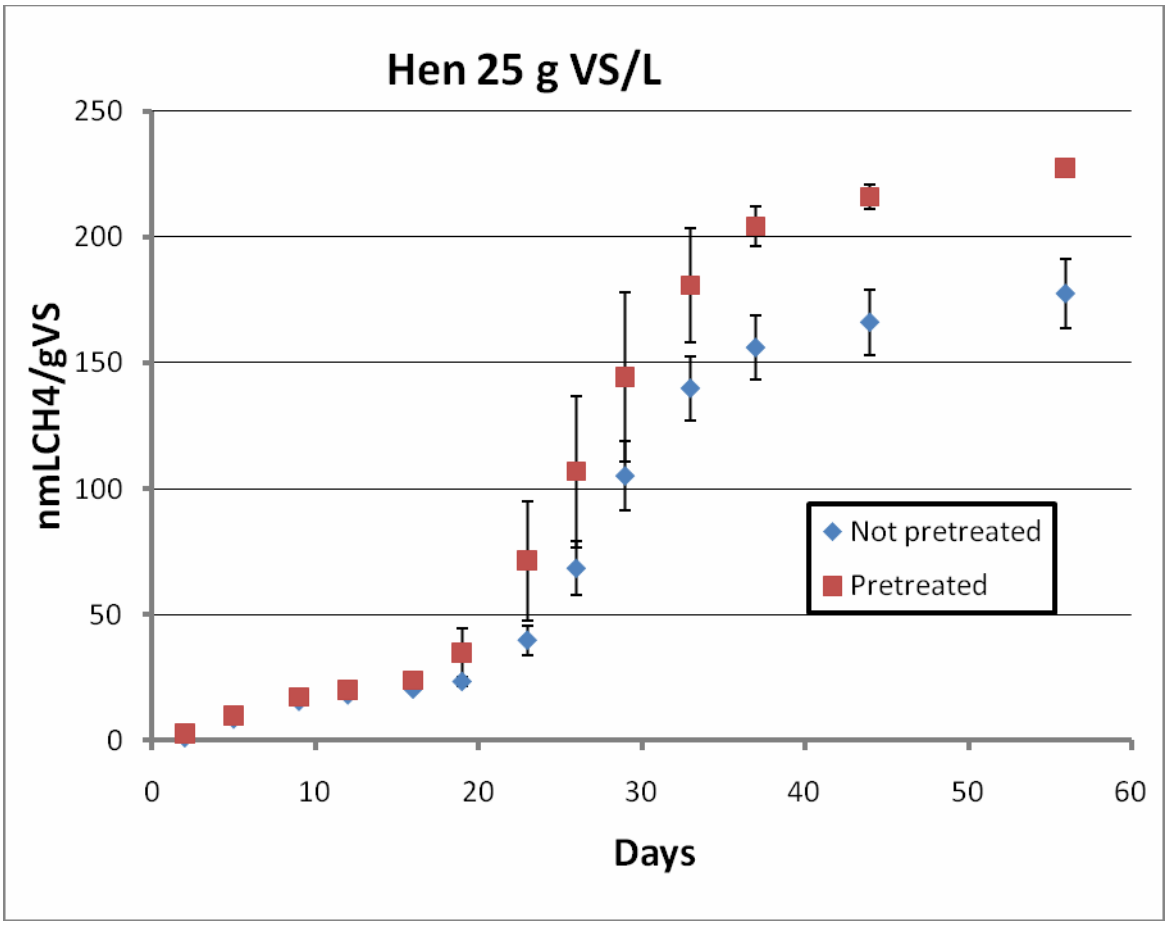

Figure 1. Accumulated methane production for 25 g VS/l (6-double) Standard deviations of the summarized methane production for each 6-double measurement point are shown in the figure.

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

- 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 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.

8.2. Evaluation of test data quality

The data quality is evaluated to be at scientific level and standard deviations of repeated measuring were all very low, which is a good indicator that repeated tests will show same results and therefore the data can be used as a good indicator. However the method being of batch laboratory test set up does not simulate the real conditions in biogas plants.

8.2.1. Control data

The test results were checked using parallel tests in two laboratories of the following parameters:

- Dry matter (DM), Volatile solids (VS), selected tests of Methane Potential. –see testreport

8.2.2. Audits

No audits were performed.

8.2.3. Deviations

Standard deviation of all relevant parameters are calculated and depicted as bars on the graphs in the testreport for methane potentials.

The test plan has been followed - No deviations from test plan are registered. Initial presampling program for calibration of weight and determination of variation was performed as described.

8.3. Compilation of additional parameters

8.3.1. User manual

When sold as a separate unit a manual shall be provided. In particular the manual, should bear instructions for:

- Operation of the system
- Prevention of and dealing with incidents
- Occupational health and safety measures
- Service and maintenance
- Surveillance of the installation

No separate manual for the pressure cooker existed when the test was performed on this existing plant where the pressure cooker is an integrated part of the feeding system for the biogas reactor.

8.3.2. Occupational health and environment

Has not been evaluated specifically but GFE biogas plant is regulated and controlled under Danish laws including APV (working place evaluation)

9. Liability exclusion

ETV verifications are based on an evaluation of technology performance under specific, predetermined operational conditions and parameters and the appropriate quality assurance procedures. DTI makes no expressed or implied warranties as to the performance of the technology and do not certify that the technology will always operate as verified.
The end user is solely responsible for complying with any applicable regulatory requirements.

10. Quality assurance

All documents are reviewed by internal and external experts according to the Quality plan for the verification, see Table 4.

Table 4 QA plan for the verification

Reviewers	**DTI**	**Experts**
Plan document with application definition, verification protocol and test plan	NHN	TQF, LDMO
Report document with test report and verification report	NHN	TQF, LDMO

Reviews were done using the DTI review report template.

Appendix 1 Terms and definitions used in the verification protocol

Terms and definitions used in the protocol are explained in Table 1:

Table 1 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

Word	DANETV	Comments on the DANETV approach
		experts
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	None

Word	DANETV	Comments on the DANETV approach
	for the application	
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 (verification protocols, requirement documents, standards, methods)

1. DANETV. Centre Quality Manual, DTI 2009.
2. European Parliament and Council. Directive 2006/42/EC of the 17th May 2006 on machinery and amending Directive 95/16/EC (recast).
3. European Council: Directive 89/655/EEC of 30 November 1989 concerning the minimum safety and health requirements for the use of work equipment by workers at work (amended 2007/30/EC).
4. ISO 12100-2:2003: Safety of machinery - Basic concepts, general principles for design - Part 2: Technical principles.
5. Measurement protocol for biogas potential measurements for ETV tests at DANETV.
6. Anders Peter Jensen. Notat. Status over dokumentation af NIX-koncept, 6. marts 2009.

Appendix 3 Application and performance parameter definitions

This appendix defines the application and the relevant performance parameters application as input for verification and test of an environmental technology following the DANETV method.

A3.1 Applications

See 5.1

A3.1.1 Matrix/matrices

See 5.1

A3.1.2 Target(s)

See 5.2

A3.1.3 Effects

See 5.3

The effects claimed by the vendor are presented in Table 2:

Table 2 Performance parameters and vendor claims

Performance parameter	Vendor claim of performance
Biogas potential	25 % increase of methane production pr. kg VS depending on fibre type
Removal efficiency of ammonia	>50 % removal of NH4-N from manure fibres

Appendix 4 Test report

The test report is attached to the verification report as a separate file