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An integrated approach for biogas production with agricultural waste

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CO	Confidential, only for members of the consortium (including the Commission Services)	X

1. Preface

This report comprises the results from the work accomplished under task 3.2 of the Collective Research project AGROBIOGAS “An integrated approach for biogas production with agricultural waste” which is co-financed by European Union’s the 6th Framework Programme. The report was elaborated under leadership of the Swedish University of Agricultural Sciences (SLU) with assistance from the following partners:

- BOKU (Austria)
- ELBE (Germany)
- HG (Sweden)
- BME (Germany)
- SK-BIOM (Slovakia)
- SLU (Sweden)
- TTZ (Germany)
- UB (Spain)

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1. Preface	2
2. Introduction	5
2.1. Sampling procedure	5
2.2. Schedule of sampling.....	5
3. The Parameters	1
3.1. Working reactor conditions.....	1
3.2. Influent parameters needed.....	1
3.3. Overview monitoring.....	1
3.4. Reactor content during the monitoring period (four weeks)	1
3.5. Detailed monitoring	1
4. Large scale experiments.....	2
4.1. Hagavik Gårdsbiogas (HG), Sweden	2
4.1.1. General description.....	2
4.1.2. Process parameters and substrates	2
4.1.3. Process logs	2
4.1.4. Chemical analyses.....	5
4.2. Hohenberg-Krusemark, Germany	6
4.2.1. General Description.....	6
4.2.2. Process parameters and substrates	6
4.2.3. Process logs	6
4.2.4. Chemical analyses.....	8
4.3. Kleisthöhe, Germany	10
4.3.1. General Description.....	10
4.3.2. Process parameters and substrates	10
4.3.3. Process logs	10
4.3.4. Chemical analyses.....	13
4.4. Nebauer, Germany	15
4.4.1. General Description.....	15
4.4.2. Process parameters and substrates	15
4.4.3. Process logs	15
4.4.4. Chemical analyses.....	16
4.5. Kolinany, Slovakia	18
4.5.1. General Description.....	18
4.5.2. Process parameters.....	18
4.5.3. Process logs	18
4.5.4. Chemical analyses.....	18
4.6. Norrköping, Sweden.....	19
4.6.1. General Description.....	19
4.6.2. Process Parameters.....	19
4.6.3. Process logs	19
4.6.4. Chemical analyses.....	20
5. Deviation from technical annex	22

2. Introduction

Six large-scale biogas plants in three different European countries were included in the large-scale experiments (LSE) as described in D15. The specification of parameters and the sampling schedule for these large scale experiments are presented in D16. All six included biogas plants, in assistance with their RTD partner, have agreed to perform the schedule as presented in D16. Due to unfortunate circumstances some plants (as detailed below) was either excluded or exchanged for other plants.

To be able to perform an applicable optimisation of the AD simulation toolkit all plants started their monitoring program after harvest and collection of fresh crop material, to be used as a substrate. This deliverable is a summarization of the monitoring period and will only present some of the data as the major part of the collected data is in the form of process logs and tables of chemical parameters. The complete data set is sent to RTD partner Barcelona to be used for validation purposes of the mathematical model used in the toolkit.

The different parameters to be investigated in the large-scale experiments are described in detail in D15 but these parameters are also shortly summarized below.

- During the large-scale experiments the hydraulic retention time (HRT) and temperature as well as any changes of these critical parameters should be continuously noted. Also, the substrates composition at each time of feeding should be determined. This includes total solids (TS) and volatile solids (VS) of all in-going substrates as well as the final composition of the mixture. The time of each feeding should also be noted.
- To overview process performance, sampling for chemical analysis will be performed according to the schedules presented in D16. The investigated parameters include; Volatile Fatty Acids (VFA), Chemical Oxygen Demand (COD), Dry Solids (DS), Volatile Solids (VS), Alkalinity, N-NH_4^+ , Total Kjeldahl Nitrogen (TKN) and pH. In addition also the gas production/composition will be determined.

It was proposed in D15 that Long Chain Fatty Acids (LCFA) also should be included in the monitoring parameters, but due to the lack of an efficient analytic method the LCFA was excluded from the monitoring schedule.

2.1. Sampling procedure

Liquid samples was taken at the biogas plants and stored frozen, and later sent to the RTD partners for chemical analysis. The sampling of reactor liquid was performed just before substrate addition. The exact number of samples varied from plant to plant due to different HRT and a sample schedule for each plant was presented in D16.

2.2. Schedule of sampling

Sampling schedules for each biogas plant is presented in D16. The plan was that sampling according to two different schedules should be performed. The first schedule represented monitoring of normal process performance for one HRT (or at least for a month). The second schedule sampling was for detailed monitoring in between two feeding occasions. The sampling frequency varied between the plants depending on the prevailing HRT and feeding frequency. In addition to the analyses shown in the schedules also HRT, temperature, gas production/composition and the substrate composition was to be determined during the experimental period.

Due to a very high feeding frequency (each 15 min) the short monitoring period was excluded from the Neubauer plant. For some plants (as noted below) the short monitoring did not give any further information, as the dynamics between two feeding occasions was too small to register with the used analysis methods.

3. The Parameters

The aim was to perform the following monitoring program:

3.1. Working reactor conditions

- The hydraulic retention time (HRT). This should be continuously noted during the monitoring period on a daily basis.
- The reactor working temperature, this should be constant during the monitoring period, but if it changes it is important to note the time of change.

3.2. Influent parameters needed

Although characterisation of substrate is available from work package 2 (WP2), the following data should also be available:

- Identify the substrates added to the reactor at each time of feeding (and the percentage if a mixture of substrates is used).
- Total solids (TS) and volatile solids (VS) of the substrate must, due to its variability, be continuously logged if possible, otherwise at least noted on a daily basis.
- Feeding schedule, if semi-continuous what is the frequency of feeding.

3.3. Overview monitoring

The reactor should first be monitored for at least one HRT with the following parameters daily;

- Biogas production
- Biogas composition
- pH performed as soon as possible after sampling (with correction for temperature).

This is performed to establish that the process is working at steady state.

3.4. Reactor content during the monitoring period (four weeks)

The sampling for these parameters should be done before feeding.

- Biogas production (Daily or if possible logged continuously).
- Biogas composition (daily or if possible logged continuously), required constituents are carbondioxide and methane.
- VFA (volatile fatty acids) (2-3 times a week), total amount as well as the concentrations of acetate and propionate.
- COD (twice a week)
- TS, VS (twice a week)
- Alkalinity (once a week)
- pH (Daily) performed as soon as possible after sampling with correction for temperature.
- N-NH₄ (twice a week)
- TKN (once a week)

3.5. Detailed monitoring

During one day of normal operation the following sampling schedule should be performed hourly (depending of feeding frequency it can be shortened to every 15 minute). This is performed to see if there is any short time dynamics in the reactor, mainly between two feedings. This is only performed at reactors where it is relevant (due to feeding regime or monitoring possibilities).

- Biogas production
- Biogas composition, required constituents are carbondioxide and methane.
- VFA, total amount as well as the concentrations of acetate and propionate.
- pH performed as soon as possible after sampling (with correction for temperature).

4. Large scale experiments

4.1. Hagavik Gårdsbiogas (HG), Sweden

4.1.1. General description

The company Weltec-Biopower, in cooperation with JTI, built this plant in 2003. The plant is operated by the owner, farmer Krister Andersson. The plant is a CSTR with intermittent stirring with an active volume of 450 m³. Initially the plant was feed with silage and horse manure but this was later change and since one year the main substrates are bakery waste and poultry manure. The biogas is used for production of electricity (max. 900 Mwh/year) and heat (max.1400 Mwh/year).



Figur 1: Hagavik biogas plant

4.1.2. Process parameters and substrates

The biogas plant of Hagavik is presently running with an average organic loading rate (OLR) of 3,7 kg VS/m³/day and with a hydraulic retention time of 100 days. The process is run at mesophilic temperature (39°C) with a gas production of approximately 1100 m³/day. The digester is feed with a mixture consisting of starch rejects from agroindustry, poultry manure and bakery waste. The composition of the mixture is varying over time, depending on the performance of the process. However approximately 1.4 ton agroindustrial starch and 1.4 poultry manure or, depending on availability, bakery waste are added daily. The plant in Hagavik continually monitors the gas production, gas composition (CH₄, H₂S) and pH is measured once a day.

4.1.3. Process logs

The loading of the biogas reactor is irregular due to a variable access of the different substrates. The feed is put in a tank where it is mixed and then feed into the reactor. As the HRT of the mixing tank is larger than a day (in general) the loading schedule as presented below is somewhat misleading. The substrates entering the biogas process is actually a mix of the last three to four days of feed as presented in Figur 2.

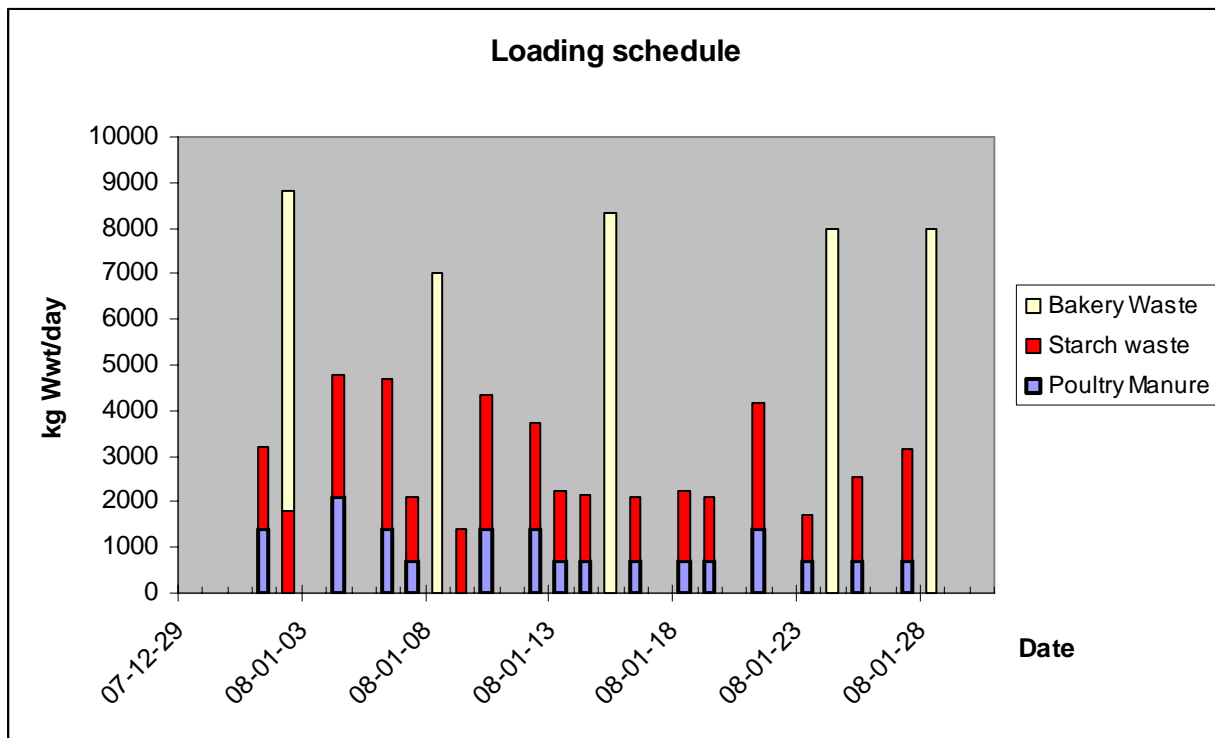


Figure 2: Loading schedule of the Hagavik biogas plant.

The monitoring equipment at the plant is somewhat basic and can be described as at-line in most cases. The biogas production is here given in daily production rather than a production rate (Figure 3). The variation is due to the loading schedule and the different digestion rates of the substrates.

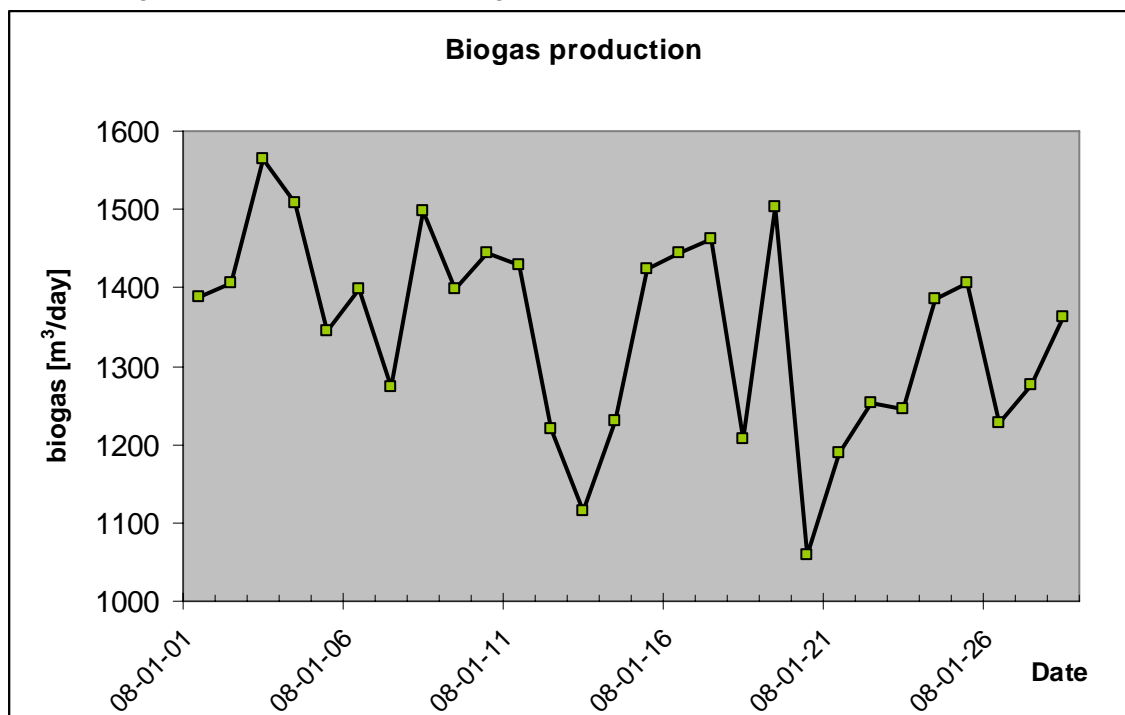


Figure 3: Biogas production at the Hagavik biogas plant, observe that the numbers are given as the sum of daily production.

As can be expected the methane concentration is varying in a way similar to the biogas production. This is a consequence of the loading rate and changes in the substrate mix (Figure 4).

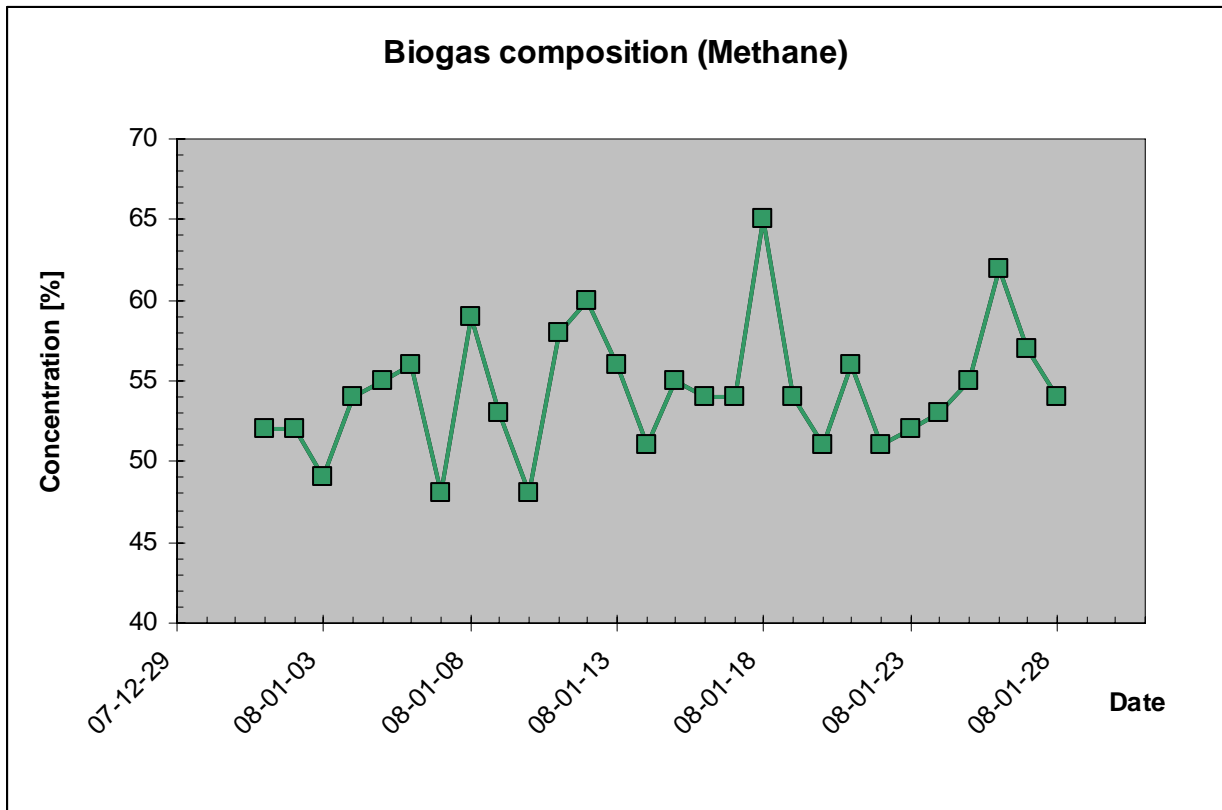


Figure 4: Methane concentrations in the biogas produced at the Hagavik biogas plant.

Initially the reactor was not working at a steady-state which is apparent from the pH, but in the second half of the period there seems to be a stabilization of the pH (Figure 5).

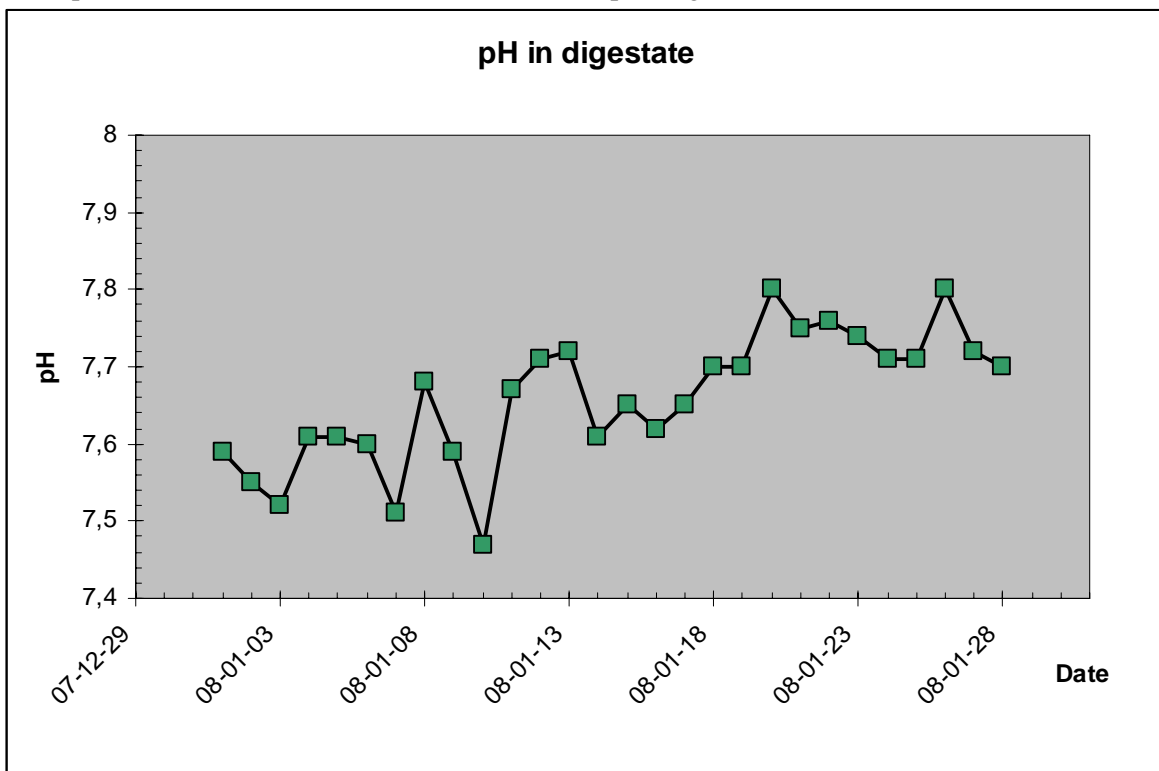
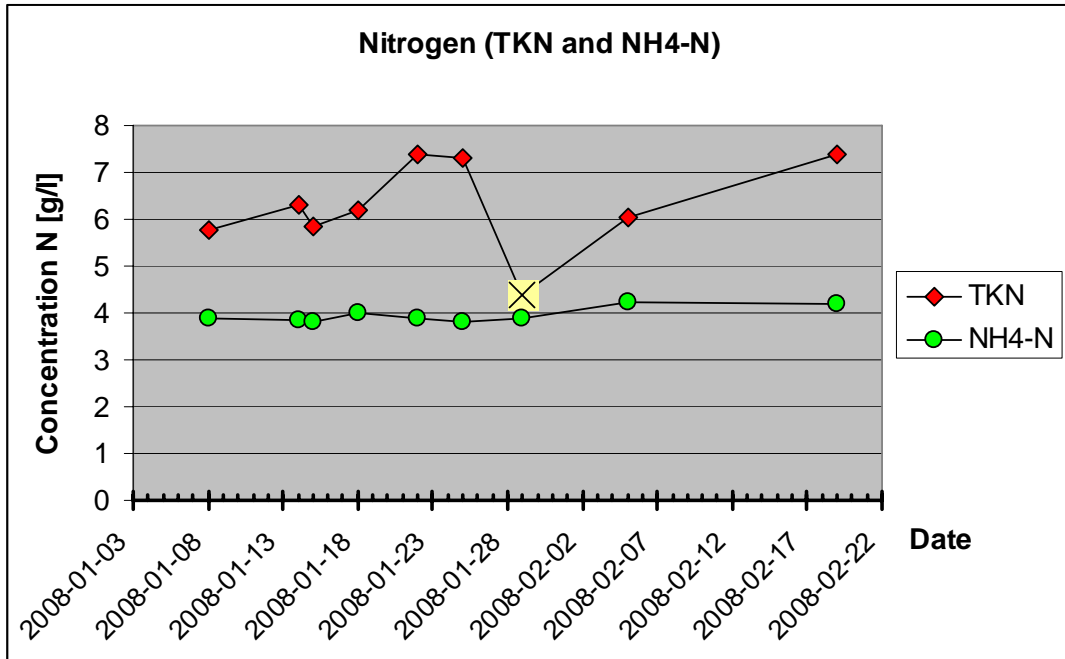


Figure 5: pH in the digestate from the Hagavik biogas plant.

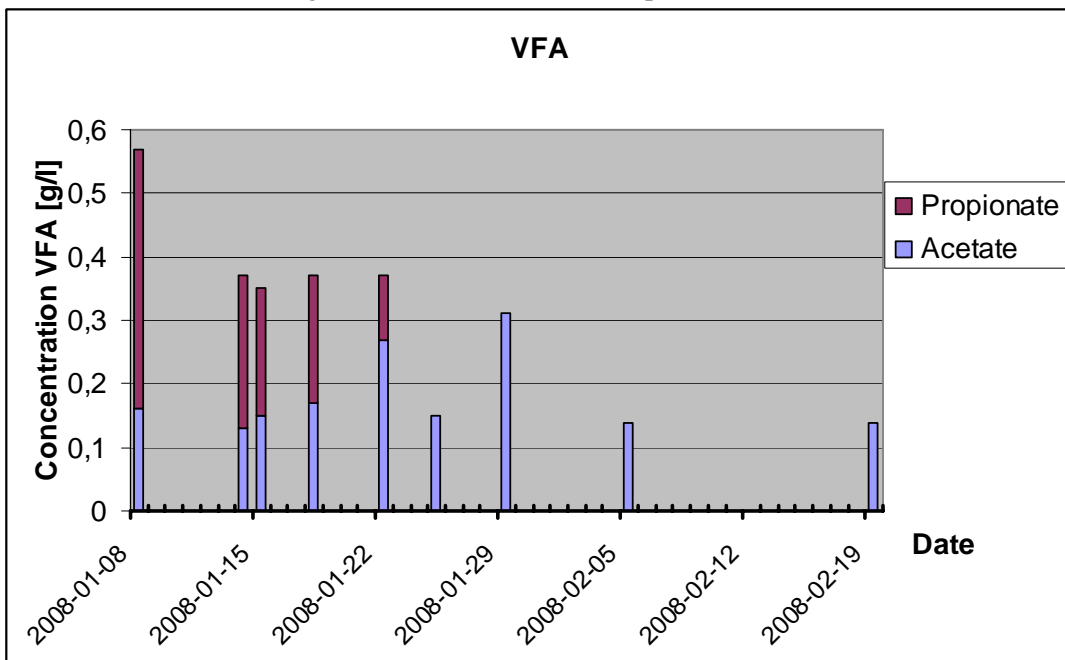
4.1.4. Chemical analyses

The digestate from Hagavik was a challenge to analyse as it had a nearly gelatinous consistency, probably caused by the starch industrial. The relatively high ammonia concentration (Figur 6) as could be expected from a plant running with such a long HRT and the VFA values were low (Figur 7) as also could be expected from the long HRT.



Figur 6: The analyses of nitrogen in the digestat from Hagavik. The TKN sample marked with X is probably due to an alaysis error, but can be noted that the TKN varies more than usual.

Interesting to note is that the concentration of propionate was decreasing over time. Propionate is typically being accumulating during instability and decreasing concentration is a sign of a process recovering from an unstable state. However the propionate in the Hagavik plant could also originate from the bakery waste that on some occations contains significant amount of this compound.



Figur 7: Analyses of VFA in the digestate from the Hagavik plant. The decreasing propionate concetrations should be noted.

4.2. Hohenberg-Krusemark, Germany

4.2.1. General Description

The biogas plant Hohenberg-Krusemark is an agricultural plant engineered by Elbe Bioenergie and in operation by Biogasanlage Hohenberg-Krusemark GmbH & Co. KG. The plant was started in January of 2007 and has since the beginning of March 2007 been in stable operation with the same organic loading rate. Hohenberg-Krusemark is a one stage biogas system (two CSTR run in parallel and without recirculation) with continuous stirring (slowly rotating large scale propeller mixer). The biogas is used for production of electricity. Since start, the plant has been in operation with a mixture of cow manure and maize silage but currently experiments with solid manure is ongoing and also experiments with grass are in preparation.



Figur 8: Hohenberg-Krusemark biogas plant

4.2.2. Process parameters and substrates

The biogas plant Hohenberg Krusemark is running at mesophilic temperature (34-38°C) with an organic loading rate (OLR) of 3 kg VS/m³/day. The hydraulic retention time is about 50 days. The substrate mixture used by this biogas plant is cow manure (60-70 % of wet mass) and maize silage (30-40 % of wet mass). The plant performs routine analyses of gas production rate, gas quality (CH₄, O₂, H₂S, and H₂), dry matter, organic dry matter, organic acids, pH and alkalinity.

4.2.3. Process logs

The biogas production from the two process tanks was for the major part of the monitoring period very stable (Figur 9), it was only during the first week the production was showing some fluctuations.

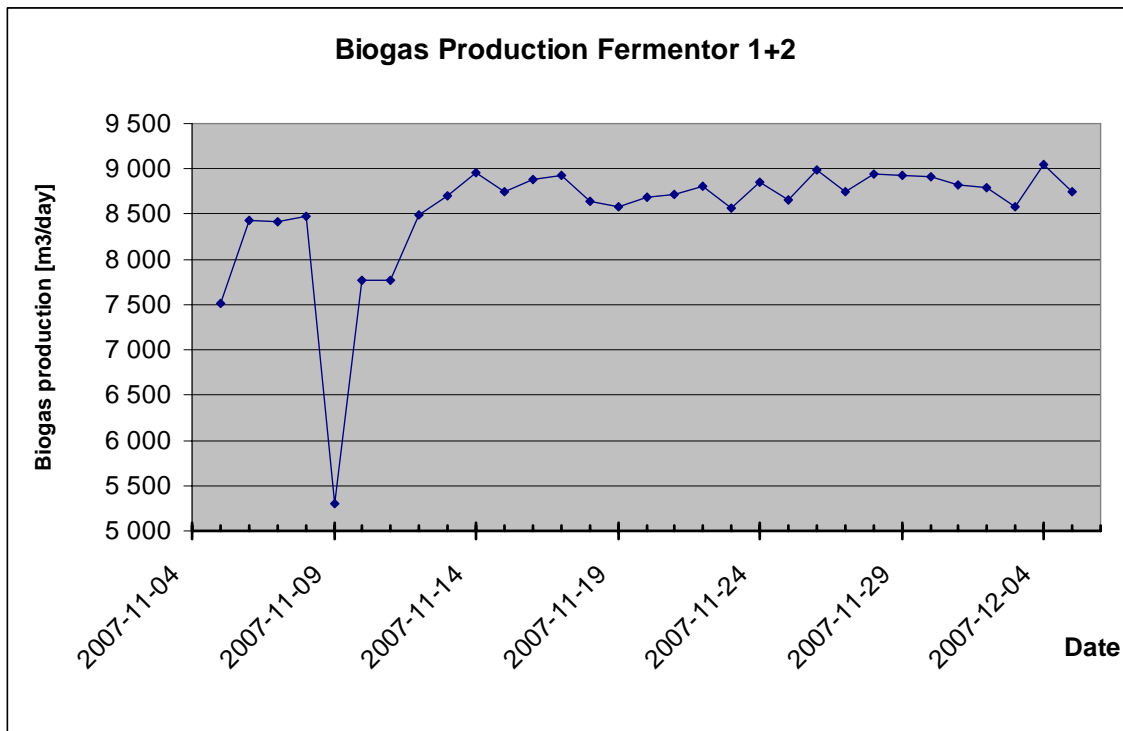


Figure 9: Biogas production from the two parallel reactors at the Krusenmark plant

The loading rate during the monitoring period was with only two exceptions constant (Figure 10).

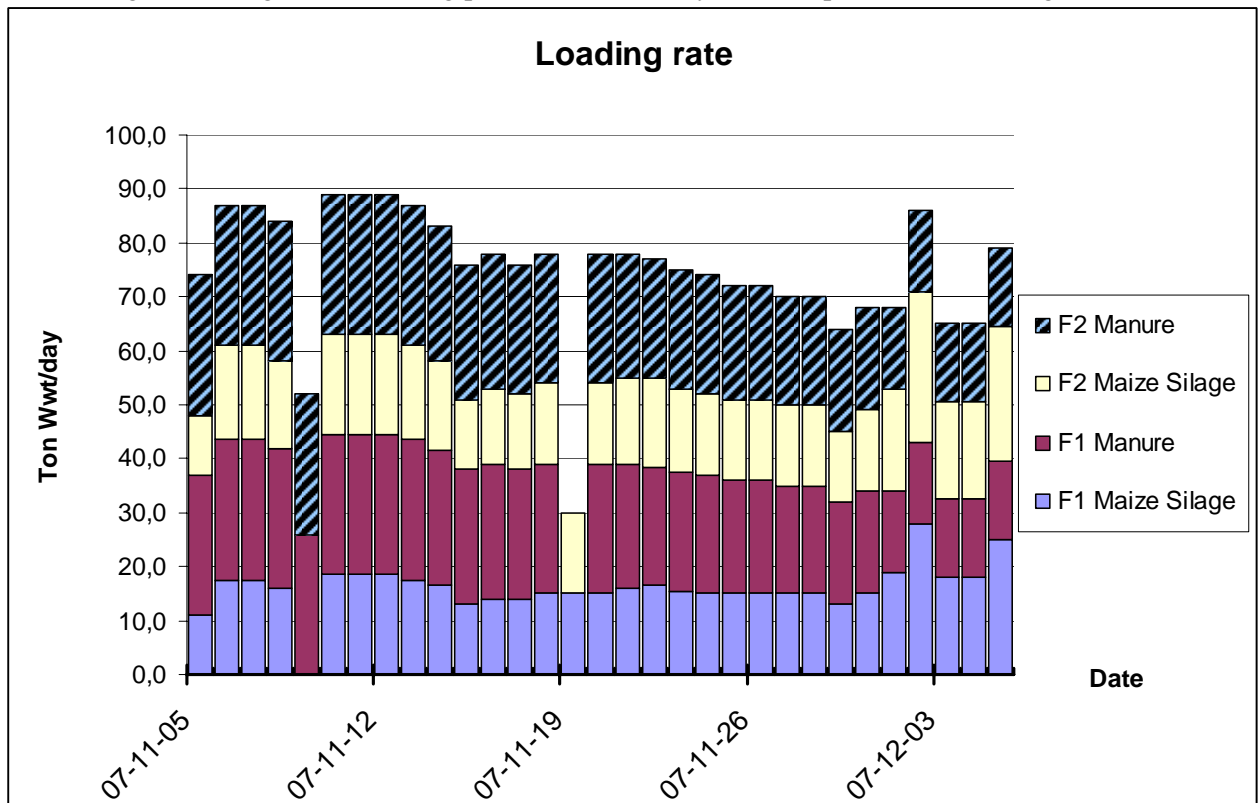


Figure 10: The Loading of the two reactors at Krusenmark.

The organic loading rate (OLR) is calculated as it gives a better description of the amount of organic matter that the process uses for the methane production. In this graph (Figure 11) the reason for the drop in biogas production (Figure 9) even easier to see than in (Figure 10) as the maize silage gives a larger relative contribution than manure to the OLR.

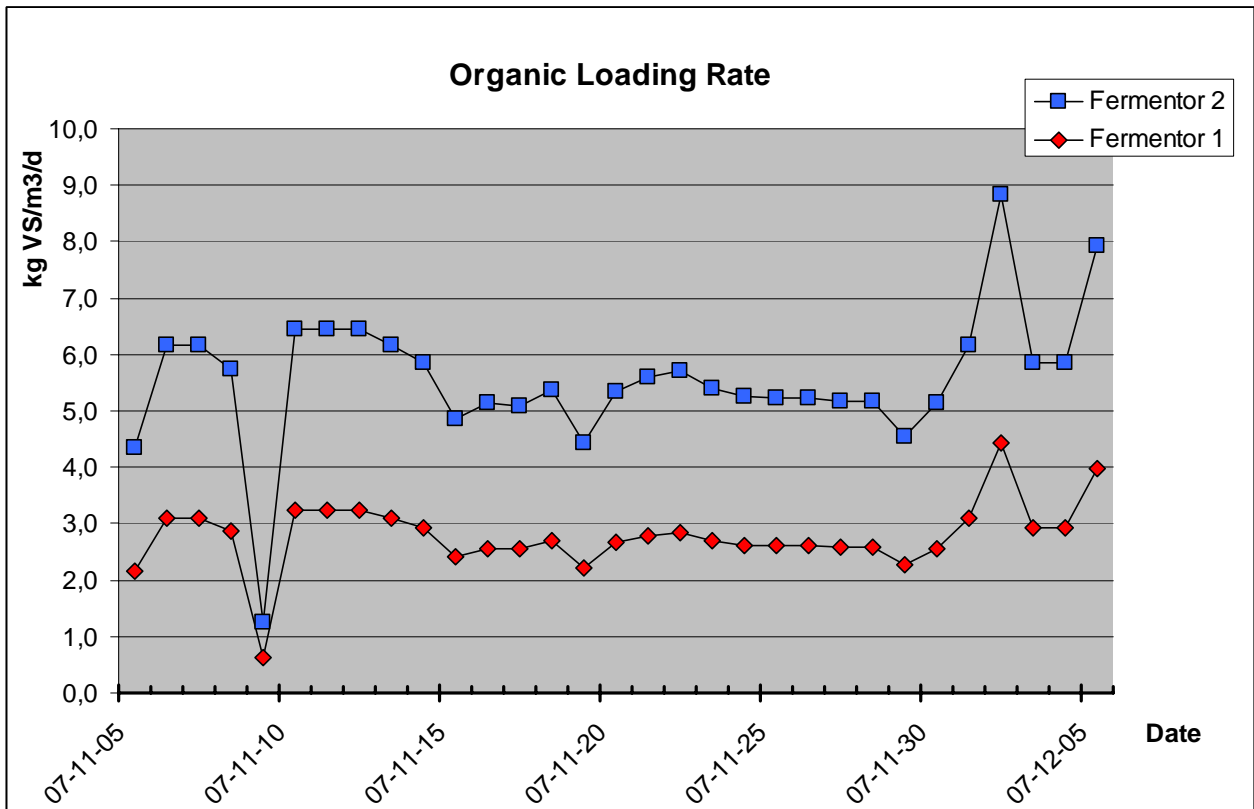


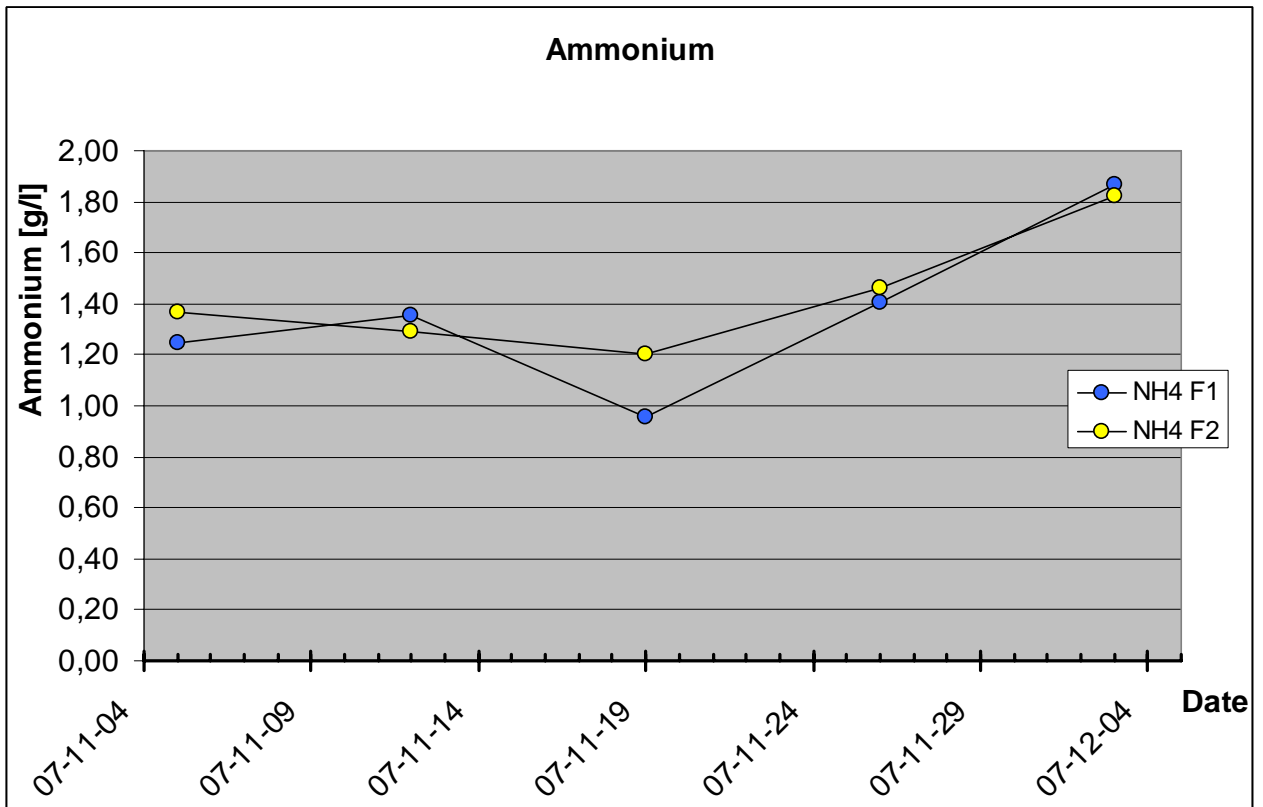
Figure 11: Organic loading rate (OLR) of the two reactors at the Kruenmark plant.

The methane concentrations in the biogas was very stable during the period ($50,1 \pm 0,34$, not shown). The HRT varied only slightly during the monitoring period (not shown).

4.2.4. Chemical analyses

Due to undetermined reasons some of the chemical analyses from this plant produced values that could not be found in digestate from a functioning reactor and therefore had to be excluded. Below is the ammonia analysis that was decided together with the SME and RTD partners to be reliable.

The ammonia concentrations (Figure 12) was low but increasing slightly towards the end of the monitoring period, but as the manure can contribute different amount of ammonia directly to the process this increase can not be seen as significant.



Figur 12: Ammonia concentrations in the digestate from t he Krusenmark plant

4.3. Kleisthöhe, Germany

4.3.1. General Description

The biogas plant Kleisthöhe is an agricultural biogas plant engineered by Elbe Bioenergie in cooperation with ENERTRAG AG. Since December 2006 this plant is operated by ENERTRAG Bioenergie GmbH & Co. KG. This plant is a single stage process with recirculation possible by separator (used if total dry substance increase to more than 10 %). The plant has two reactors of each 2350 m³ and the process is continuously stirred (slowly rotating large scale propeller mixer) and uses external biological desulphurisation. The plant is feed with energy crops exclusively and trace elements are added to ensure a stable bioprocess. Optimization of the process, including optimization of the trace element addition, is still in progress and the final organic loading rate are planned to be reached during autumn/winter 2007. The biogas is used for the production of electricity.



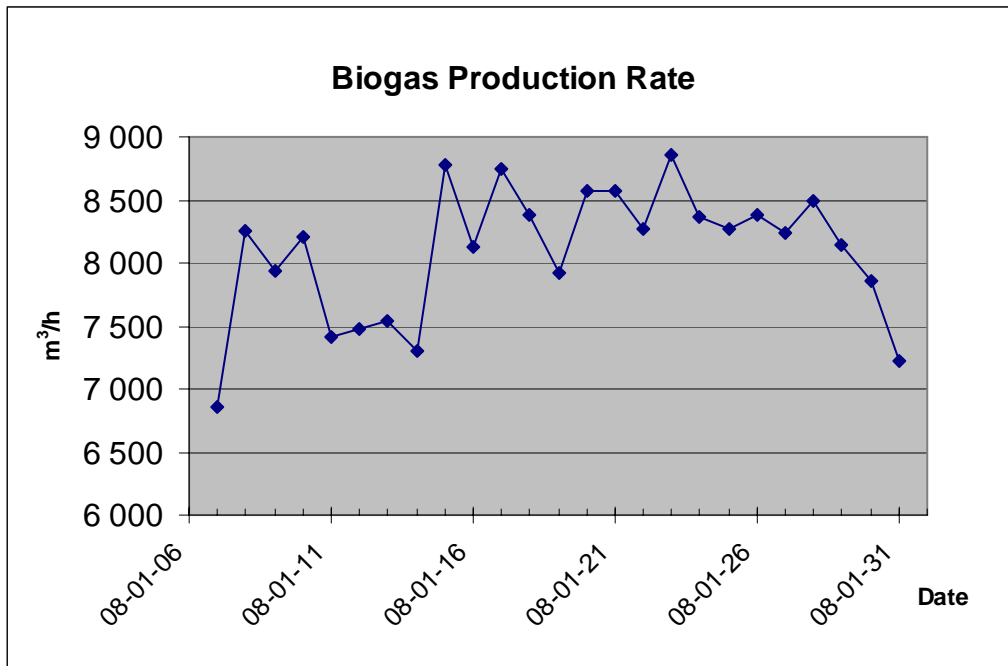
Figur 13: Kleisthöhe biogas plant

4.3.2. Process parameters and substrates

The biogas plant of Kleisthöhe is running at mesophilic temperature with an organic loading rate (OLR) of about 2,5 kg VS/m³/d and a HRT of about 120 days. The substrate used for biogas production is maize and rye silage. The plant performs routine analyses of gas production rate, gas quality (CH₄, CO₂, O₂, H₂S, and H₂), dry matter, organic dry matter, organic acids, pH and alkalinity.

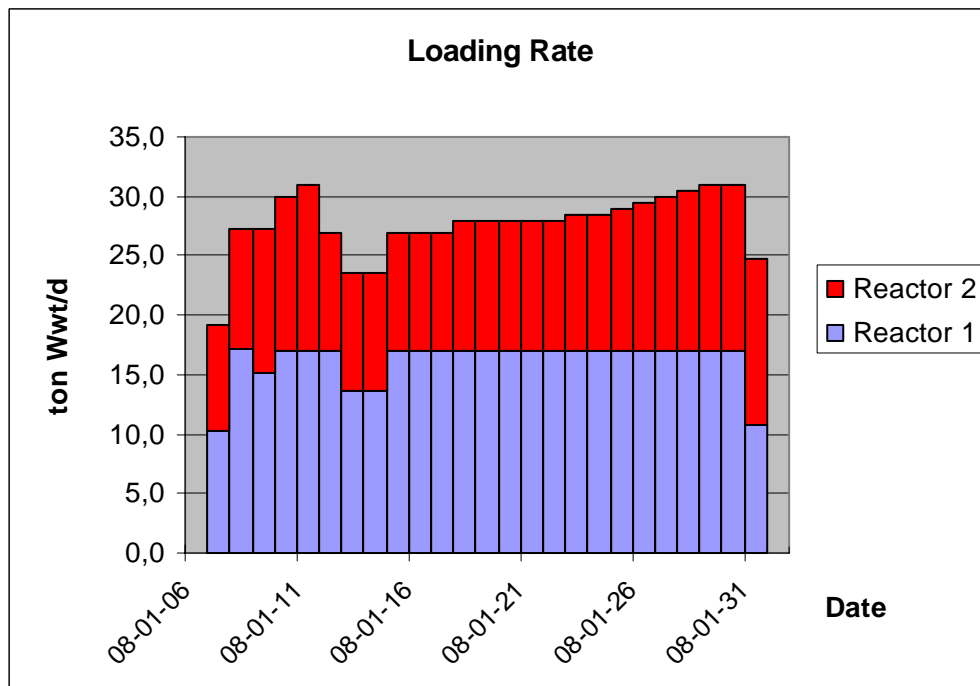
4.3.3. Process logs

During the period there was considerable dynamics in the process with variation in the biogas production and in the load of the reactors. The biogas production logs are reported as sum of the two reactors individual production (Figur 14).



Figur 14: The sum of the biogas production of both reactors at the Kleisthöhe biogas plant.

Although the loading rate of the reactors varied slightly during the period a constant substrate composition was kept. The substrate load of the reactor can be expressed in absolute numbers (Figur 15) or as an organic loading rate (OLR) (Figur 16). If the load is expressed as OLR, the variations can be explained in a better way.



Figur 15: Superimposed substrate loading rate expressed in terms of raw weight (as ton wet weight of 1:1 mix of maize and rye silage) at the two reactors in at the Kleisthöhe plant.

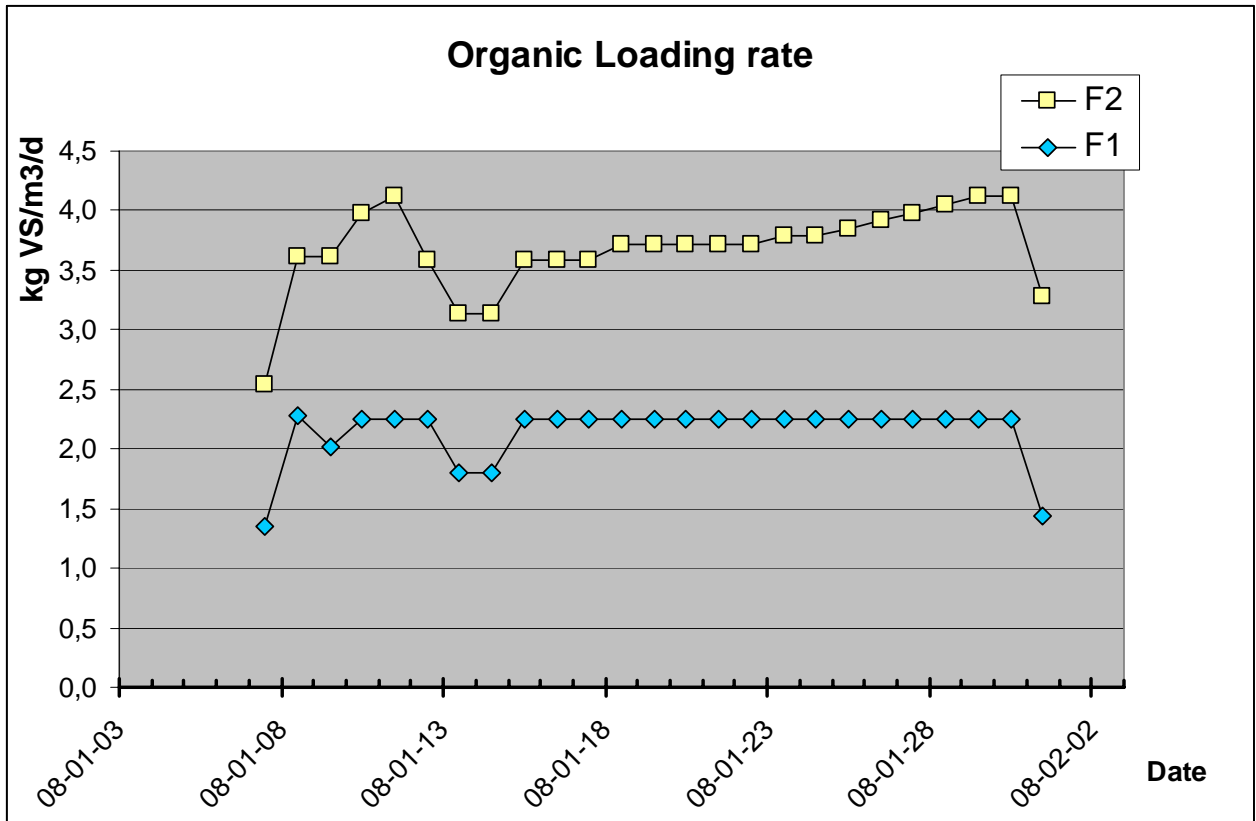


Figure 16: The substrate load expressed as OLR of the two reactors at the Kleisthöhe plant.

There were also some slight changes in the HRTs during the period (Figure 17).

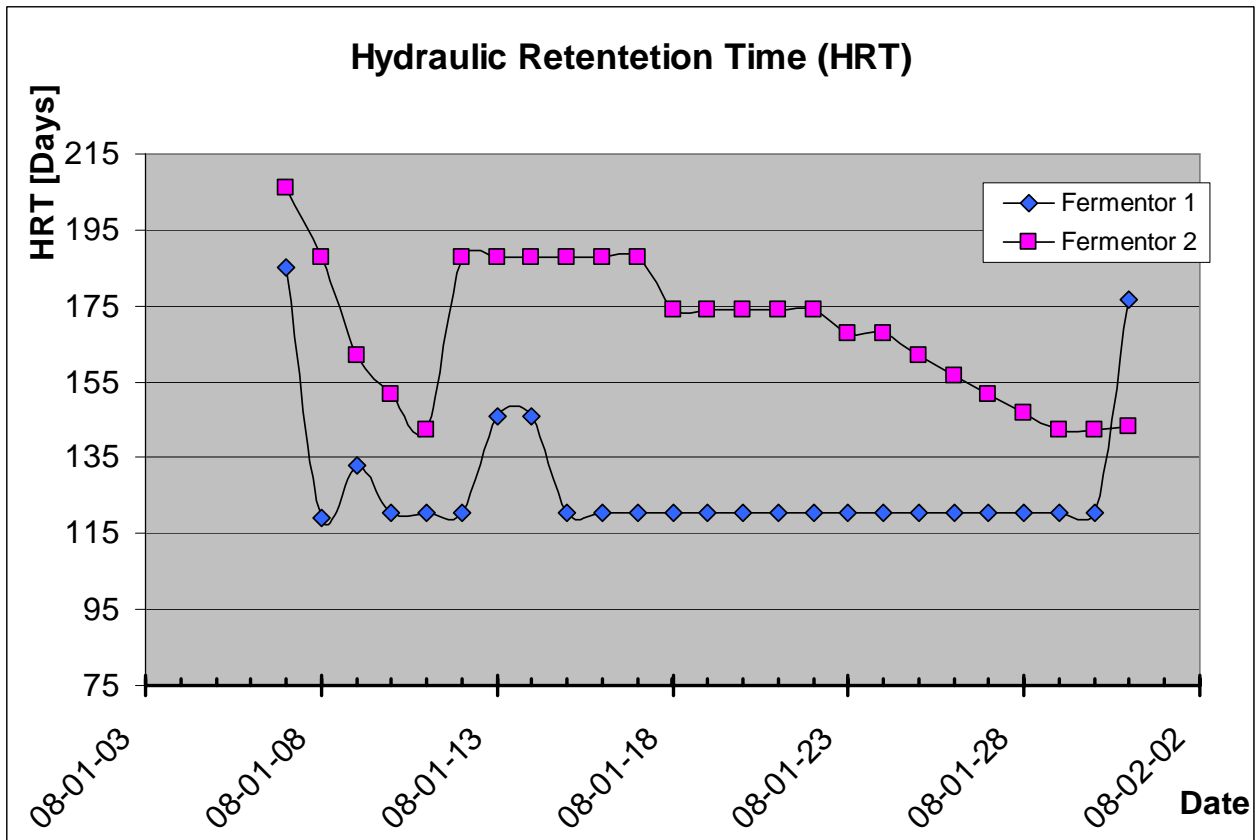


Figure 17: The Hydraulic retention times of the two reactors at the Kleisthöhe plant. Observe that the effect of these changes usually takes considerable time to affect the process.

The methane concentration was stable during the period ($49,7\pm 0,8$, not shown). The gas quality monitoring also contains information about the amount of hydrogen concentration in the biogas (Figur 18). Hydrogen is often proposed as a parameter useful for detecting disturbances in the process. If the hydrogen indeed is an indicator for this systems stability it shows here that for the min part for the period the process was running at steady state.

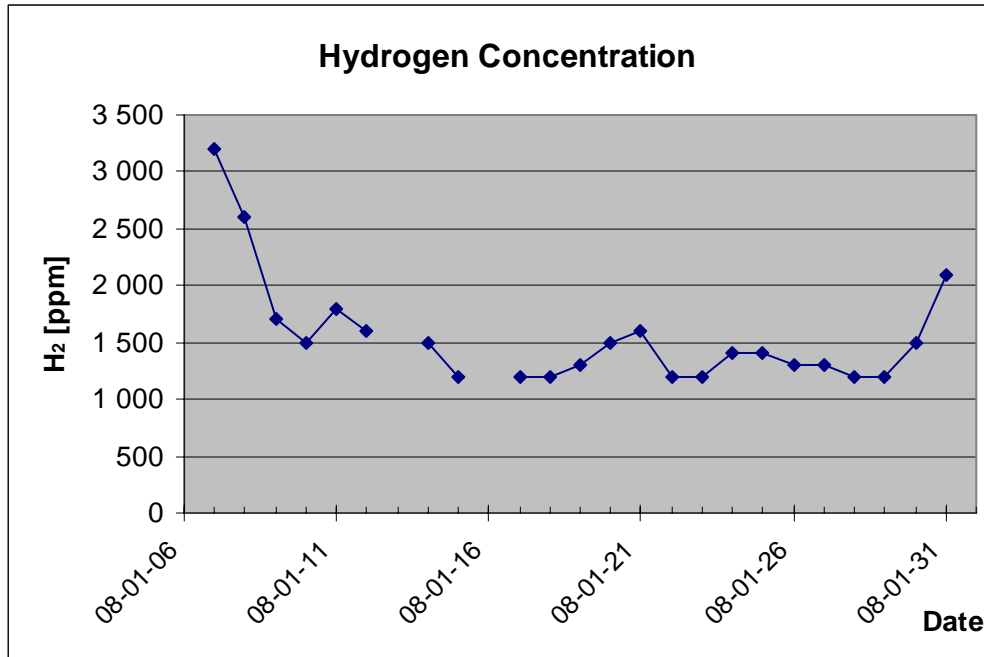
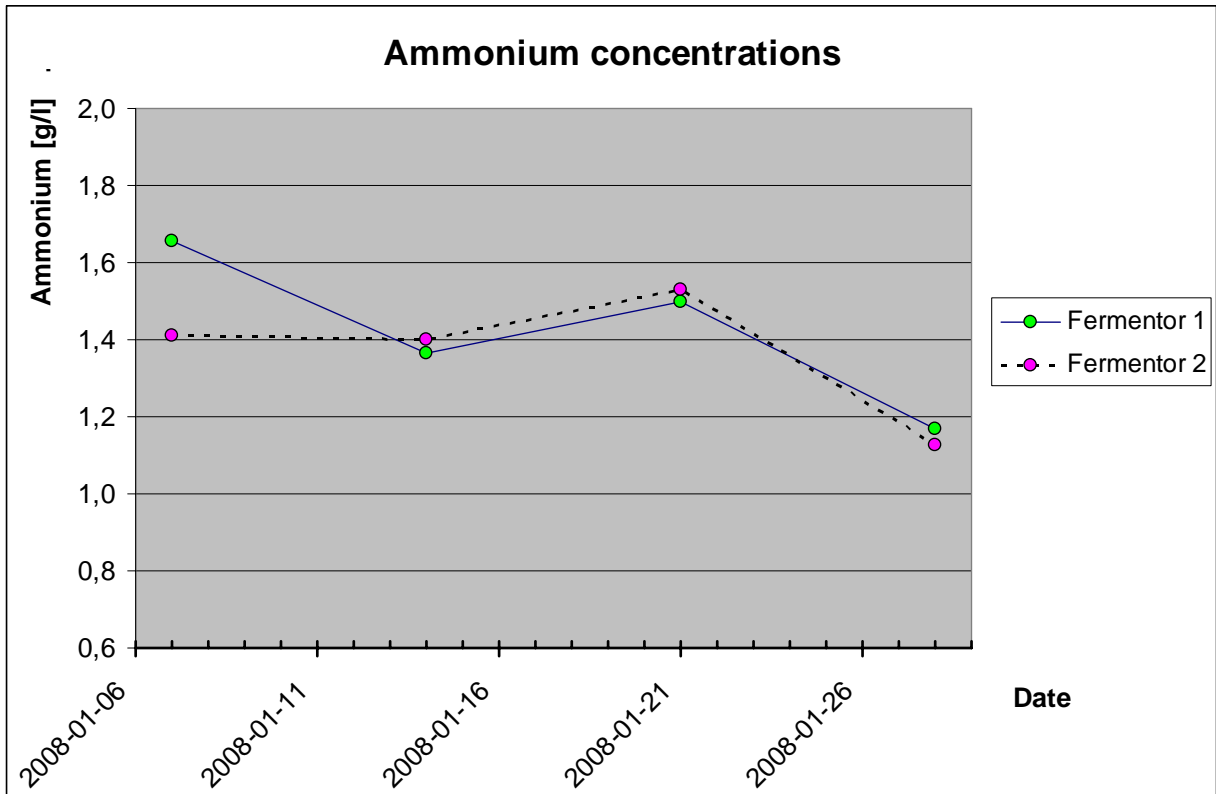


Figure 18: Concentration of hydrogen in the biogas from reactor 1+2 at Kleisthöhe biogas plant

4.3.4. Chemical analyses

Due to undetermined reasons some of the chemical analyses from this plant produced values that could not be found in digestate from a functioning reactor and therefore had to be excluded. Below is the ammonia analysis that was decided together with the SME and RTD partners to be reliable.

The ammonia levels in the twin tanks was similar (Figure 19) but showed a tendency of declining towards the end of the monitoring period. In the case of fermentor 2 this could be explained as an effect of a reduction in HRT (Figure 17), in fermentor the reduction of the HRT during the period was less but could be a contribution.



Figur 19: Ammonia concentrations in the digestate from the Kleisthöhe plant.

4.4. Nebauer, Germany

4.4.1. General Description

This plant was started in 2006 and is a CSTR with a volume of 1200 m³ (1100 m³ digestate volume). The substrate used for the biogas production is pre-hydrolysed (acid) for 2-3 days. After the hydrolysis the liquid material are pumped to an acidification tank. The liquid from this tank are then, every half hour, pumped into the biogas digester. The process uses biological desulphurisation for cleaning of the biogas, i.e. air is pump into the digester in order to remove H₂S by the formation of S₂. The biogas is used for production of electricity.



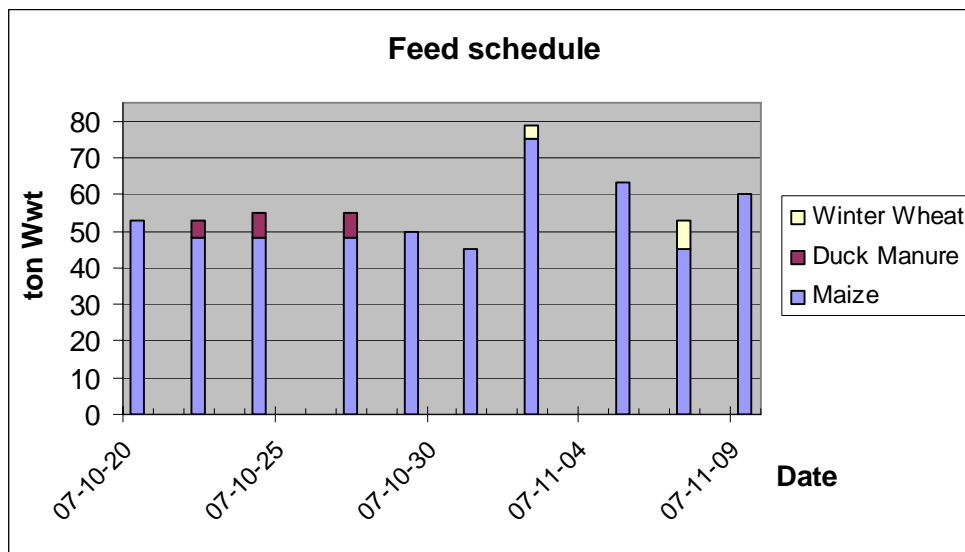
Figur 20: Nebauer biogas plant

4.4.2. Process parameters and substrates

The process is run at mesophilic temperature (40°C) with a HRT <10 days and an OLR of 7 kg VS/m³/day. The substrate used for biogas production consist of a mixture of duck manure (25%), maize silage (40%), wheat whole plant silage (10%), rye whole plant silage (10%) and grass silage (15%).

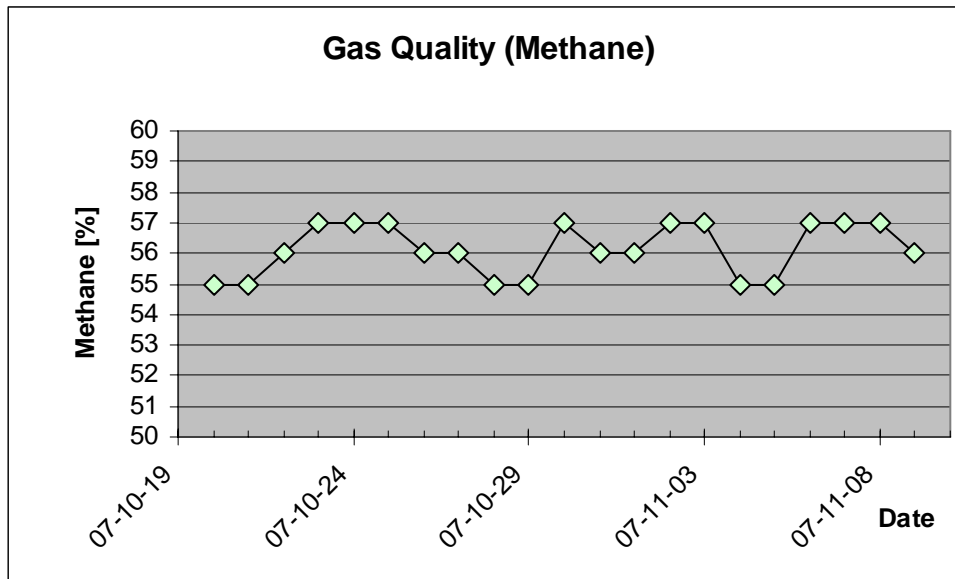
4.4.3. Process logs

During the monitoring period Maize silage was the main substrate with only small additions of duck manure and wheat grain (Figur 21). As the feeding of this reactor was of a very high frequency (every 20th minute) it was decided that a short monitoring wouldn't show any process dynamics. Thus the plant only executed the long term monitoring schedule.



Figur 21: Load of the reactor in wet weight, distributed on the different types of substrates.

The methane concentration in the biogas was stable ($56,1\% \pm 0,9$) (Figur 22).

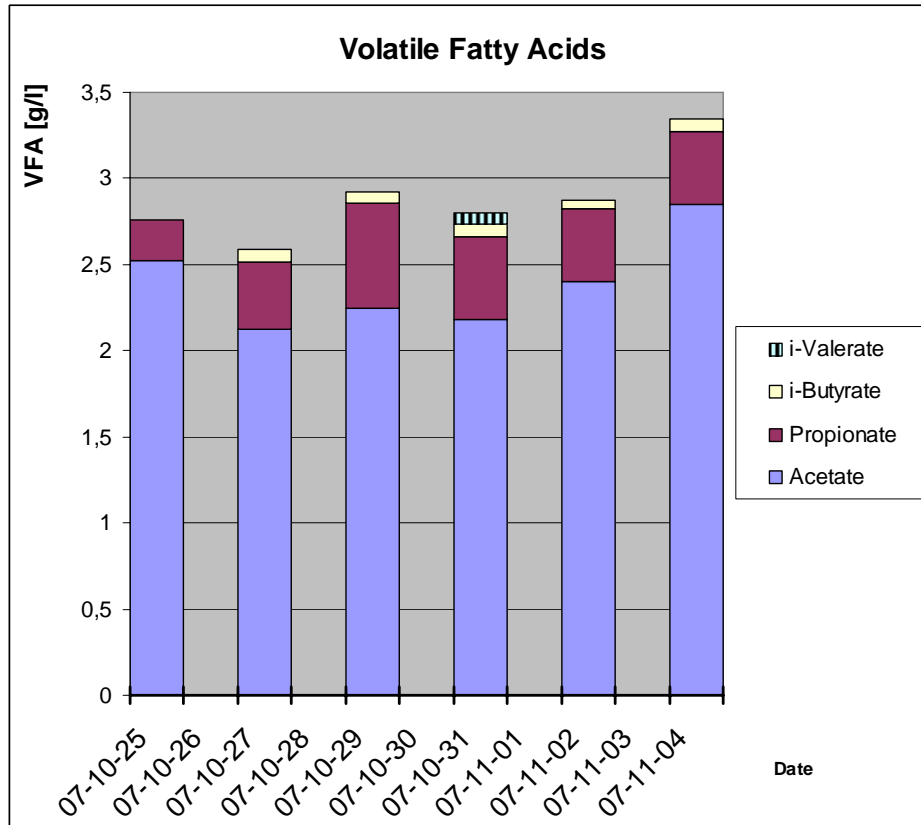


Figur 22: Gas quality expressed as methane concentration of the produced biogas at the Nebauer plant.

The biogas production was not monitored but was calculated from the production of electricity (not shown) and was stable at $3080 \text{ m}^3/\text{d}$.

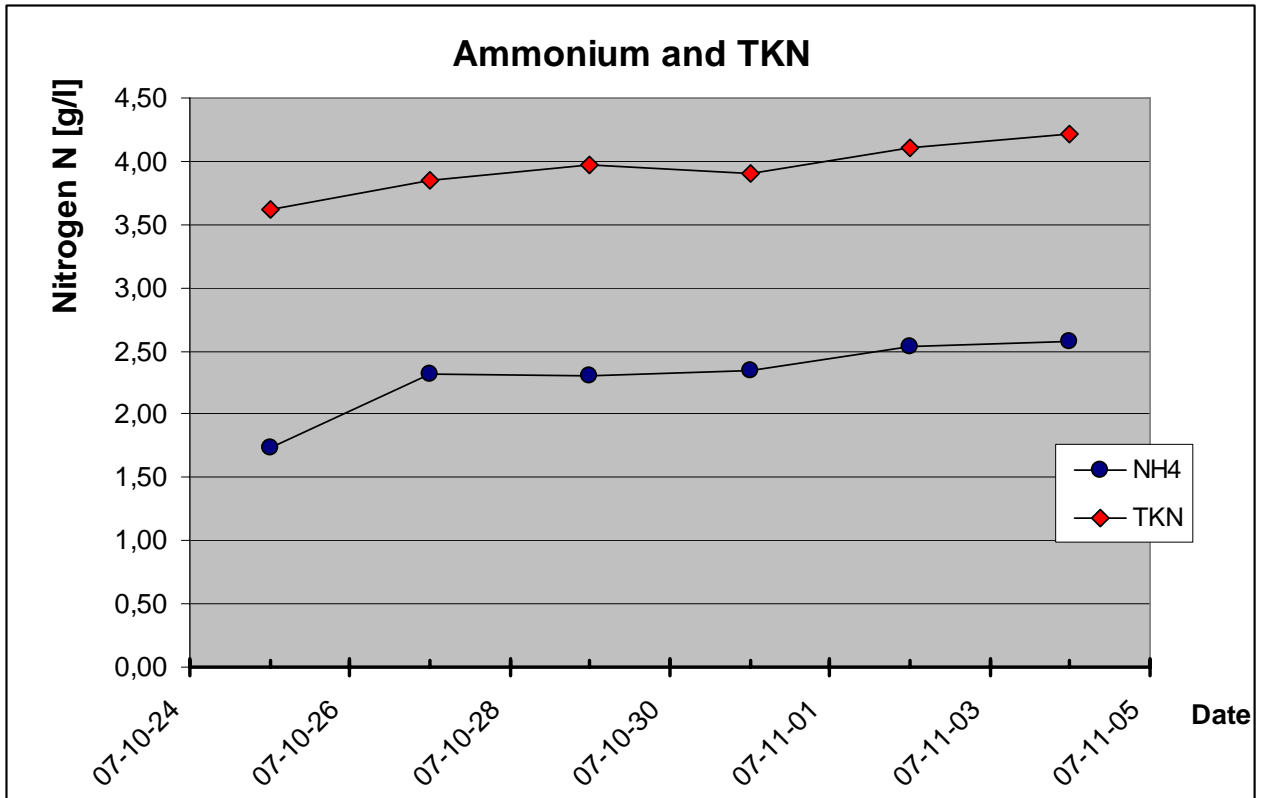
4.4.4. Chemical analyses

The chemical analysis was performed by BOKU and is only presented here as a summarization of some of the results. The analysis of the volatile fatty acids (VFA) showed that there was significant presence of acetic acid but lower concentrations of the higher order VFA (>2 carbon atoms) (Figur 23).



Figur 23: A summary of the result of the VFA analysis of digestate at the Nebauer biogas plant.

The nitrogen content of the reactor slightly increased during the monitoring period, which implies that that steady state was not yet achieved (Figur 24).



Figur 24: The nitrogen content in the Nebauer reactor

4.5. Kolinany, Slovakia

4.5.1. General Description

For the experiment purposes there were used facilities of the Slovak University of Agriculture in Nitra (Figur 25). The experimental equipment consisted of a 5 m³ pilot reactor, homogenisation tank, co-mixture tank for co-fermentation mixture preparation, biogas holder and storage tank of the digested sludge. The pilot reactor was in parallel operation with a large scale one (100 m³) of the university biogas plant.



Figur 25: plant of the Slovak University of Agriculture in Nitra

4.5.2. Process parameters

The biogas plant in Kolinany is operating at mesophilic temperature (38°C) with an OLR that varied during the experimental period (Tabell 1) and with a HRT of 20 days. The plant monitored a large number of parameters (not shown, see 4.5.3).

Tabell 1: Organic loading rate[OLR] and Total Solid of substrate [TS] (CM - cattle manure, KW - kitchen waste, CS - corn silage, GS - grass silage, FG - fresh grass)

Cycle	Monitoring period [Days]	Used substrate	OLR [kg COD/m ³ /d]	TS [%]
I	60	100 % CM	3,19	4,82
II	32	40 % CM + 60 % CS	3,12	5,29
III	33	60 % CM + 40 % CS	2,86	5,98
IV	42	90 % CM + 10 % FG	1,85	4,92
V	48	92,3 % CM + 7,7 % KW	2,7	3,59
VI	53	90 % CM + 10 % GS	3,77	5,2

During the monitoring period (after a stabilization period) the substrate was changed in order to study the dynamics of the process. The substrates are described in Annex 1 together with a summary of the experiment.

4.5.3. Process logs

Due to a hard drive failure at the plant no process log with time-stamps or chemical analyses could be delivered. The data as delivered thus is not useable for validation of the model.

4.5.4. Chemical analyses

See 4.5.3 above

4.6. Norrköping, Sweden

4.6.1. General Description

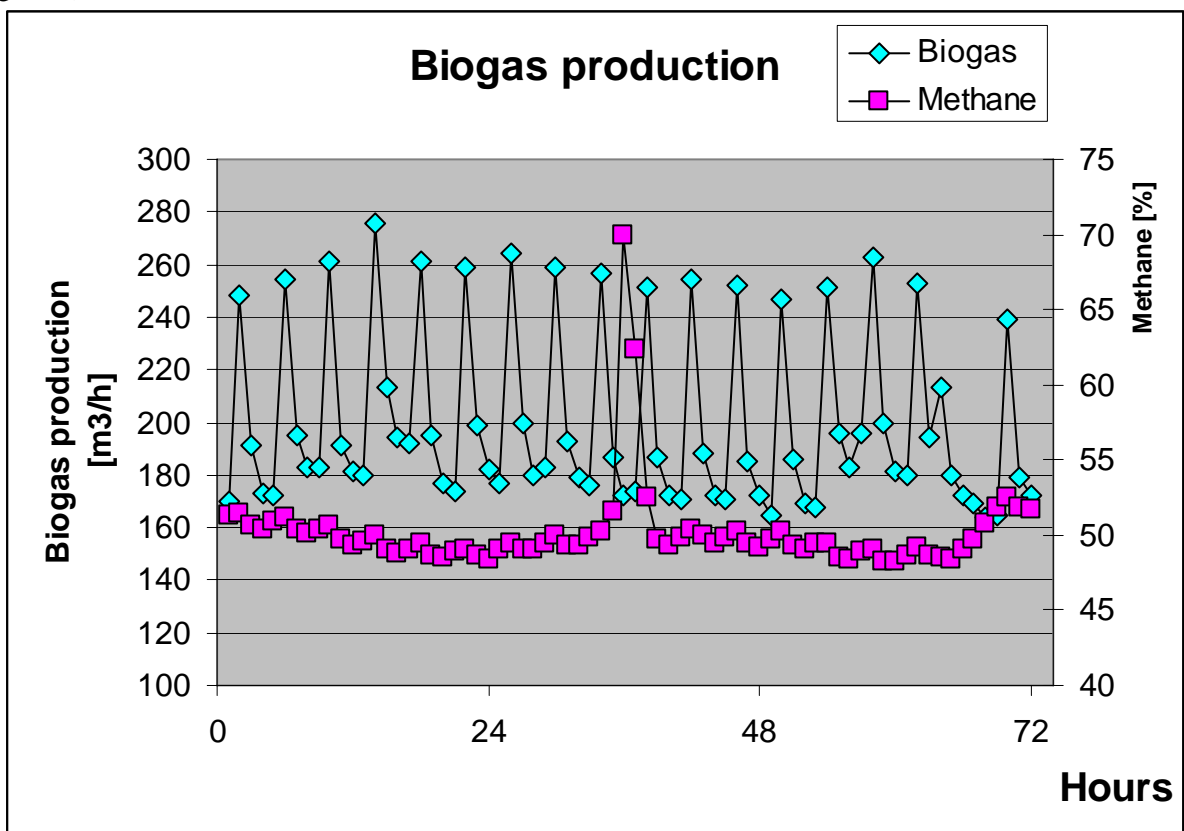
Wheat and wheat screenings are received and stored in a silo. The liquid substrate, distillers waste from a closely situated ethanol production plant is pumped into a buffer tank. The distiller waste is transported in tubing's from the bio ethanol plant. Wheat and screenings is grinded in a hammer mill and are mixed in batches with the distillers waste in a preparation tank. The mixture is then pumped into the biogas digester tank. To obtain an efficient process and to lower the content of hydrogen sulphide in the produced biogas, a nutrient mixture (KMB1) and iron(II)chloride is added to the process. The digester tank is 2000 m³ and the active volume is 1850 m³. Intermittent stirring is performed.

4.6.2. Process Parameters

On basis of organic content (% volatile solids) the mixture is normally 45/65 of wheat and distillers waste, however during the monitoring period the distillers waste was the main substrate. The organic load is approximative 4 kg/m³/day, the hydraulic retention time is 40 days and the process temperature is 37°C. The plant routinely performs analyses of VFA, pH and NH₄⁺ and continuously logs gas production and gas quality.

4.6.3. Process logs

The feeding of the reactor was for the whole monitoring period constant and consisted solely of distillage with the exception of the first day when an addition of wheat was made. As the Norrköping plant has on-line registration of gas quality and production the logs are very detailed and only a small selection of the production log is presented. The gas production numbers clearly shows the process dynamics at the feeding occurrences where the easily digestible part of the substrate give increase in gas production for a short time (Figur 26).



Figur 26: Excerpt from the data logs from the Norrköping biogas plant, observe the distinct dynamics in the biogas production corresponding to the feeding occasions. The dynamics in the methane concentrations is not as notable but can be seen.

4.6.4. Chemical analyses

The analysis of VFA shows high values of propionate (Figur 27) which indicates an unstable or recovering process, thus the process is probably not running at steady state. This conclusion is supported further by the analysis of the nitrogen content (Figur 28) which shows remarkable high concentrations of ammonia. It has been suggested that the process is suffering from sulphate reducing organisms' competing with the methanogens for substrate. Thus resulting in a lower biogas yield than could be expected. This all indicates that the plant is not optimal for validation purposes for the toolkit model.

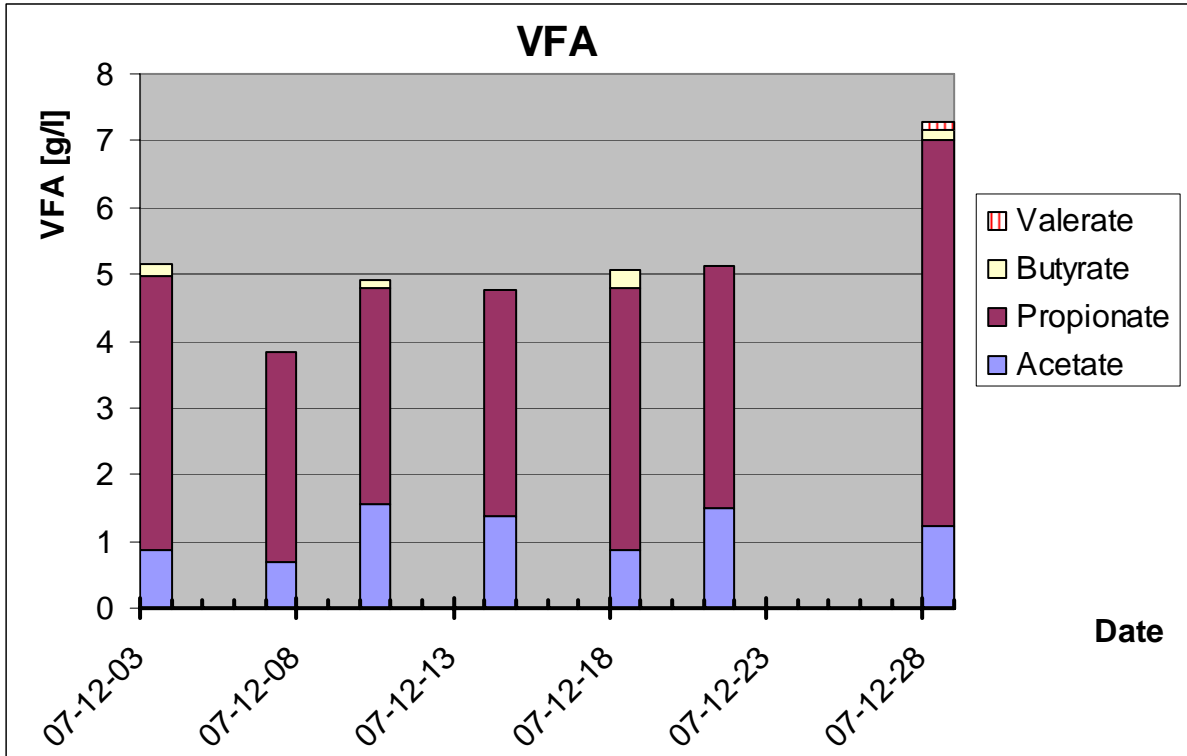


Figure 27: VFA analysis of the digestate from Norrköping, the high amounts of propionate should be noted.

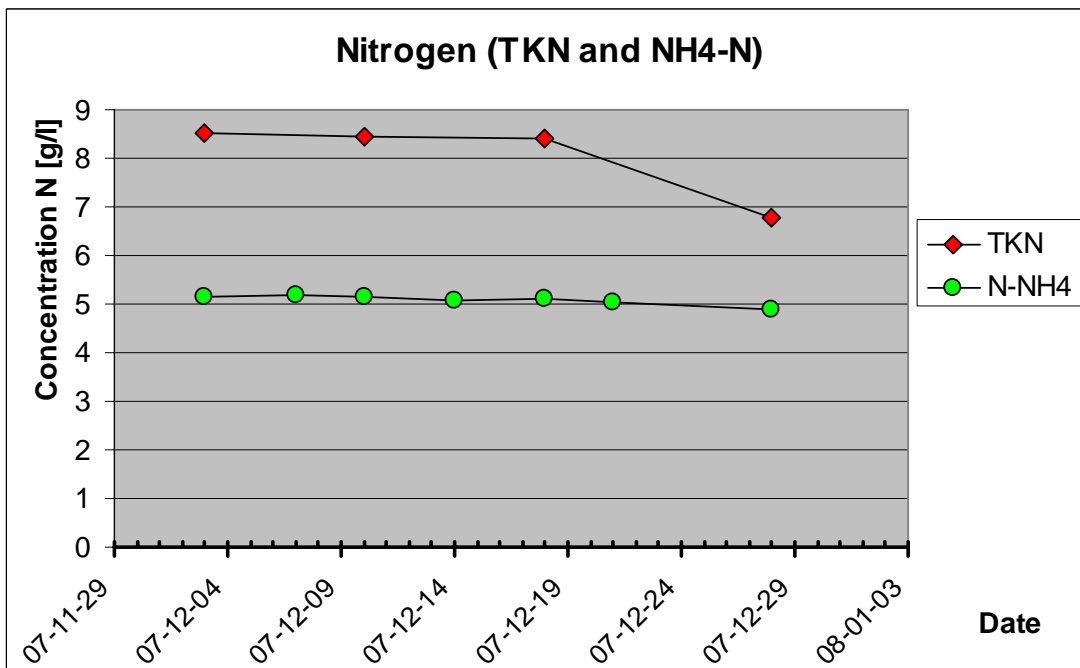
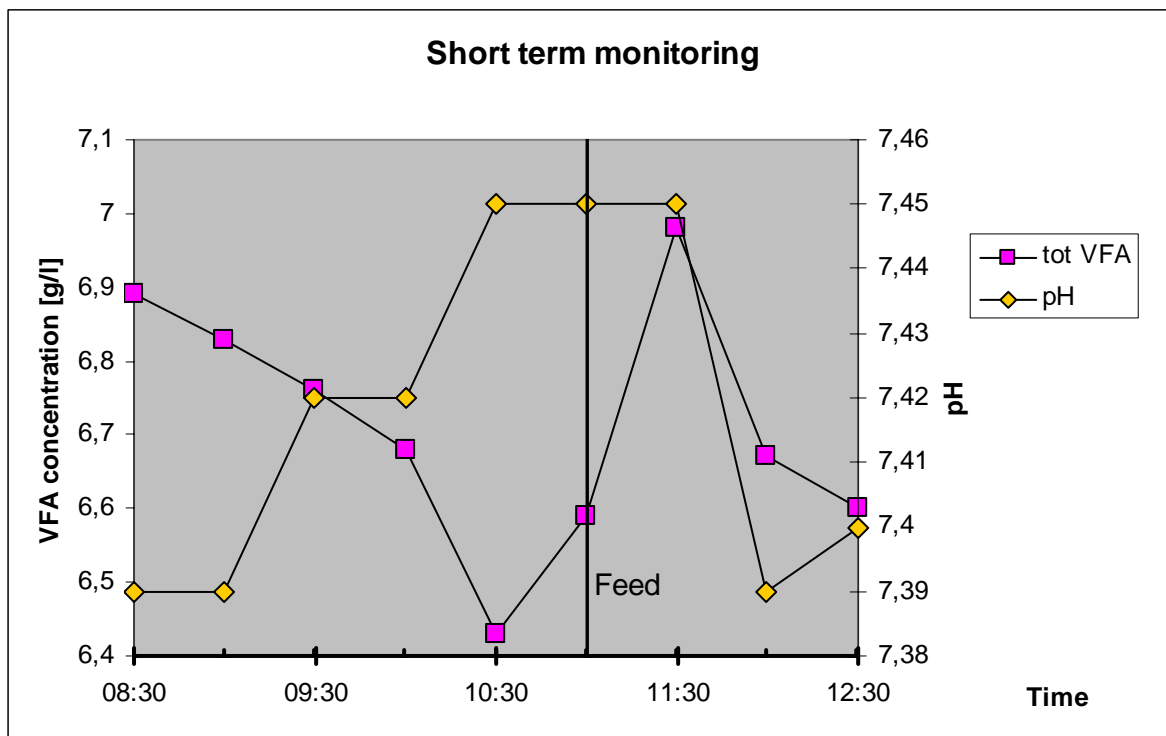


Figure 28: Nitrogen analysis of the digestate from Norrköping. The high amount of ammonia is of note.

The short term monitoring was only partly a success as the sampling was badly coordinated with the feeding and thus did not catch only some of the dynamics of the process. The graph, (Figur 29), do show the expected dynamics with a increase in biogas production soon after the feeding occasion with a corresponding drop in pH due to the metabolites released.



Figur 29: Short term monitoring of the norrköping plant. The vertical line indicates the feeding occasion.

5. Deviation from technical annex

- Due to several different reasons the time schedule as outlined in the technical annex not realistic to keep. All plants are but one is connected to farms and was not able to perform the monitoring period until after the harvest season. There was also deemed essential to have a stable process and thus there was further delay at several plants as the operating condition needed to stabilize.
- As the plant (Kolinary) named in D15 was not able to reach stable operating conditions SK-BIOM decided to exchange it for the pilot plant operating at the University of Nitra.
- Due to a harddrive failure at the plant of Nitra (SK-BIOM) no process logs or chemical parameters could be delivered in a usable format. Thus the plant is effectively excluded from the Large Scale Experiments.
- As the biogas plant connected to the partner EARL was changing their substrate to types which was not characterized in the project and also was not well characterized in literature the consortium decided to shift the monitoring of a Swedish plant using substrates better in agreement with the aim of the project.