# A TOTAL CONVERTING AND BIOSAFE LIQUEFACTION COMPARTMENT FOR

# MELLISSA

## TECHNICAL NOTE 86.1.1

## Maximum Methanogenesis

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June 2001

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## 1. Introduction

Anaerobic degradation of organic waste is an environmentally attractive way for the conversion of organic waste on the one hand in an energy rich off-gas (biogas) and on the other hand into a recalcitrant fibre-containing residue.
The aim of this first technical note was the carrying out of preliminary experiments with a synthetic model substrate and the characterisation of the reactor performance and its mass balances.
As a whole, the anaerobic decomposition of organic waste is generally considered to be a four step process: hydrolysis, fermentation, acetogenesis and methanogenesis. The first step, namely the solubilisation of solid reactants, is generally found to be the slowest and rate-limiting step in the anaerobic biodegradation process (Schieder 2000). Therefore, the computing of the hydrolysis of the C and N compounds during digestion and their subsequent conversion into biogas by the methanogenic microbiota was the main objective of this work. Beside the main objective, the buffer capacity and a VFA-analysis was carried out in order to determine the stability of the digester.

## 2. General procedures and experimental set-up

### *Dimensions*

- 10 Liter PVC cylindrical anaerobic reactor (height 24 cm, diameter 22 cm) with a liquid volume of 5.5 Liters and a headspace of 4.5 Liters
- plastic tubings with an internal diameter of 1.5 cm
- biogas liquid column of 12 Liters

### *Experimental set-up and scheme*

A 10 Liter anaerobic PVC-reactor is used for the anaerobic digestion of the defined feed. As indicated in Figure 1, the digester is maintained at a constant temperature of 34°C by means of placing it in an incubator. The reactor is a CSTR-type one (continuously stirred tank reactor) and is shaken two minutes/hour on a shaker platform (INNOVA shaker) at a constant rate of 90 rounds/minute.

The feeding of the reactor is fed-batch wise at regular time intervals. When the reactor is at the feed-mode, valve 2 (biogas outlet) is closed while valves 1 and 3 are opened. By means of a peristaltic pump, the feed is pumped in at a rate of 200ml/min. The feeding causes a

replacement of a part of the liquid present in the reactor by the freshly added feed, resulting in a release of the effluent through the effluent pipe (valve 3). Consequently, for each volume of the feed fed to the reactor, a same volume of effluent is withdrawn simultaneously.

When the reactor is at the non-feed mode, valve 1 and valve 3 are closed. Valve 2 is opened permitting the biogas to escape from the reactor. Subsequently, the biogas passes by an electronic milligascounter device (Fachhochschule Bergedorf, Hamburg-Harburg, Germany) with a resolution of 1 ml and an accuracy of 3%. By means of a double-check, the biogas is captured in a liquid column after passing the gascounter device. As a result of the biogas pressure, the liquid height in the column is decreased. The decrease of the acidified liquid can be measured with a resolution of 100 ml.

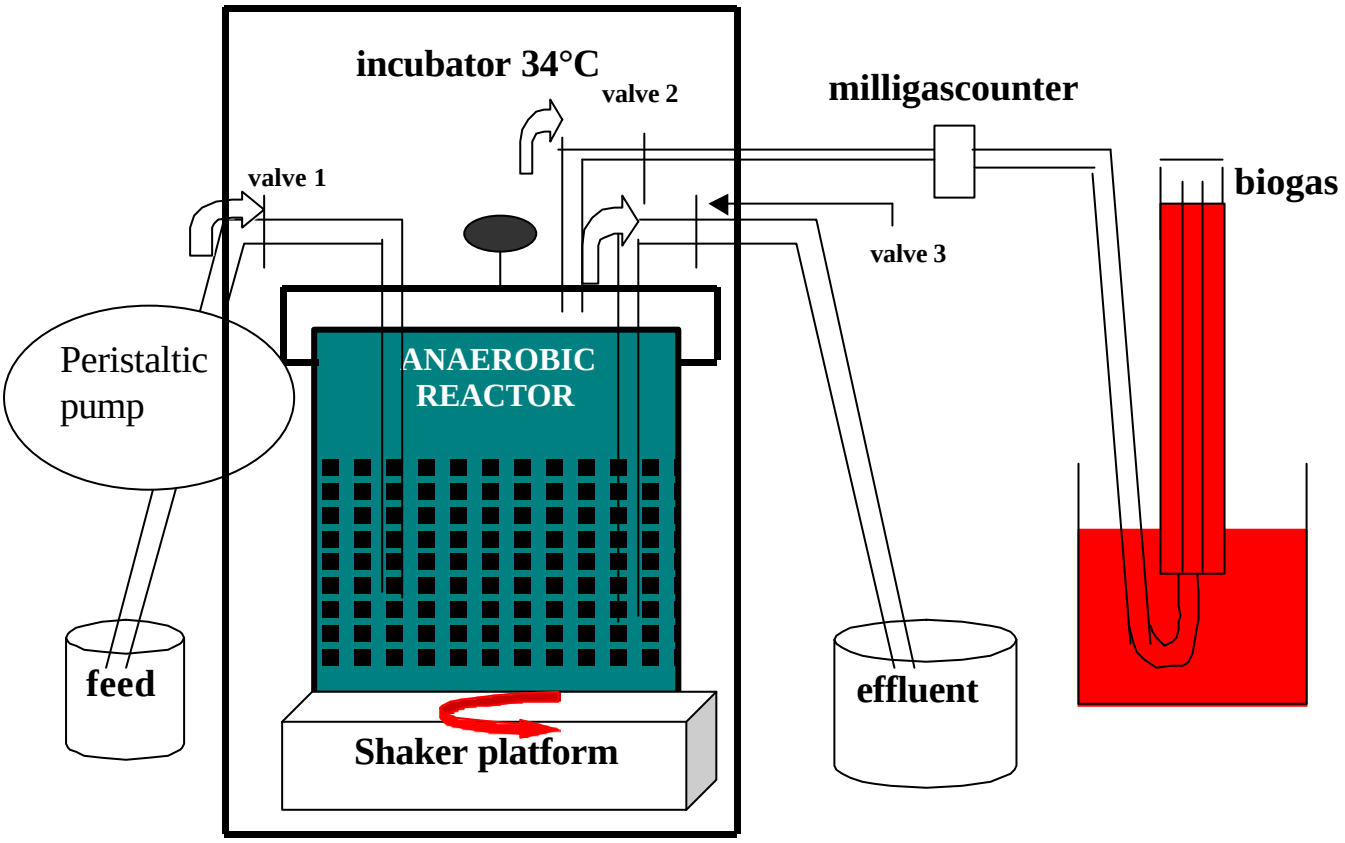


**Figure 1: Experimental set-up of the anaerobic digester and the biogas measurement**

*Feed preparation*

Feed preparations were done batch wise in amounts of 20 Liters. According to the defined feed as discussed on the progress meeting in Ghent on the 2nd of april 2001, the different ingredients were mixed. Spirulina algae were bought from a French company (Technature),

wheat straw was delivered by a local farmer, fresh green cabbage was available in a local supermarket, dried soya was bought from a Belgian company (RADAR) and fecal material was also locally produced.

To 20 Liters of tap water, the following amounts of the previously mentioned ingredients were added: 90 grams of spirulina powder, 630 grams of plant materials (including 210 grams of wheat straw, 2100 grams of fresh green cabbage and 210 grams of soya powder) and 1800 grams of fecal matter. The dry matter content both of the green cabbage and the fecal material was found to be 10% (after drying in an oven at 105°C). All other ingredients were considered to have a DM-content close to 100%. The wheat straw was chopped and ground in dry conditions with a kitchen mixer until particles with a diameter < 4mm were obtained. The cabbage was first cut in smaller parts and subsequently mixed (kitchen mixer) while adding tap water. The final dry matter content of the feed was found to be 2.8-2.9%.

## 3. Results and Discussion

### *Feed characterisation*

In order to compute mass balances for the anaerobic digestion process, the feed was first characterised in terms of C and N composition. In Table 1, the most important features of the prepared feed are given. All analyses were performed according to the standard procedures.

**Table 1: Feed characterisation**

| DM-content | COD | TAN | Kj-N | VSS | ash-content |
|---|---|---|---|---|---|
| 2.8% | 21 g/L | 0.41 g/L | 1.2 g/L | 24 g/l | 4.4 g/l |

### *Conversion efficiencies and Reactor performance*

In terms of reactor performance, the volumetric loading rate was calculated. Given that 1.75 liter of influent is fed to the reactor in a period of 7 days implies that 0.25L fed on a daily basis. Consequently, the daily COD-feed of the reactor is 5.25 g COD/day or the $B_v$ (daily g COD input per liter digester per day) is 0.95 g COD/L.d. The pH of the reactor remains at a constant value of 7.3-7.4. This is also confirmed by the high buffer capacity of the reactor

(results see later). In table 2, the current conversion rates of the digester are calculated by computing the mass balances.

**Table 2: Overview of the achieved conversion rates in the anaerobic digester compartment**

| Parameter | Influent | Effluent | % Conversion |
|---|---|---|---|
| COD (g/l) | 21 | 3 | 85% |
| TS (g/l) | 29 | 8 | 73% |
| VSS (g/l) | 23 | 5 | 78% |

From Table 2, it can be concluded that 15% of the COD is not converted into biogas. Consequently, this 15% is problematic in terms of anaerobic digestion and mainly exists of undigested lignocellulose complexes (from the wheat straw and fecal material mainly) and macromolecules (i.e. from pigments from *Spirulina platensis*). As a matter of fact, the breakdown of long-chain biomolecules (like lignocellulose complexes) during anaerobic digestion is low, both from a chemical and biological point of view (Schieder et al., 2000; Angelidaki et al., 1999; Angelidaki et al., 2000). In manure for instance, up to 40-50% of the total solids consists of biofibers. Biofibers consist of a core of carbohydrates, holocellulose (cellulose and hemicellulose) which makes up 63-78% of the fiber lignocellulose structure (Crawford, 1981). The remaining 15-38% is attributed by lignine, which is a natural and a very stable binder for the hollocellulose complexes (Angelidaki et al., 2000).

Subsequently, since 85% or 18 g/l of COD is removed, the theoretical biogas production (per day and per liter reactor volume) can be calculated. As a rule of thumb, in anaerobic digestion half a liter of biogas is obtained per gram of COD converted (personal communication, W. Verstraete). Consequently, from the volumetric loading rate it can be estimated that approximately 2.3 liters of biogas is produced on a daily basis or 0.42 liter/L.d. This was found to correspond with the average daily biogas production.

**Table 3: Nitrogen levels in influent and effluent of the anaerobic digester**

| Nitrogen | Influent | Effluent |
|---|---|---|
| Kj-N (g/l) | 1.2 | 1.1 |

| | | |
|---|---|---|
| TAN (g/l) | 0.4 | 1.1 |

Concerning the nitrogen mass balances (Table 3), the following conclusions can be drawn. First of all, a part of the organic bound nitrogen is converted during anaerobic digestion into solubilized ammonia (increased TAN-level in the effluent while the Kj-N mass balance is close to zero). The complete or nearly-complete hydrolysis of organically bound nitrogen and proteins into ammonia during anaerobic digestion is confirmed by several authors (Christ et al., 2000; Angelidaki et al., 2000).

Secondly, almost all nitrogen of the effluent is in the soluble phase (supernatant) since the TAN-level of the supernatans was found to be similar to the TAN-level of the mixed liquor. Finally, almost all nitrogen of the effluent is under the ammonia form, very little is organic bound. The latter confirms the data on C-conversion which indicate that most organics are solubilized during digestion.

### *Biogas composition*

The current biogas consists of 61-65% of methane and 39-35% of carbon dioxide gas (GC-measured).

### *Buffer capacity*

The buffer capacity both of the influent and effluent were determined by means of a downtitration (acid addition). In both figures (Figure 2 and 3), two distinct buffers could be identified. The first buffer is situated around a pH-value of 6.3 and is identified as the bicarbonate buffer. As can be seen, the bicarbonate buffer capacity of the effluent (320mg/l) is about 4 times higher in comparison with the influent (80mg/l). This result can also is confirmed in literature and in conventional textbooks on anaerobic digestion technologies.

The second buffer at pH-value of 9.5 clearly shows the presence of an ammonia buffer. The ammonia buffer of the effluent is about 2-3 times higher compared to the influent. These results are also confirmed by the TAN-analysis (Table 3). It should be remarked though that an up-titration is required in order to determine the ammonia buffer concentration since part of the ammonia is stripped of during the preparation of the downtitration (sodium hydroxide addition). For the influent, a third buffer could be noticed but remained unidentified (around pH-value 3.3). A possible explanation for this buffer is the presence of high weight proteins

and/or acids. The fosfate and sulfate buffer capacity was found to be very low both for the influent and effluent.

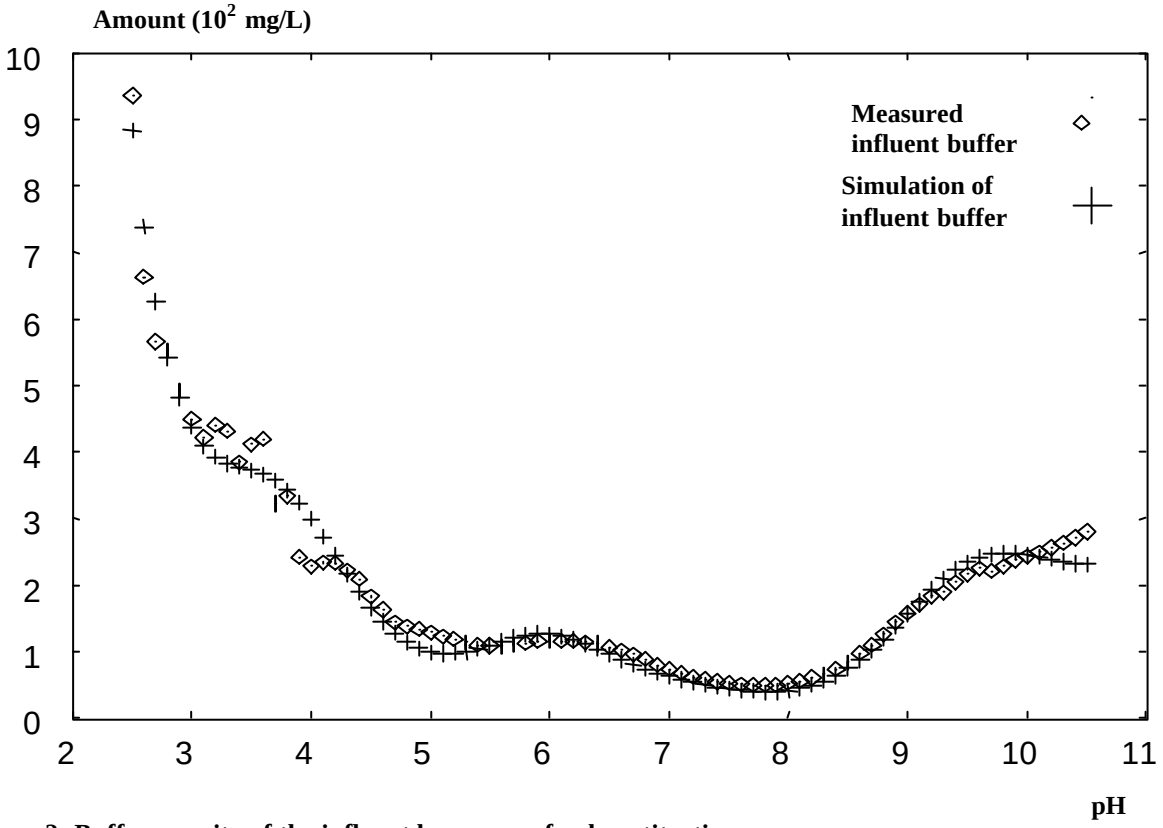


**Figure 2: Buffercapacity of the influent by means of a downtitration**

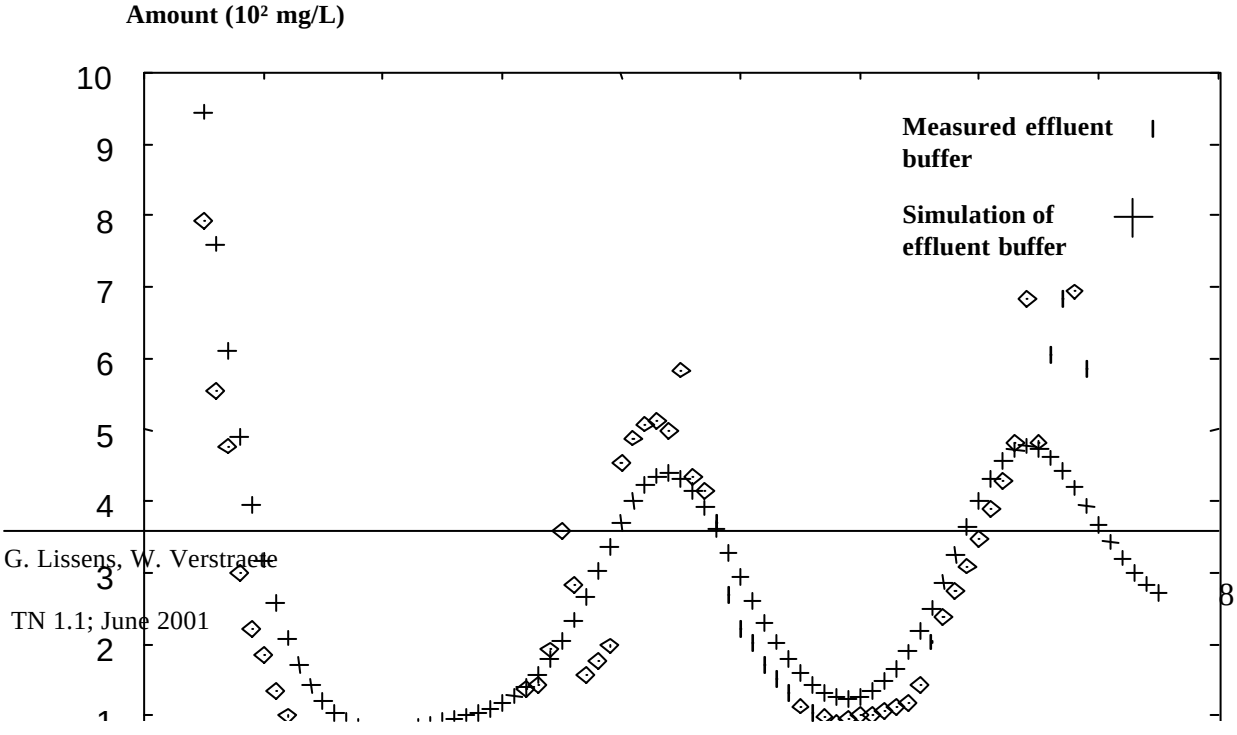

**Figure 3: Buffer capacity of the effluent by means of a downtitration**

*VFA-analysis*

Volatile fatty acids where extracted from the digester effluent with diethylether and analyzed with GC-FID (with internal standard). The following fatty acids have been determined: acetic acid (10mg/L), propionic acid (3mg/L), isobutyric acid (1.6mg/L), butyric acid (2.6mg/L), isovaleric acid (0.6mg/L), valeric acid (1.5mg/L), iso capric acid (1.3mg/L) and capric acid (5mg/L). It can be concluded that all VFA-concentrations were found to be very low (< 20 mg/L). This clearly indicates the high organic carbon removal and the stability of the digester (Bonmati et al., 2001).

## 4. Conclusion

The objectives of work package 1.100 are fulfilled. Preliminary tests with the defined synthetic substrate are carried out and the carbon and nitrogen mass balances are computed. The CSTR-type mesofilic digester shows satisfactory stability. This can be proven by the constant biogas yield, the low VFA- content of the effluent and the constant monitoring of the digester pH (around 7.4 continuously). With the current conditions, the average methane content of the produced biogas is found to be 60-65% or 13 g COD-$CH_4$/Liter substrate.
The digester residue (15-20% of the COD initial) mainly consists of recalcitrant substances in the liquid phase and fibre containing material in the solid phase (mainly lignocellulose complexes and macromolecules originating from the algae biomass).

## 5. Future perspectives

In the nearby future, the optimisation of the biogas production is aimed at. This means that both maximisation of the biogas production and particularly the methane production is

focussed on. To achieve this, an increased solubilisation of particulate matter (15% remaining COD, mainly insoluble) is necessary. This objective can be reached by two means; either by enhancement of the reactor performance (increase of hydrolysis during digestion, i.e. effect of temperature) or by means of the development of novel physico-chemical pretreatment methods such as thermal hydrolysis and electrolysis. Study of the kinetics and characterisation of the microbiota by means of molecular techniques (FISH, DGGE,…) will be necessary in order to get a clear view on the determining processes for the most rate-limiting step in the digestion of particulates, namely the hydrolysis step. For the development of novel physico-chemical techniques, the main critical parameters to evaluate the different techniques will be the increase in $COD_{soluble}$ , DOC/TOC and the increased biogas production (by means of small batch fermentation tests).

Other techniques such as the supercritical aqeuous treatment of organics (TUHH, Germany) and the hydrolysis of particulates by means of extremophilic bacteria (TUHH, Germany) are also considered. Therefore, during the coming months, digester residues will be sent to the partners of the MAP-project and the residues will be subsequently tested in different runs.

## 6. References

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