# A New Concept to Prove the Degradation Rate of Solid Biomass during Anaerobic Digestion

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**SUMMARY:** For production of high electrical current and for an optimal efficiency of a biogas plant, the biogas quantity, as well as a high methane content of the gaseous products (i.e. the biogas potential), is a fundamental economic characteristic property. Following the carbon path of the digestion process enables the prognosis, where the carbon remains, in methane or in residuals or elsewhere. The following concept takes up a simple carbon analysis of the input material and the residual substances of the digestion process, including an analysis of volatile compounds by gas chromatography (GC). The complete carbon balance of a biogas plant can be obtained by the parameters C<sub>solid</sub>, C<sub>liquid</sub> and C<sub>gaseous</sub>. The concept for calculating the theoretical possible yield of biogas based on a carbon determination makes the assumption that according to the general gas law equimolar gases exhibit the same volume, i.e. 1 mol carbon (12 gram) has the volume of 22.414 litres under conditions of standard temperature and pressure (STP). 1 g carbon could reveal 1.81 l biogas as outlined. In the case of solid matter, the total inorganic carbon (TIC) can be neglected. However, for the determination of carbon in the fraction of suspended solids, precautions are necessary, since the suspension liquor contains many dissolved compounds being volatile. The concept of carbon flow and of the reported analytical parameters for process stability has been validated for three years on 4 different large-scale installations.

### **1. INTRODUCTION**

In the past, mainly determinations of the biochemical groups like carbohydrates, protein and fat of the organic test substrate were performed. Also anaerobic batch digestion tests are used to predict the biogas resp. methane potential. The alternative concept for calculating the theoretical possible yield of biogas based on a carbon determination goes back on the general law that equimolar gases exhibit the same volume, i.e. 1 mol carbon (12 gram) possesses a volume of 22.414 litres (STP). A carbon balance with the parameters  $C_{solid}$ ,  $C_{liquid}$  and  $C_{gaseous}$  allows the verification of the gas yield of a laboratory batch test or of a large scale biogas plant.

## 2. MATERIALS AND METHODS

The anaerobic batch digestion tests were performed according to the procedures as outlined in VDI 4630 (Bergedorfer batch digestion test, guidelines for anaerobic digestion of organic matter, VDI 4630, 2006). The scheme of the experimental set-up used for anaerobic batch tests is shown in Figure 1. 1.1 litre gas tight glass vessels with a rubber plug were used for the anaerobic batch digestion tests. The vessels (n=3) were filled with 300 g of laboratory reactor effluent (supernatant) containing only 1.3 % volatile suspended solids (VSS). The continuously driven

reactor was processed for 6 years absolutely free of manure. With sugar beet silage (Scherer P., Dobler S. & al 2003; Scherer P., Lehmann, K. & al 2008). 20 g of frehly mashed substrate was added (sugar beets SB, pH 3.4-3.7, came from KWS Saat AG, Einbeck,). Dry matter content of SB: 17.30%, C<sub>solid SB</sub> dry: 39.46%, C<sub>liquid SB</sub> wet: 0.951% (volatile fatty acids, alcohols, about 60:40). 40 mM added NaHCO<sub>3</sub> and the initial pH of 7.3 guaranteed an alkalinity of about 5000 mg CaCO<sub>3</sub>-equivalents/l and a sufficient high pH above 7.0 after the incubation time of 11-20 days at 42°C. 10 mM NaHCO<sub>3</sub> revealed 500 and 40 mM NaHCO<sub>3</sub> 2000 CaCO<sub>3</sub>-equivalents/l. The assays were filled up with demineralised water up to 500 ml. Finally, the pH of each assay was adjusted with 1 M KOH to 7.0-7.3.



Incubator with Anaerobic Batch Digesters

**Figure 1.** The experimental set-up used for anaerobic batch digestion tests. The electronic instruments provide a precise determination of the gas yields online, they were developed at the Hamburg University of Applied Sciences.

Gas production from each assay was measured with a Milligascounter® type MGC-1.0 (Ritter, Bochum, Germany, <u>www.ritter.de</u>; www.bluesens.de). Gas yields were monitored online using a data logger and software, which were developed in the Laboratory of Applied Microbiology at the HAW Hamburg. A speciality of this volumetric gas determination is the measurement without overpressure. This revealed generally higher gas yields as measured with instruments generating an overpressure (Logan B, Oh SE. & al 2002).

The degradation of the test material was evaluated using the measured gas yields. The measured gas yields were calculated as ml under STP. The moisture content was also subtracted (VDI 4630, 2006). This resulted in a gas yield of about 9 % lower (under STP) than the measured values. 1 g of carbon reveals 1.81 litres gas according to the physical law that 1 mol of gas has a volume of 22.4136 litres under waterless and STP conditions. This means that 1 g C (mol = 12 g) can generate 1.81 litres gas at STP (including 3 % carbon uptake by bacterial biomass) (Scherer PA., Schultz KH. & al 1990; Scherer PA., 2007). By the carbon content of the used 20 g SB substrate it was calculated that 100 % degradation corresponded to 3797 ml <sub>STP</sub> biogas generation.

The volatile suspended solids (VSS) content was measured according to DIN Methods (DIN 38414-8, 1985). Volatile fatty acids (VFA) and alcohols were determined using a HP 5890

Series II GC (Agilent) with a flame ionization detector (FID) and a BP 21 Bonded FFAP Fused Silica column.

### **3. RESULTS AND DISCUSSION**

### 3.1 Considerations about carbon and efficiency calculations

For the carbon determination (total carbon, TC, total organic carbon TOC, total inorganic carbon TIC) of solid NawaRo, a carbon analyzer is required. With a rather uniform input of biomass only a few carbon analyses are needed. In the absence of special instruments, the carbon analysis could be replaced by a rule of thumb. This was validated by a publication of Navarro AF, & Cegarra J 1993. According to the authors, 1 gram total carbon (TC) means 1.8 - 2.2 gram of organic dry weight, thus, 2.0 gram organic matter (on ave.). On the other hand, 1 gram TS (total solids) corresponds to approx. 0.4 - 0.5 gram carbon (approx. 40 - 50%). For application on liquors with only small amounts of TOC, but CO2 or carbonates in it (water/wastewater), a modified carbon analytics had to be used, the error would be otherwise too large. For this, the inorganic carbonate portion (TIC) had to be determined separately. With a high organic content of solids, as for example NawaRo, one does not necessarily need to take into consideration the dissolved inorganic carbon in the form of  $CO_2$  or carbonate. The total organic carbon (TOC) becomes the TC. Thus, the process balance over the carbon path is simplified. But for the determination of carbon in the suspended solids, GC analyses are necessary, since the suspension liquor contains many dissolved digestion residuals being volatile. In our cases of operational analytics, the GC analyses of the dissolved substances represented mainly fatty acids, but also alcohols, with a proportion of 60 to 40. The possible error could be up to 100%.

The gas chromatographic analysis (GC) is in competition with other meaningful methods of analysis, e.g. ion chromatography (IC) or high pressure liquid chromatography (HPLC). GC is a little trouble-prone technique, but expert knowledge is required. For example, humic acids could be a serious problem, especially for HPLC. GC analysis supplies indirectly the carbon content by summing of the dissolved carbon data. Furthermore, GC delivers by the analyzed fermentation metabolites at the same time important parameters for the assessment of the operating stability of a biogas plant.

The principle to prognosticate the theoretically possible biogas yield of a substrate and the gas composition can be dated back to 1932, as Buswell and Boruff formulated a stoichiometric equation, which uses a carbon balance and allows estimation of the degradation efficiency as well as the methane content in the gas of a biogas plant:

$$C_{a}H_{b}O_{c} + \left(a - \frac{b}{4} - \frac{c}{2}\right)H_{2}O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right)CH_{4} + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4}\right)CO_{2}$$
(Buswell equation)

One can accurately calculate the quantity of gas, which can derive from 1 gram carbon. 1 kg carbon results in 1.81 standard cubic meters fermentation gas  $(m^3_{STP})$ , under standard temperature and pressure conditions. This means that the volume of any gas, corrected by the water content, by the temperature under measuring conditions (instead of 0°C) and by the atmospheric pressure (STP), contains 1 mole, independently if the fermentation gas contained a little or a high percentage of methane. That's another question and depends on the redox balance of the organic substrate. It is assumed that "biogas" contains  $\leq 1\%$  by-products like H<sub>2</sub>S, H<sub>2</sub> or NH<sub>3</sub> besides CH<sub>4</sub>, CO<sub>2</sub> and water vapour. Therefore, the gas volume has to be converted first into a volume under STP conditions. But the theoretical value of  $1.81_{(STP)}$  litre biogas per1 gram

carbon should be actually 3 % higher (see also VDI guideline No. 4630, 2005). 3 % was already subtracted from the value 1.81, as during fermentation a part of carbon is turned into bacterial biomass and therefore doesn't stand any longer for disposal to produce biogas (Figure 2).

If one considers 10 % carbon-loss by formation of bacterial biomass under standard conditions, only 1.692 m<sup>3</sup> of fermentation gas could be produced. Investigations in Weihenstephan/Bavaria, during balancing the anaerobic digestion of bear draff resp. spent grain of barley, revealed a value of approximately 3 % new bacterial biomass by biogasification, as recognized by different methods, e.g. DNA determination (Scherer PA., Schultz KH. & al 1990).

Aivasidis (1995)\_assumed a factor of 1-5 % for building of new microbial biomass during anaerobic waster water treatment. Pavlostathis and Giraldo-Gomez (1991) cite papers regarding the microbial growth yields as based on single substrates for some bacterial groups, e.g. 3.2 % for acetate, 3.0 % for  $H_2/CO_2$  and 15 % for carbohydrates, related to 1 g COD (chemical oxygen demand), i.e. approximately to 2 g VS resp. VSS (Navarro AF., Cegarra J al 1993).



Figure 2. Simplified scheme of anaerobic, microbial food chain (Aivasidis, 1995).

However, data for the increase of biomass by a mixed bacterial digester population, besides the own ones (Scherer PA., Schultz KH. & al 1990), could not be found in literature. Therefore, the experimentally determined growth yield was used for a mixed carbohydrate resp. brewers spent grain being 3.0 % (Scherer PA., Schultz KH. & al 1990). Possibly a higher value should be considered for substrates with a high fat and energy content.

### 3.2 COD value as a basis for the calculation of biogas yields?

350 ml CH<sub>4</sub> is assumed to correspond to 100 % degradation of 1g COD (chemical oxygen demand, an indirect measure of organic matter). In practice by parallel formation of new microbial biomass, this should result in only 320 ml gas yield. This assumption goes back to the 2. Work Report of the German ATV working group 7.5 (ATV resp. DWA Report of the group 7.5, 1993). The calculation cannot be used for the reversed conclusion, in order to prognosticate

a biogas yield by the COD content of a given substrate. However, the COD is suitable for the characterisation of a fermentation process with uniform carbon feeding. Under certain circumstances the COD causes a substantial error, especially in the case of manure which contains oxidizable nitrogenous compounds. A precondition to use the COD measurement is that the carbon is actually present in a dissolved state. On the other hand, there still exists no validated method for the determination of COD in solid organic matter to our knowledge. Recently, a method was published in order to determine the COD of solid organic matter (Raposo F., de la Rubia M.A. & al 2008).

## 3.3 Example given for an efficiency analysis in the case of maize

Maize silage of a pile contains approximately 34 % TS (it depends above all on the sort and the harvest time) and an average carbon content of 43 % per gram of dry weight. Thereby for the conversion in fermentation gas 150.5 kg carbon are available from 1 Mg resp. ton of maize silage (one can assume a loss of 15% of carbon by rain water washing and lactic acid fermentation, if a cover or a seeping water feedback is missing). Based on the carbon content of maize silage, a maximum theoretical biogas yield  $(CH_4 + CO_2)$  potential of 272.4 m<sup>3</sup> per Mg of fresh maize silage can be calculated anticipating the above calculation of 1.81 litres biogas per 1 gram carbon. Thus a biogas yield of 220 m<sup>3</sup> per ton resp. Mg maize silage would represent about 80.7 % degradation efficiency. With the current state of the art this can be regarded as a good value. The occasional reported gas yield of 230 m<sup>3</sup> per ton of silaged maize (total plant) would result in an efficiency degree of 84.4 %. This seems the maximum gas yield obtainable from maize. Therefore, any further enzyme addition (Parawira W., Murto M. & al 2005) or any mechanical disruption would not top such a high biogas yield. This computation based on the carbon content should demonstrate how simply the degradation efficiency of a biogas plant can be examined worth-neutrally. It helps to make the appropriate considerations about the useful pre-treatment procedures and the following profit from a biogas plant.

# **3.4** Example for efficiency computation of a biogas plant by analysis of dissolved, volatile carbon compounds

For operating analytics of biogas plants the knowledge about the content of dissolved volatile compounds is of paramount importance. Therefore, the VFA (C<sub>2</sub> to C<sub>6</sub>), alcohol and the lactic acid (determined enzymatically) content of the biogas reactor liquid are determined. With municipal sewage digesters a stable operational behaviour could be reached with retention times of 21-30 days. In such a state the content of VFA amounts generally  $\leq = 500$  ppm (DWA M 380, in preparation, set of technical rules for good practice of co-digestion, www.dwa.de). The common VFA are acetic, propionic, butyric, and sometimes valeric and capronic acid, whereby in particular the relation of acetic acid to propionic acid can give a statement about the stability and efficiency of a plant (Ahring BK., Sandberg M. & al 1995). In the HAW laboratory, in particular with so called dry anaerobic digesters for maize, very high contents of these dissolved VFA were measured in biogas plants, which frequently ranged between 3-5 thousand ppm VFA in the discharge. Additions of trace elements (especially cobalt and nickel) reduced dramatically the VFA below 1000 ppm (unpublished observations, found only for maize). Nevertheless these biological gas facilities run very well. Primarily, the pH value is important, which should not be below 7.3. This derives from the buffer capacity or "alkalinity", sometimes also called "lime reserve" of the reactor liquor. Total Alkalinity ("TAC") includes the sum of buffer capacity of bicarbonate alkalinity and of VFA-alkalinity, by titration down to 4-4.5 (Speece 1996).

However, high concentrations of dissolved digestion residuals resp. VFA in the reactor discharge cause a loss of electrical current production. Table 1 demonstrates this decreasing

process efficiency. Thereby the profit loss of 13680 Euro per year by the lacking use of the electrical current is not unrealistic. This refers to a 500 KW electrical engine (2000 m<sup>3</sup> biogas reactor). Thereby, the electricity loss caused by suspended digestion residuals, instead of dissolved residuals, are higher around a multiple. By a second stage of an anaerobic digester only 5 - 10 % additional carbon can be converted into biogas on the average. In the methane reactor, if the total solids (TS) contents are about 5-11 % (being a realistic value for a so called dry fermenter), the TS content in the disposal stage should be in the range of 4-10 %, i.e. the carbon contents are lying between 2-5 %. Thus, the loss of biogas resp. electricity by TS discharge would lie between 20000 - 45000 Euro/a, only for a 500 kW producing biogas plant.

Volatile Fatty Acids (VFA C <sub>2</sub> -C <sub>6</sub> ) and Alcohols [ppm]	500 [ppm]	1000 [ppm]	2000 [ppm]	3000 [ppm]	4000 [ppm]	5000 [ppm]
Reactor Volume [m <sup>3</sup> ] of the						
Reactor						
500 (ca. 11 Mg/day)	570€	1140€	2280€	3420€	4560€	5700€
1000 (ca. 22 Mg/day )	1140€	2280€	4560€	6840€	9120€	11400€
2000 (ca. 44 Mg/day)	2280€	4560€	9120€	13680€	18240€	22800€
3000 (ca. 66 Mg/day)	3420€	6840€	11400€	17100€	22800€	34200€
4000 (ca. 88 Mg/day )	4560€	9120€	18240€	27360€	36480€	45600€

Table 1. The annual electricity profit loss of a biogas plant, as shown by the operating analytics.

\* VFA and alcohol values were converted into carbon values. It was assumed that 1000 ppm VFA and alcohols (60:40) reveal 0.905 standardized litres biogas (litre<sub>STP</sub>). On the average 1000 ppm fatty acid/alcohols (60:40) correspond to about 500 ppm carbon (determined 480-520 ppm). The methane content of the biogas deriving from a biogas plant fed only with maize silage (without manure) was assumed to be 53.5% (sometimes only 52.5% are measured). In terms of economics, a hydraulic retention time of 50 days was assumed in Table 1, whereby 10% of the input materials were considered to be water vapour loss over the gas outlet. According to the Buswell equation, the water loss is dependent on the TS content of the input matter, whereby the retention time in the reactor extends again. The retention time is further increased by the common practice of recirculation of process water from the second stage or the discharge tank back to the main biogas reactor. Therefore, a process balance is often made more difficult by partial recirculation of the fermentation liquor. Furthermore, for efficiency computations a remuneration of 17.9 cent per a kW/h was assumed. The efficiency of a central electricity producing engine (central heating power station) was supposed to be only 40%.

# **3.5** Example for efficiency computation of a laboratory digestion test with sugar beet silage following the carbon path

Sugar beets harvested in the year of seeding contain nearly no lignin (< 0.5%). Therefore, more than 95 % of the carbon of the substrate could theoretically be converted into biogas (Scherer PA., Dobler S. & al. 2003; Scherer, 2007).

However, Speece (1996) outlined that a minimum of 6000 ppm CaCO<sub>3</sub> buffering capacity (alkalinity) is required for anaerobic digestion to reach a pH > 7. Sugar beet silage (SBS) contains only a capacity of 3000 - 4000 (Scherer P., Lehmann, K. & al 2008), and the animal manure contains up to 21000 ppm CaCO<sub>3</sub> equivalents. Raposo F., Banks CJ. & al (2006) adjusted their batch digestion tests with maize by addition of NaHCO<sub>3</sub> to 9100 mg/l equivalents

of CaCO<sub>3</sub>. Therefore, SBS needs a buffer or a pH control for complete anaerobic digestion. Quite different behaves grass silage or barley "full plant silage" being rich of nitrogen. During anaerobic digestion of barley an overplus of buffering ammonium originates. Therefore, such a substrate doesn't need an extra buffer or a pH control

In Figure 3a and b, the degradation results of a small scale batch digestion test (Bergedorfer batch digestion test, VDI 4630) is presented. In this experiment, 3534 ml biogas under STP conditions (53-58 % CH<sub>4</sub>) originated from 20 g wet and mashed beets, buffered with 40 mM NaHCO<sub>3</sub>. Assuming 23.23 % dry weight (dw) and 41.70% carbon/(dw) the test substrate of 20 g wet and mashed beets corresponded to 1.93 g solid carbon. By GC-analysis it was found that the mashed sugar beets were somewhat ensilaged. They contained VFA and alcohols by the sum of 0.840 % dissolved carbon. Therefore, the incoming substrate had to be corrected by additional 0.168 g carbon. That means that 1.93 gsolid + 0.168g carbonliquid (2.098 g) generated 3534 ml<sub>STP</sub> biogas (Figure 3a and 3b). The theoretical gas yield would be 2.098 x 1810 ml = 3797 ml<sub>STP</sub> biogas. This means that the generated 3534 ml<sub>STP</sub> biogas coming from 20g wet sugar beets were equal to 93 % degradation.



**Figure 3a/b.** Anaerobic digestion batch tests with sugar beets (SB) after 11-20d. The cumulative biogas production as a function of carbon conversion resp. degradation of SBS into biogas (column) (A) and of time (B) is given.

## **4. CONCLUSIONS**

The new concept to prove the degradation rate of solid biomass during anaerobic digestion takes up a simple carbon analysis of the input material and the residual substances of the digestion process. The generated biogas volume is converted into carbon, too. By an analysis of VFA and alcohols by GC also the dissolved carbon of the fermentation liquor is included. The complete carbon balance of a biogas plant is represented by the parameters  $C_{solid}$ ,  $C_{liquid}$  and  $C_{gaseous}$ . In the case of solid matter, the total inorganic carbon (TIC) can be neglected. The concept to follow the carbon path, not the biochemical determinations of carbohydrates, protein and fat, has been validated since three years, on 4 different large-scale installations, since these facilities are weekly analysed by the HAW Hamburg. Among these large-scale installations are the biogas facilities Lanken of the property Wotersen (2.1 1 MW, energy crops), the ProEn (Protein + Energy) company in Soltau (> 4.3 MW, energy crops) as well as the Wuesthof biogas plant in Soltau (> 4 MW) and the Biowerk Hamburg (1 MW) for overlaid food and kitchen leftovers.

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