COMPARISON OF TEST SYSTEMS FOR THE DETERMINATION OF THE BIODEGRADABILITY OF ORGANIC MATERIALS UNDER ANAEROBIC CONDITIONS

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1. ABSTRACT

The determination of the biodegradability of organic substances is of crucial importance for the product launch and for the disposal of these products. Biodegradable materials can be treated under aerobic as well as under anaerobic conditions. The investigation of biodegradability under aerobic environment conditions alone is not sufficient, for there are some materials, which are biodegradable under aerobic conditions, but an anaerobic biodegradation cannot be observed to the same extent. This is to be examined by use of standardised test methods.

For the determination of the biodegradability under anaerobic conditions bench scale studies were carried out using on two different test systems according to the ISO CD 14853. These were then compared. In one of these test systems, the gas production was measured with an Eudiometer using the principle of displacement volume. In the second test system, the gas production was measured via determination of gas pressure. Materials tested were Polyhydroxybutyrate (PHB), Poly-e-caprolacton (PCL) and Ecoflex®. The assessment of the degree of biodegradability was carried out by determining gas production. The examinations have demonstrated, that with both test systems comparable results can be achieved.

2. INTRODUCTION

In modern industrial societies plastic materials have been established in all areas of life. They are used for the production of a broad range of goods. As a result the amount of plastics in solid wastes to be disposed off increases steadily. The recycling of mixed plastics is still in its infancy. Plastic materials being used as packaging material in the food industry and in the fast-food sector in addition are heavily polluted by organic residues. As an alternative to the traditional plastics biodegradable materials have been developed throughout the last years with great success. Compared to conventional plastics they offer the advantage that they can be disposed off not only in an incineration plant or on a landfill but can also be reprocessed in a biological treatment step together with organic waste. Processes of biological treatment to be used in this context are composting and anaerobic fermentation.To ensure an environmentally sound behaviour of these materials the biodegradability in principle has to be determined under defined standards. For the examination of these plastic materials tests have to be carried out under aerobic as well as under anaerobic conditions.

During preliminary assessment studies at the Department of Waste Management at the Technical University Hamburg-Harburg comparative tests have been carried out for the examination of biodegradability under anaerobic environment conditions according to ISO CD 14853 (Anonymus, 1997). The biodegradability tests on 3 different materials have been carried out in 2 different test systems in order to assess their suitability. Test methods to be assessed were based on the volumetric and the manometric determination of gas production which used as an indicator of the biodegradability.

3. MATERIALS AND METHODS

The tests for the examination of the biodegradability under anaerobic conditions were carried out according to the draft guidance ISO CD 14853 (Anonymous, 1997).
Three different materials have been tested for biodegradability:

- Poly-β -hydroxybutyrate (PHB) with the specification BX GO8 (powder) produced by SENECA;
- Poly-ε -caprolactone (PCL tone polymer 767) produced by UNION CARBIDE (powder); and
- Ecoflex® produced by BASF (organic waste plastic bags, particles size d<5mm).

The carbon content of the different materials is presented in Table 1. In addition the theoretical rates of biogas production (*Thbiogas)* as well as the theoretical rates of CH_4 and CO_2 production of the different materials, $ThCH_4$ and $ThCO_2$, respectively, are compared.

The maximum theoretical amount of carbon (*ThC*) to be transformed into gaseous phase expressed in mol is given by Equation 1.

$$ThC = \frac{m * X_c}{M_c} \quad [1]$$

Where:

- ThC is the theoretical conversion org C into the gas phase, [mol];
- m is the mass of the test material, [g];
- X_c is the carbon content of the test material; and
- M_c is the relative atomic mass of carbon, (12 [g*mol^{-1}]).

The maximum theoretical amount of biogas produced (Thbiogas) expressed in cm^3 at standard conditions is given by Equation 2.

$$Thbiogas = ThC * V_m \quad [2]$$

Where:

- Thbiogas is the theoretical amount of biogas, at standard conditions (S.T.P.), [cm^3];
- ThC is the theoretical gaseous carbon, [mol]; and
- V_m is the molar volume of an ideal gas at standard conditions, (= 22414 [cm^3/mol]).

The maximum theoretical amount of CO_2 and CH_4 produced are given by equation 3 according to (*Buswell and Mueller, 1952*)

$$C_cH_hO_o + \left(c - \frac{h}{4} - \frac{o}{2}\right)H_2O \rightarrow \left(\frac{c}{2} + \frac{h}{8} - \frac{o}{4}\right)CH_4 + \left(\frac{c}{2} - \frac{h}{8} + \frac{o}{4}\right)CO_2 \quad [3]$$

Test material	[% dry weight basis]	PHB $C_4H_6O_2$	PCL $C_6H_{10}O_2$	Ecoflex®
Carbon content		55.81	63.16	62
Theoretical biogas production	[cm^3 mg^{-1}]	1.043	1.797	1.158
Theoretical methane production	[cm^3 mg^{-1}]	0.585	0.738	
Theoretical carbon dioxide production	[cm^3 mg^{-1}]	0.455	0.442	

Table 1. Characteristics of the materials tested

The Test medium and the inoculum have been prepared according to the ISO CD 14853 in a glove box under anaerobic conditions. The sludge being used as an inoculum was stabilised sewage sludge from the wastewater treatment plant of Hamburg-Köhlbrandhöft. The loss on ignition of sewage sludge was 1.9 (dry weight/volume), and the pH 7.6. Prior to its use, the sludge was washed with the test medium to attain a dissolved organic carbon (DOC) of C_{DOC}<10 mg/l. The total solids content of the washed sludge in the medium was TS=2.96 g/L.

For the determination of gas production two different test systems containing 12 reaction vessels each were set up. The employed test systems were the volumetric test system of the TUHH (Eudiometer) and a test system (Sensomat Meßsystem) of the company Aqualytic, Neu-Isenburg, Germany that works based on the manometric principle. The test vessels in use were modified glass Schott flasks of 500 ml each having two gas sampling ports at the upper end of each flask.

The test vessel of the volumetric test system is connected to a gas collection tube with a capacity of 200 ml via a Viton tube (Figure 1). The pH value of the barrier liquid is pH=2.0. The reading precision of the gas volume is of 1.3 ml per scale unit. For the determination of the gas volume produced the reservoir tank gets balanced via the flexible connecting tube until both liquid columns in the gas collection tube and in the reservoir tank respectively coincide. The gas sampling for the determination of the concentration of gas contents takes place discontinuously via a gas sampling syringe which is inserted into the septum on the gas collection tube. The sampling of liquids is carried out via the septum on the reaction vessel itself. The samples are intermittently mixed using magnetic stirrers.

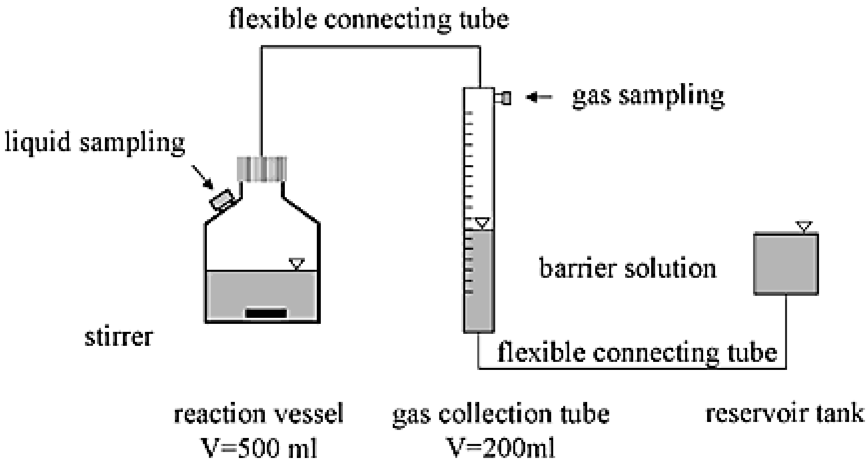

Figure 1. The volumetric test system

In the manometric test system (Sensomat Meßsystem) the amount of biogas being produced is indirectly measured by a pressure meter on the upper end of the reaction vessel (Figure 2). The actual pressure as well as the stored pressure data can be transferred into and be evaluated by a computer via an IR sensor. The sampling of liquids as well as the discontinuous gas sampling for the determination of gas concentrations takes place via a gas sampling syringe which is inserted into the septum on the reaction vessel. The samples in the vessels are intermittently mixed using magnetic stirrers.

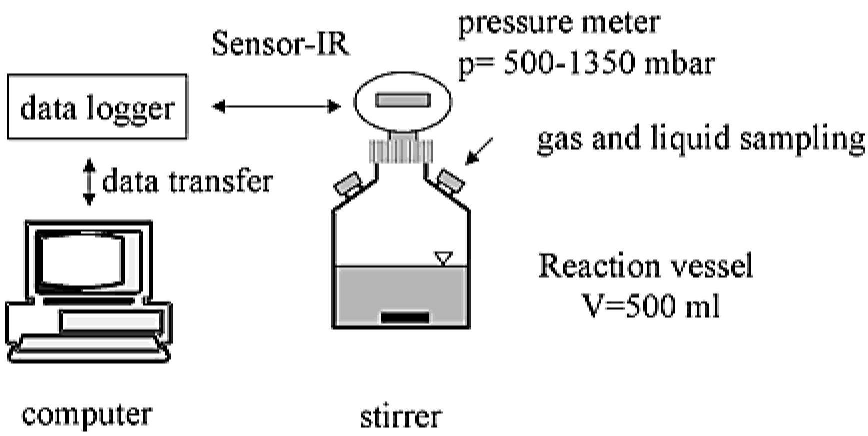

Figure 2. The manometric test system

The tests were carried out in a climatic chamber with a temperature of T=35°C±1°C during a testing period of 30 days and 60 days, respectively. The set-up for each test system is presented in Table 2. The three materials and the inoculum were examined each as a triple test. The concentration of the examined test materials was fixed to a total organic carbon content (TOC -C_{TOC}) of 100mg/l. In the volumetric test system there were inserted 500 ml of medium and 50 ml of inoculum. 50 ml of the suspension were sampled for analysis. The manometric test system was filled with 300 ml of the test sample. All reaction vessels were purged with nitrogen before being incubated.

The determination of the pH value, of the TOC, DOC, dissolved inorganic carbon (DIC), and of the solids content in the suspension was carried out at the start and at the end of the tests. The analysis of the gas volume was carried out on each working day for the volumetric test system and for the manometric test system discontinuously every 40 minutes. The gas concentration was measured discontinuously during the whole testing period.

Flasks:	Test material	Reference material	Inoculum
F_{T1-T3} Test	Poly-ε -caprolacton		+*
F_{T4-T6} Test	Ecoflex®		+*
F_{B1-B3} Blank			+*
F_{c1-c3} Inoculum check		Poly-β -hydroxybutyrate	+*

* +: runs which featured inoculum addition.

Table 2. Scheme of the test procedure

The amount of produced biogas at standard conditions in cm^3 is given by Equations 4 and 5.

$$V_n = \frac{(p_t - p_w)[mbar] * V_t[cm3] * T_n[K]}{T_t[K] * p_N[mbar]} \quad [4]$$

$$V_{NBG} = V_{Nt} - V_{Nt0} \quad ?[5]$$

Where:

- V_N is the amount of biogas at standard conditions, corrected for water vapour pressure expressed in cm^3 at time t;
- P_t is the atmospheric pressure (volumetric method) or pressure in the headspace of the test flask (manometric method) at the time of reading t of the produced biogas expressed in mbar;
- P_W is the water vapour pressure at the given incubation temperature T_t expressed in mbar;
- V_t is the volume of the gas phase at the time of reading t expressed in cm^3;
- T_N is the temperature at standard conditions expressed in Kelvin (=273.15 K);
- P_N is the pressure at standard conditions expressed in mbar (=1013.25 mbar)
- V_{NBGt} is the volume of biogas produced at time t, expressed in cm^3 at standard conditions;
- V_{Nt} is the volume of sample at time t, expressed in cm^3 at standard conditions; and
- V_{Nt0} is the volume of sample at time t_0 (beginning of the test), expressed in cm^3 at standard conditions.

The calculation of the percentage of biodegradation D_t (%) for both test systems based on produced biogas is given in Equation 6 .

$$D_t = \frac{((v_{NBGt})T_{1...Tn} - \Sigma(V_{NBGt})_{B1...Bn}))}{\Sigma(Thbiogas)_{1...n}} * 100 \quad ?[6]$$

Where:

- N is the number of replicates;
- $(V_{NBGt})_{T1,2..n}$ is the amount of produced biogas at time t at standard conditions in test flasks F_{T1}, F_{T2},...F_{Tn} expressed in cm^3;
- $(vNBGt)_{B1,2,..n}$ is the amount of produced biogas at time t at standard conditions in blank flasks F_{B1}, F_{B2},...F_{Bn} expressed in cm^3;
- $Thbiogas_{1,2,..n}$ is the amount of theoretical biogas calculated by equation 2 in the respective test flasks F_{T1}, F_{T2},...F_{Tn}.

4. RESULTS AND DISCUSSION

The comparison of the volumetric and the manometric measuring method for the determination of the biodegradation of organic materials under anaerobic conditions according to the draft guidance ISO CD 14853 is presented by using as an example the degradation of PHB.

The course over the time of the calculated rate of biogas production (standard volume) of the samples to be tested containing PHB and without PHB (blank), respectively, is presented in Figure 3, as an example for the volumetric measuring method over a testing period of 30 days. According to the *Buswell and Mueller (1952)* equation the inserted amount of PHB can theoretically produce 93.4 cm^3 Thbiogas in total. The triplicate parallel set-ups of the samples tested show each a similar course-trend of biogas production. The degradation of PHB starts simultaneously in all the different PHB_{FC1-3} set-ups after approximately 3 days. The exponential phase of biogas production is already terminated after approximately 7 days. After a testing period of 30 days a total amount of about 84 cm^3 biogas is produced, the standard deviation is 53 cm^3. The curves of biogas production of those samples having been inoculated ($blank_{FB1-2}$) show, following an initial biogas production, almost a linear course during the whole testing period. After 30 days the biogas production of the inoculum was at an average value of 22.7 cm^3.

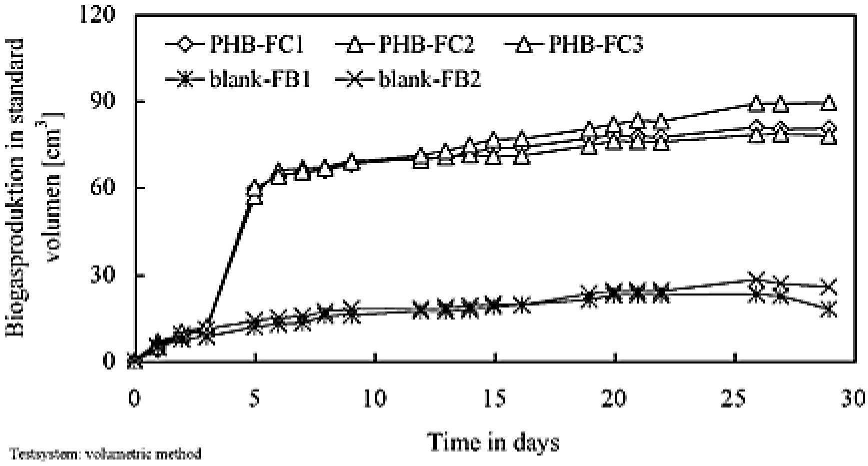

Figure 3. Production of biogas (standard volume) of the tested samples PHB and inoculum during a testing period of 30 days in a volumetric test system (see also Table 2)

The comparison of both test systems for the examination of the anaerobic degradation behaviour of PHB is demonstrated in Figure 4 using the average curve of the parallel set-ups on the basis of the maximum theoretical rate of biogas production according to *Buswell and Mueller (1952)*.

After a testing period of 30 days in both test systems almost identical rates of biogas production have been observed. Approximately, for the volumetric test system this was 65% while for the manometric test system 67% of the theoretically attainable rate of biogas production. The lag-phase began for both test systems simultaneously after about 3 days. The biodegradation phase of PHB in the manometric test system took about 1 day longer than in the reference experiment (volumetric test systems). This is probably due to the higher excess pressure of 160 hPa in the manometric system. At higher gas pressure more gas is theoretically dissolved in the liquid phase. This phenomenon is subject to further investigations. Altogether in the manometric test sample there is attained already briefly after the end of the biodegradation phase an of about 5-10% higher biogas production rate. By the end of the testing period of 30 days the curves have converged again.

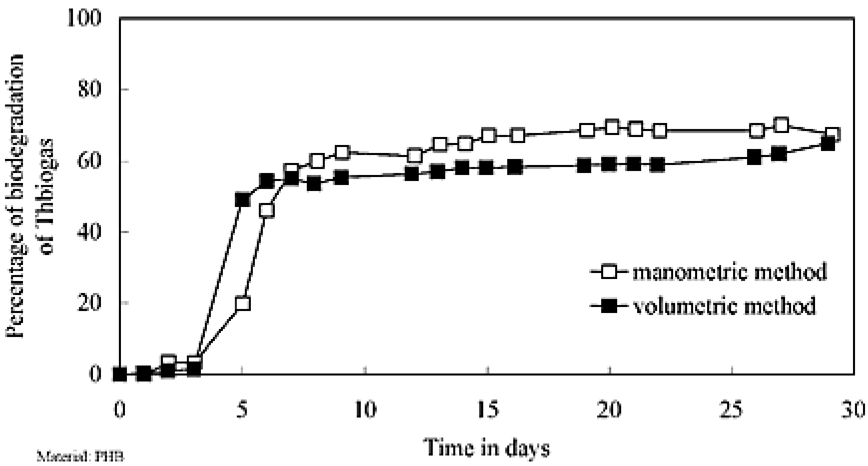

Figure 4. Percentage of PHB-biodegradation of Thbiogas according to *Buswell and Mueller (1952)* in comparison to the manometric and volumetric measuring methods.

In addition to the testing of PHB, experiments regarding the biodegradation of the materials Ecoflex® and Poly-ε -caprolactone were carried out in both test systems (Table 1). For both of the materials no significant anaerobic degradation according to ISO CD 14853 after a testing period of 60 days could be detected. Concerning the Ecoflex® , there are available extensive results of experiments regarding the aerobic degradation behaviour. These results indicate that, according to DIN V 54900, this material is aerobically completely biodegradable (BASF, 1998). Should the material be treated by using anaerobic fermentation, a sufficient post-treatment by using composting will be necessary.

5. CONCLUSIONS

The anaerobic biodegradation of Poly-β -hydroxybutyrate (PHB), Poly-ε -caprolacton (PCL) and Ecoflex® was examined according to the draft guidance ISO CD 14853 by using two different test systems. The results have demonstrated that during the degradation of PHB in both test systems, following a testing period of 30 days, a biogas production rate of 65 % and 67 %, respectively, of the theoretical gas production rate has been measured. Here the soluble part of the produced CO_2 in suspension was not taken into account. Both test systems are thus suitable for the examination of the biodegradability of organic substances according to the ISO CD 14853. However, the influence of the higher gas pressure on biodegradation results, in the manometric test system, remains to be examined.

No significant biodegradation of the materials PCL and Ecoflex® under anaerobic conditions during a testing period of 60 days could be detected. The material Ecoflex® is however biodegradable under aerobic conditions. The assessment of the biodegradability of so-called biodegradable plastic materials under aerobic and/or anaerobic conditions is of crucial importance, when increasing amounts of those materials will be biologically treated in the future.

6. ACKNOWLEDGEMENTS

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