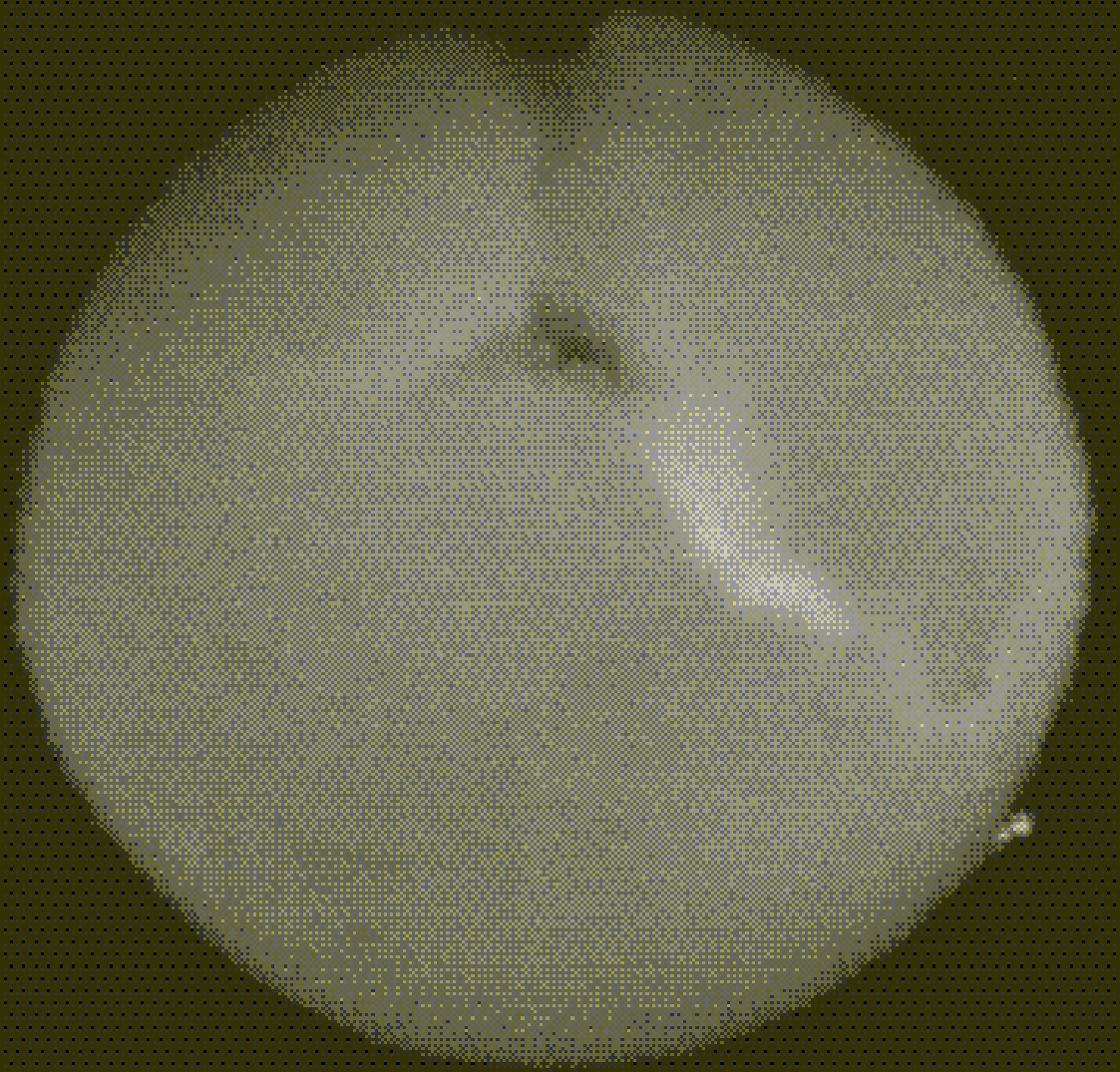
Innovations in composting pig manure



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Innovations in composting pig manure

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Innovations in composting pig manure

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Abstract

Composting the solid manure fraction on farm has many advantages, but usually burdens the environment through gaseous emissions. Notably, large quantities of ammonia and smell can be emitted. On a farm, the composting process is controlled by less knowledgeable operators, which increases the risk of odour and ammonia emissions, and the production of a low quality compost. This thesis focuses on the possibilities to improve the compost process by analysis of the three main aspects of composting: process control, feed composition and bed structure. Based on this analysis the composting process was improved with respect to ammonia emission and compost quality.

A low cost solution to the ammonia emission has been developed in the form of a composting process at low oxygen concentration that decouples the heat removal from the oxygen supply, decreasing the amount of waste gas. The control and operation of such a system have been investigated, and the reduction in emitted ammonia quantified. The system can reduce ammonia emissions with up to 78%, but requires a careful control of the start up, and therefore of the feed composition and bed structure.

Our analyses of (bio-)chemical properties of solid pig manure showed that the composition can vary in time. In order to optimise the feed mixture from available ingredients, an oxygen uptake measurement was modified so that the oxygen uptake rate (OUR) of feed material can be measured on farm. A complete growth and mass transfer model of OUR measurements based on pressure change methods was developed to investigate these measurements in detail. From the analysis an improved protocol to quantify the stability from the OUR, by measuring the hydrolysis rate, is derived. A conceptual model of how the degradation during composting can be predicted from the initial hydrolysis rate is presented. With these tools, the feed composition can be optimised to yield compost that is sanitized as well as dry and stable. This work has also yielded measurable criteria to assess the accuracy of pressure based activity (OUR and anaerobic methane production) measurements.

The influence of the bed structure was investigated by comparing several compost runs using a mixture of wheat straw and solid pig manure. Two models, one of which not validated until now, predicting bed activity as a function of bed air porosity were tested and found applicable. Further analysis revealed however that not the initial porosity, but the weakness of the compost bed's structure, which leads to a diminished porosity at higher temperatures, was more important.

Finally, the results of this thesis are combined with the particle based composting model. It is shown how the acquired insight can be used to optimise the composting process.

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Cover: Sphere of fungus; grown in a shaken growth medium.

Recipe: a mixture of: 190 ml of a solution containing 1M PO_4^{2-}, 0.77M NH_4^+, 0.46M Na^+ and 0.36M K^+; 5 ml solution B, 0.2 ml solution C and 2.5 ml solution D (see section 5.4); 0.6 g of glucose and a drop of compost extract, is shaken at 120 RPM at 30°C for several days. Ensure the liquid has enough room to slosh in its container and that sufficient oxygen is present or supplied.

1

Introduction

1.1 Background

The attitude of society towards pig production is changing. Society demands that nuisance, from smell, noise, and pollution of soil and ground water, are minimised and that produced food is safe. In the near future this will be extended with demands for further reduction in the environmental burden and for the introduction of stricter ethical standards for animal husbandry.

Pig production, like other industries, has to reform to keep abreast of these changes and to keep production in the Netherlands possible. To meet these demands pig production is constantly changing and innovating. Changes in production methods normally involve added technology that further improves the process. The new demand for more animal friendly housing presents technological difficulties for current pig rearing systems as it tends to compromise other design criteria like abatement of emissions of pollutants and of smell. Also the costs can be a bottleneck.

In the Netherlands project Hercules was set up to design a more sustainable pig rearing process. Within this project the complete pig production chain was redesigned. By doing this, demands that seem conflicting in current production facilities, can be met simultaneously (Bos et al. 2003). To ensure acceptance by the pig rearing industry various businesses and knowledge institutions related to agriculture collaborated in the project. The work presented in this thesis was conducted at Wageningen University as part of the Hercules project. The objective was to design a composting system working at low oxygen concentrations that can process separated solid pig manure on a farm working according to the Hercules system.

1.2 The Hercules Project

It falls outside the scope of this thesis to completely describe the Hercules pig rearing system. Instead a brief overview of the system and a detailed description of the mass flow through the system will be given. More details on specific aspects of the Hercules system can be found in the following publications: (Ogink et al. 2000a; Ogink et al. 2000b; Willers et al. 2000; Ogink et al. 2001).

The concept

In the Hercules project the housing system and the complete pig rearing chain were redesigned. The sustainability of the complete chain was of prime consideration. Social acceptance, economic viability and environmental impact were all considered. This meant that farmers' workload and ergonomics were considered as well as e.g. animal behaviour and environmental impact of feed,

gaseous emissions and excrements. This led to a new housing design, with innovations like floor cooling, twin aisles for better accessibility, and an improved airflow design over the pigs living area.

One of the key features of the Hercules concept was the improved utilisation of agricultural by-products and organic wastes. In the system the pigs are fed a wet fodder mixture containing agro-industrial by-products. Care was taken that this did not compromise pig health or meat quality. Suitable processes were also developed for the treatment of the faeces and urine. This entails better handling and storage properties, lower transport costs, fertilizing properties more suited for modern agriculture where nutrient management is important, and less emission to the environment.

The first step in the treatment of the excrements is a separation into a liquid and a solid fraction. Separation has two advantages. First, by separating directly ammonia emissions from the pigs' housing area can be kept very low. This improves pig health, farmers working conditions, and makes the system more robust as a breakdown of the air treatment unit will not immediately cause excessive nuisance to the surroundings. Second, the faeces-urine separation diverts nearly all the phosphorous to the faeces fraction. This allows for more precise fertilizing than could be achieved with a mixed product. It is expected that this will therefore increase the value of produced fertilizers.

Mass flow

The mass flow of the Hercules system is described by the flow scheme presented in figure 1 (Ogink et al. 2000b). Pigs need air, water, feed and bedding. The pigs consume some of the air, the water and the food, converting them to body mass, heat, carbon dioxide, urine and faeces. The grown pigs are the primary product of the system, the other products are considered wastes and have to be disposed of, or upgraded to a valuable secondary product. In the Hercules system the excrements are upgraded to high quality fertilizers.

The heat produced by the pigs is removed from the pen via air ventilation. This removal occurs partly by an increase in ventilation air temperature, and partly as latent heat of evaporated water. As the ventilated air is not saturated it is used to evaporate the urine, so a more concentrated nitrogen fertilizer is produced. As the urine has to be acidified to retain ammonia during evaporation, the outlet air is simultaneously scrubbed from ammonia, reducing emissions.

The faeces and bedding material are composted to obtain a dry and sanitised fertilizer. Ammonia emitted from the composting process is scrubbed in the urine evaporating process that also scrubs the ventilation air. To further increase urine

evaporation the heat emitted from the composting process can be used to increase the temperature of the urine.

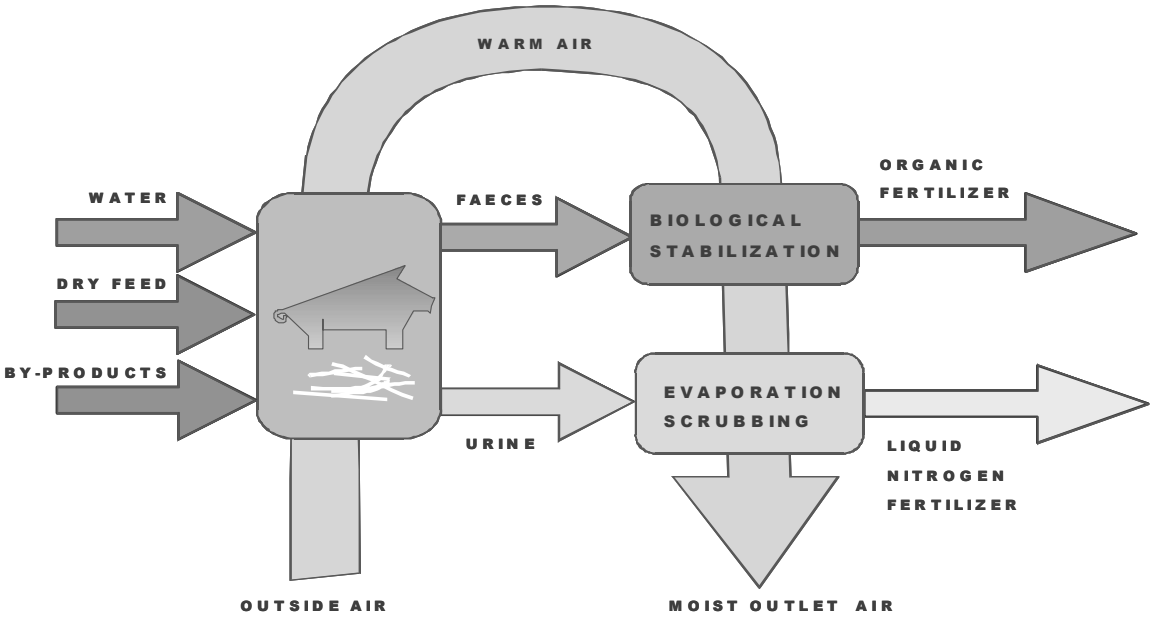

Figure 1 Qualitative flow diagram of the Hercules pig rearing system.
From: (Ogink et al. 2000b)

Feed can be either dry feed from a specialized company, or by-products that could come from various sources. By-products are waste materials from the agro-industry, and an increased use of by-products in animal feedstuffs will benefit the environment. The environmental advantage gained by using a different kind of fodder is not only the source of products used for the mix, but also the fact that it is not dry. In the Hercules concept the pigs are fed a feed slurry, whereas traditionally pigs are fed pelleted dry feed. Drying feed accounts for a large part of the energy use associated with rearing pigs. By switching to wet feed mixes the environmental impact of the system is reduced.

The flow scheme in figure 1 does not show bedding material, even though the pigs require this. It is a small amount compared to the feed, and is therefore omitted. Bedding material will be a legal requirement for pigs, and by recycling the nutrients contained in it to a fertiliser sensible use is made of resources.

Integrating the solid manure treatment

The Hercules project dealt with the complete pig rearing chain, so all stages of production were subject to optimisation during the project. Insight gained was used to modify pen design, bedding material and feed mixture during the course of the project. Some of these changes affected the properties of the manure produced. The system is optimised with regard to feed, pig production and air

emissions. The environmental gain from stabilization is small compared to the combined gains achieved by other innovations. The quality of the faeces and urine produced is a result of process decisions made. It can be expected that when the system is used commercially, adaptation to new insights and legislation will continue. Therefore, in practical application any manure stabilization process has to be able to deal with this variability in manure quality.

Stabilization of solid manure is necessary to ensure the acquisition of the manure by arable farmers and other buyers. The bulk of the water in the manure is evaporated during the process, and this reduction in weight means a larger area can be economically supplied. The stabilization has to produce a good marketable product. The production of this product should not interfere with pig production.

Constraints of the composting process

Within the concept of the Hercules project the composting of the pig manure solids had to satisfy certain requirements.

- Composting had to be on farm. This meant that the workload should be minimised, as well as the required operator knowledge. Clearly manure composting is the production of a by-product, and as such much less important then the rearing of pigs. Time and effort required of the farmer should reflect this. Also investments should be in line with benefits.
- On farm composting necessarily means that available facilities, space and time are all restricted and there is no room for adjustments to the process. A finished product has to be produced within the planned three weeks.
- Emissions resulting from treatment of wastes should not compromise advantages gained at an earlier stage. The Hercules housing system was designed to have low emissions of ammonia and smell. Emissions of the composting process should not significantly increase the load emitted from the pig pen. Therefore, ammonia had to be recovered from the process gas.
- The produced compost should have a market value higher than the untreated pig manure solids. The market value depends on the fertilizing properties of the compost, as well as on handling, transport and storage properties. Concentrating phosphorous in, and lowering the nitrogen content of, the solid manure fraction, increases its fertilising properties. Producing a stable and dry product optimises the other properties.
- To comply with EU regulations concerning export, the compost should be sanitised. This means heated to at least 70°C for at least one hour.

1.3 Composting pig manure

The Hercules project chose composting as the method for the stabilization of raw manure. This choice was based on the evaluation of the market for the fertilizer produced. Pig production in Europe is mainly concentrated in a few production areas. Within these areas, there is an excess of nutrients excreted by the animals. Useful application of these excrements necessitates transport to areas where a shortage of nutrients exists. Transport becomes easier and cheaper with a dry and stabilized product. Export, which may be transport to the nearest arable land, is subject to sanitation laws to prevent the spread of disease. These currently demand that the manure is heated to 70°C for at least one hour. These criteria are met by properly composted manure, making composting a very suitable method for processing separated solid pig manure.

One of the main advantages of the Hercules system is the low concentration of ammonia in the air emitted from the pig housing area. The composting of faeces, which is nitrogen rich, is associated with high ammonia emissions. Contamination of the expelled air with large amounts of ammonia would be unacceptable. Therefore, waste gas from the compost process cannot be treated in the same unit as the air expelled from the housing area, unless the load of ammonia is reduced. A separate stripping unit to pre-treat waste gas from the composting process is costly, and therefore undesirable. A solution was found within the composting process itself.

During composting micro-organisms degrade organic matter to carbon dioxide, water and ammonia. This process uses oxygen that is supplied by blowing or sucking oxygen rich air through a stacked pile of solid matter, called a compost bed. The oxidation of the organic matter releases energy. The organisms use part of this energy to grow, and part is released as heat. At the start of the compost process this heat is used to warm the compost, as the bed has to be sanitised at 70°C for 1h. After this, the bed has to be cooled to the optimum operating temperature of 55-60°C. Once the optimum temperature has been reached, cooling is still required to remove excess heat and maintain bed temperature.

The energy needed to heat a dry volume of air from 20°C to 55°C and saturate it with water vapour (as occurs in a compost bed) is equal to the enthalpy generated by an aerobic microbiological degradation that consumes an amount of oxygen equivalent to 2%(v/v) of the dry air. Therefore, broadly speaking, the maximum amount of energy a volume of air can remove when entering at 20°C and exiting at 55°C is equal to the energy provided by a reduction of the oxygen content from 21% to 19%. This means a composting process emits a larger volume of waste gas than the volume of air necessary to provide the quantity of oxygen consumed.

In the Hercules project a choice was made to use a composting process that would utilise a greater fraction of the oxygen in the air used. Reducing the flow of expelled air will simultaneously reduce the load emitted, as the concentration of ammonia and other noxious substances in the expelled gas is dictated by equilibria. It is not possible to simply recirculate all process air until oxygen levels have dropped because cooling is the main function of the airflow through a composting bed. Heat also has to be removed. In the system used, this was done by cooling the recirculated air. By cooling the saturated air, a condensate forms in which water soluble gasses dissolve. This further decreases emissions.

By using a greater portion of the oxygen available in the process air, the oxygen concentration within the reactor will drop. In conventional composting, a low oxygen concentration is associated with a badly functioning process. These usually compact compost beds have a limited oxygen supply. These beds heat up until the oxygen is depleted, and then anaerobic digestion takes over, producing an acidic and smelly end product. In the process proposed here, the supply of oxygen can be large, but the concentration at which it is supplied is low. It is more difficult for the biomass to take up oxygen when the concentration is low. Oxygen deprivation of the composting process may therefore occur despite a theoretically sufficient supply. One of the main aspects of this research was to find the minimum oxygen concentration required for producing a good quality compost.

Cooling the recirculated process air during composting can lower emissions to the atmosphere. There are two disadvantages. Cooling costs energy, and a waste stream of condensate is produced. The condensate is not a problem in the Hercules concept as this can be added to the urine. A major part of the ammonia emitted from the composting unit will be dissolved in the condensate. This approach will increase the nutrient retrieval of the system. The energy needed to cool the condensate has to be weighed against the advantages obtained. Without some form of gas treatment on farm composting is not a viable option. Composting the manure produces a more valuable fertilizer, and reduces the energy required for transport. Further, the excess heat energy and temperature of the recycled air are sufficient to help heat the urine as it is evaporated. Additional energy for cooling would therefore only be necessary during very active composting phases when the temperature of the ingoing air has to be low.

1.4 Research objectives

The main objective of this research was to design a composting system working at low oxygen concentrations that can process separated solid pig manure on a farm working according to the Hercules system. This meant the design has to fulfil all the requirements given earlier. In this research specifically attention was given to

reducing ammonia emission to the atmosphere, which is usually very high when composting manure, and formulating a foolproof composting guide that would allow farmers to use the system with a minimal amount of knowledge required.

At the start of the Hercules project the low oxygen composting system was still a theoretical system. The first goal of the research presented in this thesis was therefore to prove that low oxygen composting is feasible. To justify the extra investment and energy demand, this system should diminish emissions without compromising product quality. At least three demands have to be met:

1. The process produces qualitatively good stable compost, without the high volatile fatty acid contents usually found in compost deprived of oxygen.
2. The composting manure can maintain enough activity to become dry compost within three weeks.
3. The low oxygen composting system reduces gaseous emissions when compared to conventional composting, particularly of ammonia.

Having shown that the low oxygen composting process is feasible, work was done to optimise the process to meet all the Hercules criteria. Critical elements in an on-farm unit are the quality of the produced compost, and the time necessary to produce it. There is not enough reactor space, time, or knowledge for adjustments or for a prolonged or a secondary composting process. The second goal was therefore to formulate criteria that would ensure that the structure of the compost bed would enable sufficient bacterial activity to complete the composting process within three weeks.

The third goal was to optimise the compost reactor feed so that the produced compost would be both dry and stable without requiring intermediate adjustments. Therefore, a prediction of biodegradation during composting had to be achieved.

1.5 Overview of the thesis

In chapter 2 experiments are described with a novel composting system that uses the oxygen content of the air more efficiently. It was expected that this would lead to less emission of ammonia to the environment. Also the degradation after three weeks composting was compared to the degradation in a standard composting set-up.

In chapter 3 the start up phase of pilot experiments following the experiments of chapter 2 are described. Start up is far more problematic than was expected from the preliminary experiments. It is made plausible that this is due to the structure of the compost bed. It is also indicated that degradation of the manure varies, most

likely because of variations in the diet of the pigs. The relation between bed structure and start-up is investigated, and guidelines are given that can prevent start-up problems occurring.

The varying degradation during composting of the manure leads to varying product quality. To be able to control product quality better, it is necessary to characterize the degradability of the manure beforehand. A conceptual model describing a possible method to predict degradability by measuring the hydrolysis rate is presented in the introduction of chapter 4. The rest of chapter 4 analyses the suitability of the OxiTop system, for measuring oxygen uptake of suspended solids. Modifications making the system suitable for the intended purpose are described.

In chapter 5 the measurement of oxygen uptake with the OxiTop as an indication for hydrolysis rates is discussed in detail. A growth model for bacteria growing under substrate limited conditions is adapted for the specific conditions in the OxiTop. It is discussed how substrate and oxygen are supplied to the bacteria, and how a limited supply will restrict bacterial oxygen uptake. From this the measurement with the OxiTop is discussed for its use in measuring the hydrolysis rate of organic solids. A conversion factor to measure hydrolysis is defined and its accuracy estimated.

Chapter 6 is the synthesis of the research. Here it is described how the results obtained fit in with general composting theory, and how they should be interpreted. The content of this chapter is then used to formulate how to design a better on farm composting system.

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2

Composting at low oxygen pressure

2.1 Introduction

In The Netherlands, intensive pig farming is concentrated in areas that have an excess manure production. Consequently, surplus manure for use as an organic fertilizer, has to be transported over long distances, leading to higher production costs for the pig farmer. Export could be part of the solution for the manure surplus, but due to EU regulations concerning animal manure, it cannot be exported unprocessed. Composting can be an option for manure management. If composted properly, the product complies with EU sanitation rules and can be exported. In addition, compost weighs only half as much as the fresh manure, is easier to handle and store, and transport is consequently cheaper. Composting can expand the market for excess manure.

Traditional low-technology composting methods take a long time and require a lot of space. As space is scarce and expensive in The Netherlands, only high-rate composting processes are economically feasible. These high-rate processes emit a lot of ammonia when composting low C/N (ratio of carbon to nitrogen on a weight basis) materials, such as manure. Therefore, Dutch legislation demands treatment of the waste gas emitted by high-rate composting. However, the costs of this treatment can outweigh the economic advantage of composting.

According to Finstein (1983), the ventilation in temperature controlled high-rate composting processes has two functions: supply of oxygen and removal of excess heat. Veeken (1999) showed that these functions can be uncoupled by introduction of gas cooling. In the uncoupled process fresh air is added to supply oxygen, and recirculated gas is cooled for heat removal. A part of the ammonia emitted from the compost is trapped in the condensate that forms when cooling the recirculated gas. As a result, both the amount of waste gas and the ammonia emission to the environment are strongly reduced. Optimised to minimise ammonia emissions this system may be able to comply with Dutch legislation.

In the uncoupled system, the oxygen level and temperature can be independently controlled. There is a considerable literature on the choice of optimum temperature. Reference is made to Richard (1998) for a review. It is generally accepted that the best composting results are obtained in the temperature range from 55 to 60°C.

The major question regarding the uncoupled system is the optimum oxygen concentration of the off-gas. Model calculations showed that the lower this concentration is set the less air is required for composting and the less ammonia is emitted (Veeken et al. 1999). However, Richard (1999) have shown that under low oxygen levels the composting rate can be impaired. Any limitation of the process

rate leads to a slower process and consequently higher land usage as reactor volumes have to be increased. An impaired process can thus lead to higher costs.

The objective of the study described in this chapter is to investigate changes in the performance of the composting process at low oxygen levels and, if necessary, propose system changes to cope with the expected process limitations. The result will be used to design an on-farm composting unit for the Hercules project, as described in chapter 1.

2.2 Materials and Method

Three composting runs were made to compare the process at different oxygen concentrations ($[O_2]$) in the off gas. Run A had 10%, run B 5% and run C 1% ($v\ v^{-1}$) oxygen in the off-gas. Run A was run for 25 days, run B 21 days and run C for 19 days. Run C was done with a half-full reactor because of a shortage of suitable manure.

Manure was collected from a small pilot facility in Maartensdijk, in which it was separated on a convex conveyer belt as described by Kroodsma (1998). The excrements dropped onto the conveyer belt through a floor grid in the pig pen. Urine ran off the belt and was collected in two gutters at either side. The faeces were collected by turning the conveyer belt on, and scraping the manure off at the end. This was done daily.

The manure for the three runs was collected on the same day, and kept in cold storage (4°C) until used. The structure of the compost bed was improved by adding wheat straw to the manure as a bulking material. The manure was mixed with the straw manually. The ratio manure to straw was 19 to 1 on a total mass basis.

Run A was mixed by hand once a week during the composting process. The material was rewetted if necessary, and samples of compost were taken. Runs B and C were not opened during the run, so no rewetting or sampling took place.

The experiments were performed using the 80Lcomposting vessel described by Veeken (1999); the set-up is represented in figure 1. The composting vessel was aerated with dry pressurised ambient air, entering at the bottom (Q_{in}). Part of the gas at the top was recirculated to the bottom of the composting vessel (Q_{rec}) via a water-cooled heat exchanger. Excess gas was led from the top of the composting vessel through an acid-filled water-lock to the gas analysing units. This off-gas flow was driven by the overpressure induced by the inflow. The water-lock kept the vessel slightly pressurised, preventing ambient air from leaking into the system. The acid in the waterlock captured all ammonia emitted with the off-gas, and was regularly replaced and analysed.

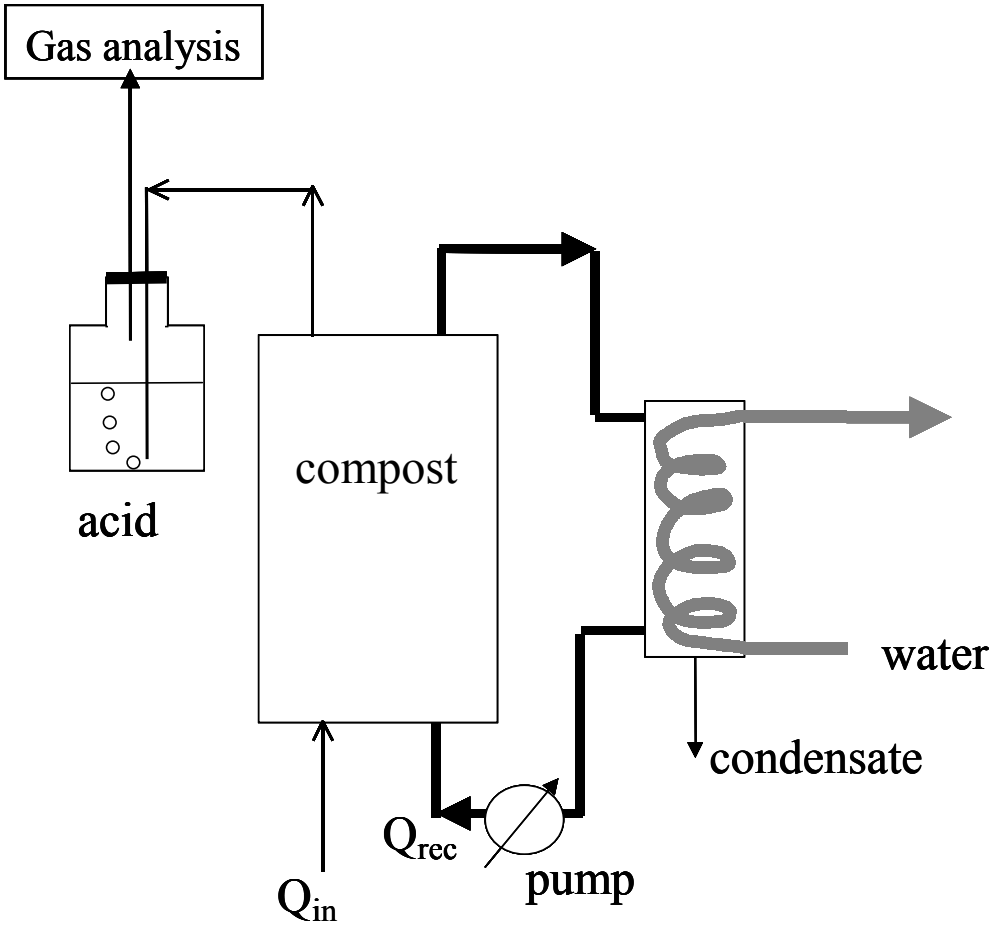

Figure 1 Flow scheme of the batch-composting unit

The composting system was controlled by a computer with an input output system (RTI-820 board, 5B modules, Analog devices, USA) using Control EG. The following parameters were measured online every 15 minutes: oxygen concentration of the off gas (Oxi 219/90R WTW, Germany), carbon dioxide concentration of the off gas (Siemens Ultramat 1, Germany), the compost temperature at five points in the bed, (thermocouples type T); and the airflow into the reactor system, Q_{in} (5850S, AIR, thermal mass flow controller, Brooks, USA). The recirculation, Q_{rec} (m^3 h^{-1}), was calculated from the pumping frequency which was recorded. The pumping frequency to gas flow relation was regularly calibrated with a manually read gas flow meter (VEG .00094, G1.6, Schlumberger, The Netherlands).

The controls of the experiments were set to keep the average compost temperature at 58°C, and the oxygen concentration in the off gas at a certain set level: run A at 10%, run B at 5% and run C at 1%. The temperature was controlled by adjusting the recirculation flow Q_{rec}. The oxygen level in the off gas was controlled adjusting the inflow of fresh air Q_{in}. Both controls were step controls, increasing or decreasing the flows with a fixed step every 5 min.

The following characteristics of the feed and compost material in and out of the reactor were measured using standard methods (APHA 1992): mass, dry matter content ($DM_{110°C}$) and pH. And further ash content, total Kjeldahl nitrogen, ammonium and volatile fatty acids all on $DM_{110°C}$ basis. The $DM_{110°C}$ measurement takes place at high temperature, so that the VFA are nearly completely vaporised (Derikx et al. 1994). This means that the weight loss during drying consists not only of water, but also of organic matter, and that the measured OM (=$DM_{110°C}$ - ash) does not include all substrate. For this reason, the DM and the OM were corrected by adding the VFA to the $DM_{110°C}$. This gives the following measured parameters:

M_{in}	Total mass of solids packed into the reactor	[kg]
M_{out}	Total mass of solids retrieved from the reactor	[kg]
$DM_{110°C}$	Retained relative mass of a wet sample after drying at 110°C	[kg kg^{-1}]
pH	Proton activity	[-]
ash	Retained relative mass of a $DM_{110°C}$ residue sample after glowing at 550°C	[kg kg^{-1}]
N_{amm}	Ammonia that can be steam stripped at high pH from a fresh sample	[g kg^{-1}]
N_{kj}	Ammonia that can be steam stripped at high pH from a fresh sample after destruction in sulfuric acid.	[g kg^{-1}]
VFA	Volatile fatty acids that are analysed in the water phase of a suspension of a fresh sample in water	[g kg^{-1}]

The composting process was followed by analysing all flows in or out of the system. The mass of condensate formed (M_c), and mass of material trapped in the acid trap (M_a) were measured at intervals depending on the amount formed. After weighing, the condensate and acid trap liquid were analysed for ammonium (N_c, N_a, respectively) using the same method as for the compost material. From the off gas analysis and the inflow of air (Q_{in}) the rate of oxygen consumption (OUR) and of carbon dioxide formation were obtained. Leachate was not formed during the experiments.

M_c	Mass of condensate formed in the cooler during the composting period; mainly water	[kg]
M_a	Mass increase of the liquid in the acid trap during the composting period; mainly water	[kg]
N_c	Ammonia retrieved in the condensate	[g]
N_a	Ammonia retrieved in the acid trap	[g]

From the acquired data the following parameters were obtained by calculation: DM and OM which are the corrected dry and organic matter content, ΔOM the degraded organic matter, and COU_{OM} the cumulative oxygen uptake per kilogram of organic matter degraded. ΔC_{OM} and ΔH_2O_{OM} are the ”degraded” or formed amount of

carbon and water, respectively per kilogram of degraded organic matter. The effectiveness of the cooler in capturing ammonia emitted from the compost is given by N_{cap}. The activity of the compost at any time is the oxygen uptake rate (OUR).

For these calculations the following formulas were used. The subscript "in" denotes the material used, the subscript "out" the resulting compost.

$$DM = DM_{110\,oC} * (1 + VFA) \quad [kg\ kg^{-1}]$$

$$OM = \frac{1 - ash * DM_{110\,°C}}{DM} \quad [kg\ kg^{-1}]$$

$$\Delta OM = M_{in} * DM_{in} * OM_{in} - M_{out} * DM_{out} * OM_{out} \quad [kg]$$

$$N_{org} = N_{kj} - N_{amm} \quad [g\ kg^{-1}]$$

$$\Delta N = N_{kj,in} * DM_{110°C,in} - N_{kj,out} * DM_{110°C,out} \quad [g]$$

$$N_{cap} = \frac{N_c}{N_c + N_a} \quad [-]$$

$$OUR = \frac{10 * Q_{in} * \frac{(20.9 - [O_2])}{22.4}}{M_{in} * DM_{in} * OM_{in}} \quad [mol\ h^{-1}\ kg_{OM_{in}}^{-1}]$$

$$COU_{OM} = \frac{\int_{time} \frac{32 * OUR * OM_{in}}{1000} dt}{\Delta OM} \quad [kg\ kg^{-1}]$$

$$\Delta C_{OM} = \frac{\int_{time} \frac{12 * Q_{in} * [CO_2]}{22.4 * 100} dt}{\Delta OM} \quad [kg\ kg^{-1}]$$

$$\Delta H_2O_{OM} = 1 + COU_{OM} - \Delta C_{OM} * \frac{44}{12} \quad [kg\ kg^{-1}]$$

The OUR and the ΔC_{OM} equations assume identical Q_{in} and Q_{out} (in dry gas volumes), following the reasoning that every mol of oxygen consumed is replaced by a mol of carbon dioxide. Although this is not fully correct corrections made for this assumption did not influence the measured OUR or ΔC_{OM}. Therefore, the simpler formulas were used.

The three composting runs were compared using the process parameters $[O_2]$, T, OUR, COU_{OM}, ΔOM, ΔN and N_{cap}. The OUR reflects the biological activity during composting. The amount of organic matter lost, ΔOM, and the cumulative oxygen uptake, COU_{OM}, are an indication for the progress in the composting process. The

amount of nitrogen lost, $\triangle N$, is important because in combination with the captured nitrogen, N_{cap}, this determines whether further gas treatment is necessary. The quality of the compost obtained from the three runs was compared using DM, OM, N_{kj}, N_{amm} and pH.

2.3 Results and Discussion

The graphs obtained from the on line measurements show fluctuations, due to the control, on short timescale that make the graphs difficult to read. Therefore, the graphs presented in this chapter are based on 5-h moving averages. That means every data point is replaced by the average of 20 data points. In this way, short-term fluctuations are smoothed out, and a clearer view of the process course is obtained.

During the start-up of Run B it became clear that at an oxygen concentration of 5% in the off gas the biological activity remained very low, and as a consequence no temperature increase occurred. To increase the temperature in the reactor to 58°C in an acceptable time, the oxygen concentration was temporarily raised to 10% until the desired 58°C was reached. Because activity in run B was negligible until the oxygen level was raised, this period of low activity was discarded. The point at which the oxygen level was raised to 10% in run B is considered as time 0, allowing a better comparison between the runs. Run C was also started with an initial period during which the oxygen concentration was 10%. After the temperature was raised to 58°C, the oxygen content in the off gas was controlled at the desired level for the run.

Because it was expected that the start-up problem would repeat itself after each mixing, it was decided not to mix the composting material in runs B and C. The material in run A had been mixed and rewetted once a week

On Line Measurements and Process Control

The measured oxygen concentrations are presented in figure 2. For all three runs the oxygen concentration is quite close to the intended concentration, except during the start and end phases. Therefore, the step regulation used in these experiments is capable of maintaining the desired oxygen concentration.

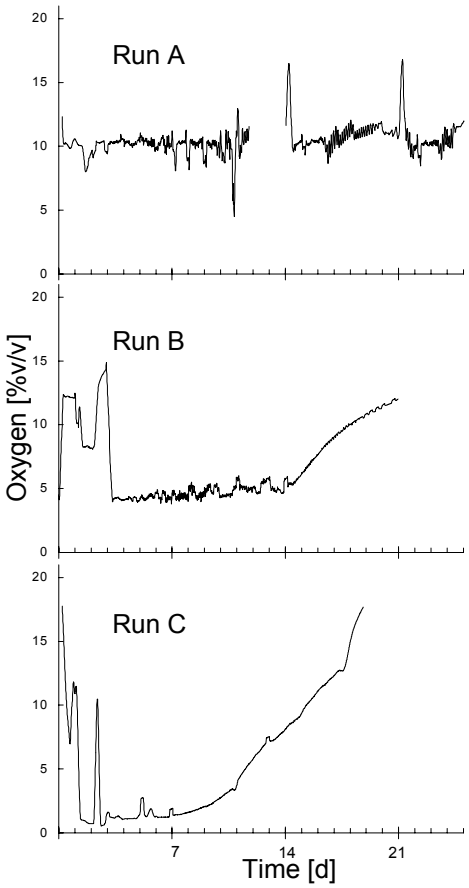

Figure 2 Oxygen concentration in the off-gas of the composting system.

The oxygen concentration in the off gas rises towards the end of the runs because a minimal net airflow through the reactor was needed to have enough off-gas for measurements. If the oxygen supply through this flow is more than needed, the low concentration cannot be maintained. In run C the 1% level could be maintained only for a week.

In table 1 the cumulative inflow and recirculation flow are given for the three runs. As expected from the model calculations of this low oxygen composting (Veeken et al. 1999), the amount of fresh air required for run C was less than that required for run B, which was less than that required for run A (table 1). An increasing portion of the available oxygen was used, so less air is needed to provide the same amount of oxygen.

As can be seen in table 1, the cumulative recirculation flow per kg initial organic matter, at the end of the runs are comparable. However, runs B and C have a peak in recirculation flow that is half that of run A (not shown). The flow is more evenly spread in time in runs B and C.

The [CO_2] graph (not shown) is an exact supplement to the [O_2] graph (figure 2), the sum of the two constant around 20%. This means every mole of oxygen consumed was replaced by a mole of carbon dioxide. The rate at which carbon dioxide was produced was in fact slightly less than equimolar to oxygen depletion in all experiments. This indicates that the degraded material was more reduced than carbohydrates.

To correct for the CO_2 captured in the condensate, it was assumed that equimolar amounts of CO_2 and NH_3 dissolved in the condensate, as $NH_4(HCO_3)$ is expected to be the main species in the condensate (Veeken et al. 1999). This assumption changes the calculated ratio of formed carbon dioxide to consumed oxygen. The corrected ratios are 0.96 for run A, and 0.95 for runs B and C. The carbon dioxide content of the condensate should be analysed in future experiments. The ratio does show that even at 1% oxygen content the OM was degraded by aerobic activity, as anaerobic degradation would form extra carbon dioxide.

Table 1 The cumulative airflows during composting.

Run		A	B	C
Total inflow; $\int Q_{in}dt$	[$m^3\ kg_{OM}^{-1}$]	3.5	2.5	1.6
Total recirculation, $\int Q_{rec}dt$	[$m^3\ kg_{OM}^{-1}$]	10.1	8.7	7.1

In figure 3 the mean temperature as well as the temperature of each of the five measuring points is given for the three runs. As can be seen, maintaining the temperature at 58°C once it was reached was no problem at either 5% (run B) or 1% oxygen (run C). In fact, this temperature could be maintained longer than for the run at 10% oxygen (A), ensuring an excellent pathogen removal. Also it can be seen that at lower oxygen concentrations the temperature gradient in the reactor is smaller. Probably because less heat is extracted from the bottom layer of compost as the cooling requirement for less active beds is lower.

Figure 4 shows the time course of the oxygen uptake rate (OUR). The times when run A was mixed and rewetted can be seen clearly. After an initial increase in the OUR, it drops in all runs at some point in time. Runs A and B show a sharp drop 2 days after start-up. In run B the drop begins before [O_2] was lowered. After lowering the [O_2] there is an almost instantaneous drop of the OUR. The OUR continues to decrease gently after the oxygen level is lowered. In run C the OUR is almost constant from day 4 through to day 10, and when the drop begins it does so despite the rising oxygen concentration.

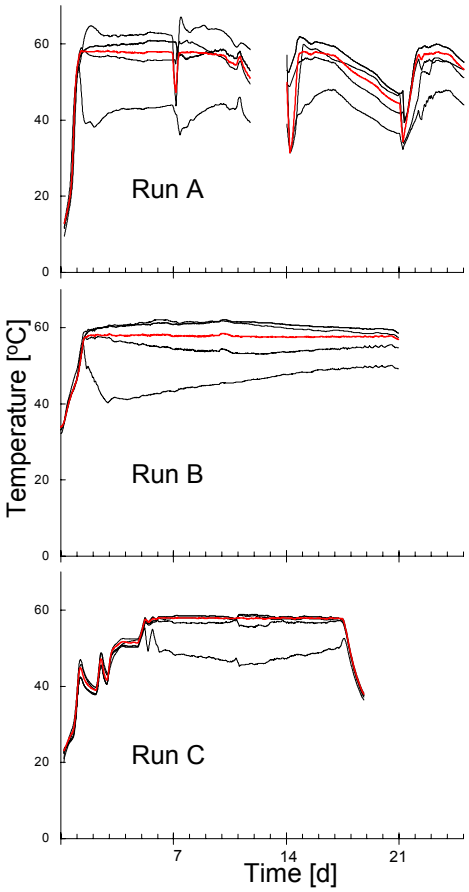

Figure 3 Temperature at five points in the compost

These results are in accordance with the predictions made by the kinetic model proposed by Hamelers (1993). In this model the microbial activity is concentrated in biofilms covering the compost material. The activity in these biofilms is limited by lack of either oxygen or substrate. Whether oxygen or substrate is limiting the composting process is determined by the size of the respective flows of oxygen and substrate to the biofilm. The oxygen coming from the gas stream, the substrate from the compost particles by diffusion through the water phase. The water phase substrate concentration in the particles does not become zero, because the particulate organic matter hydrolyses to soluble substrate.

At a fixed oxygen level in the gas phase surrounding the composting particles and temperature the potential oxygen flow to the micro-organisms in the particles is almost constant during the whole composting process. Therefore, changes in OUR may be interpreted as changes in substrate flow, which is directly related to the hydrolysis rate.

Both the inability to raise the temperature initially high enough and the ability to maintain the high temperatures during a longer period at low oxygen concentrations can be related to the significant differences in activity at the

different oxygen levels. The start up for all three runs was done at 10% oxygen. After the oxygen level was lowered in runs B and C, the activity is initially lower than in run A because of oxygen limitation. It consequently takes longer for the substrate to become limiting. The activity in runs B and C is therefore longer at a level high enough to compensate heat loss than in run A, but is too low to raise the temperature.

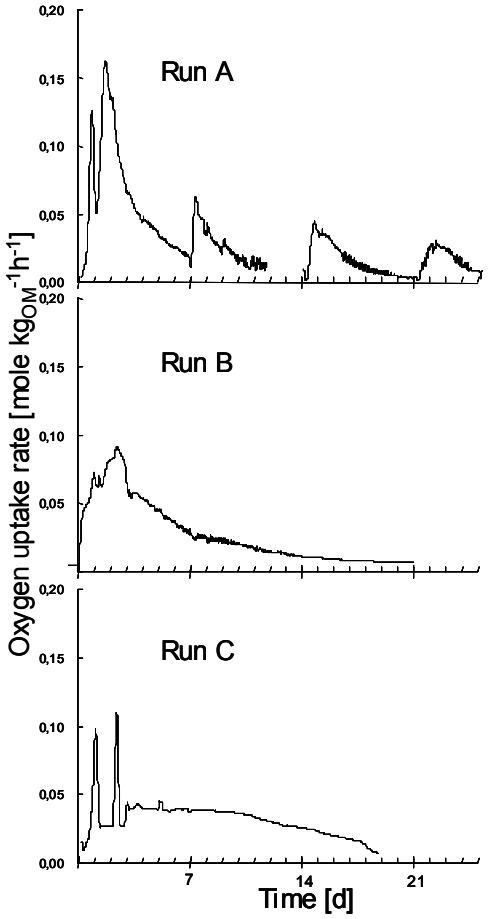

Figure 4 The oxygen uptake rate of the compost

In the kinetic model (Hamelers 1993) the available substrate is a function of stock and hydrolysis. In time, the activity stabilises at a rate equal to the hydrolysis rate of the substrate. Once this rate is reached, all initial stock has been degraded. The graphs indicate a decreasing stock of readily degradable organics and a low hydrolysis rate. The low hydrolysis rate can be seen from the low OUR at the end of all three runs. The stock of available substrate decreases, as can be seen from the decrease in OUR towards the hydrolysis rate. In run A it can be seen that the hydrolysis limited OUR is reached much quicker.

The cumulative oxygen uptake of the three runs after nearly 3 weeks was similar, even though the OUR time course differed; run A 0.48 (kg_{O_2} $kg_{OM_{in}}^{-1}$), run B 0.44, run C 0.45. This comparison time was chosen because run C was stopped at this time.

Composition of the materials

The composition of materials in and out of the reactor, before and after the composting process, is given in table 2. The analytical results of the ammonia content in the condensate and the acid trap is given in table 6.

During the dry matter analysis the VFA evaporate. However, as VFA are easily degradable organic compounds they were added to the $DM_{110°C}$ to obtain better values for the DM and OM. Without the correction for the amount of VFA the OM of all three materials would have been 0.77 kg kg_{DM}^{-1} (table 2). The ingoing material is identical for the three runs, except for VFA content. From the difference in VFA content it can be concluded that the material changes during storage.

Table 2 Composition of composting materials before and after composting

Run		A in	B in	C in	A out	B out	C out
Dry Matter (DM)	[kg kg^{-1}]	0.38	0.39	0.38	0.62	0.60	0.58
Organic Matter (OM)	[kg kg_{DM}^{-1}]	0.81	0.78	0.77	0.72	0.71	0.73
Volatile Fatty Acids (VFA)	[g kg_{DM}^{-1}]	46.20	9.30	0.94	0.00	0.00	0.00
Kjeldahl N (N_{kj})	[g kg_{DM}^{-1}]	32.10	31.50	31.80	34.29	28.56	28.10
Ammonium N (N_{amm})	[g kg_{DM}^{-1}]	14.28	14.10	14.20	8.93	8.67	9.70
Organic N (N_{org})	[g kg_{DM}^{-1}]	17.82	17.40	17.60	25.36	19.89	18.40
pH	-	7.20	7.20	7.20	8.50	8.40	8.50

In table 2 it can also be seen that the compost from the three experiments is very similar, except for dry matter content and organic nitrogen. In table 3 the calculated masses from the measured fractions in the manure and in the compost are given. It can be seen that there is a difference in the percentage of organic matter decrease during the process. In run A organic matter degradation was 40%, in run B 31% and in run C 25%. Because of the difference in initial organic matter content and composting time (table 2) it is difficult to compare these values. However, the organic matter content of the produced composts are identical (table 2).

Table 3 Mass of compost material components before and after composting

Run		A in	B in	C in	A[a] out	B out	C out
Mass	[kg]	42.00	42.00	22.10	17.68	20.70	11.60
Ash	[kg]	3.00	3.57	1.96	2.98	3.62	1.81
OM	[kg]	12.96	12.60	6.53	7.81	8.70	4.86
Water	[kg]	26.04	25.83	13.61	6.75	8.38	4.93
Total Kjeldahl Nitrogen	[kg_N]	0.51	0.51	0.27	0.37	0.35	0.19
Ammonium –Nitrogen	[kg_N]	0.23	0.23	0.12	0.10	0.11	0.06
Organic-Nitrogen	[kg_N]	0.29	0.28	0.15	0.27	0.24	0.12

[a] Values corrected for samples taken during composting.

The amount of organic nitrogen remains almost constant as can be seen in table 3. There is only a relatively small reduction that increases as the oxygen level drops. The relative increase (table 2) is caused by the decrease in OM. The organic nitrogen content in the end product of run A is 25 g kg_{DM}^{-1}; this is much higher than the 20 and 18 g kg_{DM}^{-1} in the end products of runs B and C, respectively. This is the result of both a higher decrease in DM, and lower decrease in organic nitrogen with increasing oxygen concentration.

Mass Balance

The mass balances of the runs are presented in table 4. The recovery is quite good. The mass that could not be accounted for is only 3% of either the ingoing material or of the total inflow ($\int Q_{in} dt$). The difference in the mass balance is probably caused by water lost via the off-gas. The air used for Q_{in} is dry, and the acid trap does not completely dry the off-gas. The inbalance found correspond with the amount of water needed to saturate the gas flow Q_{in} at 25°C. Because the off-gas does not pass through the cooler and therefore leaves the acid trap at lab temperature, this is very well possible.

In table 2 it can be seen that the dry matter content of the compost produced during run A is highest at 62%, run B compost has 60% and run C compost 58% DM. This can be linked to the greater oxygen uptake in run A (Table 4). In our experimental setup relatively little drying occurs that is due to convectional physical drying. The recirculated air has approximately 100% moisture content, so that the air takes up water only when heated. This means that all the energy required for drying must be provided by degrading the organics.

Table 4 Mass balance of the composting runs

Run		A in	B in	C in	A out	B out	C out
Reactor material in/out	[kg]	42.0	42.0	22.1	14.0	20.7	11.6
Water added as rewetting	[kg]	3.8					
Oxygen uptake	[kg]	7.2	5.7	3.0			
CO_2 emitted	[kg]				9.1	7.0	3.6
Condensate formed	[kg]				17.9	14.4	8.5
Acid trap mass increase	[kg]				6.6	4.5	1.1
Samples taken	[kg]				3.8		
Total	[kg]	53.0	47.7	25.1	51.4	46.6	24.8
Imbalance as mass percentage of gas flow Q_{in}					2.7	2.7	1.6

From the mass balances presented in table 4 the stochiometric formula of the degraded organic matter was calculated. The result and the calculation method are presented in table 5. The first three rows are obtained from the on line measurements and the analysis of the material in and out of the reactor. From the produced carbon dioxide the degraded amount of carbon is calculated. From the produced water the amount of hydrogen degraded is calculated. The difference between the degraded organic matter and the degraded carbon and hydrogen is the oxygen content of the degraded organic matter.

The overall elemental composition of the degraded organics of runs A and B are similar, but in run C it contains only two thirds of the oxygen content. A difference in oxygen demand per kg organic matter lost was found (Table 5). Runs A and B required 1.5 kg_{O_2} kg_{OM}^{-1}, in run C this was 1.8 kg_{O_2} kg_{OM}^{-1}. This difference indicates why less organics were lost in run C despite a similar cumulative oxygen uptake to run A: anaerobic biological activity during storage can reduce the organic matter by consuming the more oxidised compounds. The VFA degradation during storage shows that there was biological activity. Therefore, the organic matter at the start of run C would have been more stable and reduced than the organic matter at the start of run A, which is consistent with the higher oxygen demand.

The difference in the change in organic matter content between runs A and C may partly be explained by the difference in composting time, as run A lasted 4 weeks, and run C only 3. However, run A did not lose the difference, 30% of the organic matter degraded during run A, during the fourth week of composting. The cumulative oxygen uptake during this time was only 8% of the total. Therefore, the difference in composting time is considered to have little influence on the result.

Because of the difference in the initial organic matter content and in the composition of the organic matter lost, the oxygen uptake is considered the more reliable measure for degradation.

Table 5. Calculation of the elemental composition of degraded organic matter

	symbol	formula		Run A	Run B	Run C
Organic matter lost	ΔOM	ΔOM	[kg]	4.92	3.90	1.67
Oxygen uptake	COU	COU_{OM} *ΔOM	[kg]	7.14	5.72	2.97
Carbon lost	ΔC	ΔC_{OM} * ΔOM	[kg]	2.48	1.92	0.97
Carbon dioxide produced		ΔC *44/12	[kg]	9.11	7.03	3.56
Water produced	ΔH_2O	ΔH_2O_{OM} *ΔOM	[kg]	2.96	2.58	1.08
Hydrogen lost	ΔH	ΔH_2O*2/18	[kg]	0.33	0.29	0.12
Oxygen loss from the OM	ΔO_2	ΔOM - ΔC - ΔH	[kg]	2.11	1.69	0.58
Stochiometric formula	C	1		C	C	C
	H	ΔH *12/ΔC		$H_{1.6}$	$H_{1.8}$	$H_{1.5}$
	O	ΔO_2*12/ΔC/16		$O_{0.64}$	$O_{0.66}$	$O_{0.45}$
Respiration quotient		[mol_{CO_2} $mol_{O_2}^{-1}$]		0.93	0.89	0.87
%N of OM lost		100*ΔN / ΔOM	[%]	0.17	0.93	1.59

Ammonia Emission

The emitted nitrogen balance of the three runs is given in table 6. It is assumed that the Kjeldahl nitrogen equals the total nitrogen content of the manure and compost. However, in all three runs more ammonia nitrogen was retrieved in the condensate and the acid trap than was lost as Kjeldahl nitrogen from the composting material. It seems unlikely that this is the result of nitrogen fixation. Probably it is a result of the N-Kjeldahl measurement missing certain forms of organic nitrogen. It is assumed that the retrieved ammonia from the condensate and the acid trap is the more reliable measurement of the emitted ammonia.

Table 6. Mass of nitrogen components lost and ammonia retrieved

		Run A	Run B	Run C
Ammonia nitrogen in the condensate	[g]	106	131	95
Ammonia nitrogen in the acid trap	[g]	106	87	29
Kjeldahl nitrogen lost during composting	[g]	143	159	83

In figure 5 the measured ammonia emission retrieved from the condensate and the acid trap is given. In accordance with the prediction by Veeken (1999), more ammonia is dissolved in the condensate at lower oxygen concentrations. In run C only 23% of the emitted ammonia is found in the acid trap. In a composting facility this would be the ammonia emitted with the off-gas. In run B 40% would be emitted, compared to 47% in run A and 100% in conventional systems without a cooler in the recirculation.

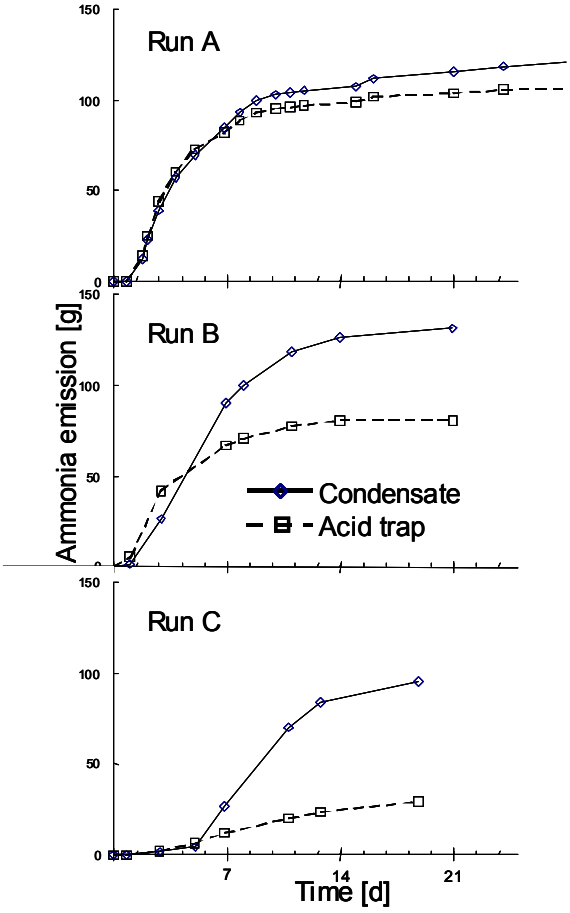

Figure 5 Total amounts of ammonia-N in acid trap (N_a) and condensate (N_c)

There is no increase in the ratio of ammonia in the acid trap to ammonia in the condensate toward the end of the runs. In this period the activity drops to the point that the minimal required flow for Q_{in} causes the oxygen concentration in the off

gas to rise. By then the bulk of ammonia has been emitted and the rise in oxygen concentration does not effect ammonia emissions.

2.4 Conclusion

As has been shown, composting can take place at low oxygen concentrations. An initial concentration of 10% is needed for start-up, but after temperature has reached 58°C, the process can maintain itself at lower oxygen concentrations.

Our data support the theory that at lower oxygen levels the activity drops. However, for a composting period of several weeks this has no effect on compost composition. This was shown by comparing the cumulative oxygen uptake. In these experiments, the degredation of organic matter was not a good indicator of bed activity. This is due to the difference in times of composting runs and differences in the composition of starting materials, especially the VFA content.

As was predicted, the gaseous ammonia emission drops when composting at low oxygen concentrations. When the oxygen concentration was 1% (run C) only 23% of the gasseous ammonia produced was emitted via the off-gas.

For the system to be applicable, a use for the condensate produced must be found. In this study the condensate, together with the separated urine, was intended as a nitrogen fertiliser.

The drop in gaseous emissions is not due to retention in the compost, but due to a higher ammonia concentration in the condensate.

The excess airflow through the system, causing the rise in oxygen concentration in the latter part of the process when the activity has dropped, does not adversely affect ammonia emissions. The compost retains the ammonia not released by then.

A step control provides sufficient control of the oxygen level in the system.

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3

The effect of bed structure on composting start-up

3.1 Introduction

Composting is a method to improve the quality of pig manure. The improvement in quality is characterised by: improved stability, better handling properties, lower transport cost due to mass reduction and lower levels of weed seeds and pathogens. In chapter 2 a new tunnel composting system operating at low oxygen concentration in the process gas was described and tested on lab scale. This new system significantly lowered ammonia emissions and off gas flow. In separate trials the performance of this system has been tested on pilot scale.

Like any state of the art composting reactor, the pilot scale system is equipped with a temperature control to prevent overheating and avert the resulting decrease in microbial activity. A typical control will tend to keep the temperature in an optimal range of 50-60°C. However, at the start of the process, the composting bed will have an ambient temperature, and the bed needs some time to reach the desired optimal temperature range. The period of temperature rise is called the start-up period.

Within the context of the Hercules project, separated pig manure solids mixed with wheat straw was used as feedstock. Contrary to earlier experiments on lab-scale described in chapter 2, the pilot scale experiments showed long start-up periods, ranging from half a day to more then ten days. Some start-up periods are so long that the practicability of the whole process is put at risk. It is therefore necessary to identify the limiting factor during start up and develop process management strategies that minimise the start-up period.

The main factors influencing the composting rate are temperature (T), organic matter (OM), dry matter (DM) and moisture (1-DM), oxygen gas pressure (P_{O_2}), and Free Air Space (FAS). During the start up period temperatures are by definition not inhibiting. During the pilot scale trials the gas phase oxygen content was automatically kept at 10% (v v^{-1}) by the control system during start-up periods. This was found to be sufficient during the lab scale experiments. The pig manure solids used in the pilot scale trials had a very high moisture content (DM = 0.19-0.26) and a high organic matter content (OM = 0.8). Given this composition and reactor control, temperature, organic matter, moisture and gas phase oxygen content can be ruled out as factors explaining the difference in start up time. Leaving the FAS as the factor most likely to explain the differences in start-up period.

In any non-mixed composting set-up, the structure of the compost bed is a critical factor. If the FAS is too low, the aerobic microbial activity will be insufficient to achieve sufficient organic matter degradation within a reasonable time span. On the other hand, too porous a bed will cost valuable reactor space. When a wet

waste, like pig manure solids, has to be composted, optimisation from an engineering point of view means something different to maximising bed activity. The objective is to compost the material in a reasonable time span, mixing in as little amendments as possible within the smallest possible volume. The start up is the critical phase, as FAS increases during the process as the bed dries.

To analyse the data gathered from the pilot scale trials the relation between FAS and the composting rate needs to be known. As compost beds are dependent on the solid material for their physical stability, there is an upper limit to the porosity that can be obtained. This porosity then has to hold water and provide passage to air. Both water and the oxygen provided by the air are essential to the micro-organisms that perform the composting process. Bed activity will be limited by a shortage of either water or oxygen in the vicinity of the micro-organisms, as neither is likely to be present to excess. Optimisation has to consider the availability of both water and oxygen.

Although water can provide extra stability by cohesion of solid particles through the capillary force, this cannot be effectively used in the composting process. The rise in temperature lowers the surface tension of the water, and with that, the capillary force. This can normally be seen by the formation of leachate at higher temperatures. The capillary force is no longer sufficient to hold the moisture in the largest pores, and a flow of moisture and small suspended solids is formed. A bed depending on capillary force for physical stability would collapse.

The objective of this chapter is to assess the usefulness of existing composting models with FAS as the key variable in explaining the delay in start up during the process and to discuss measures to improve the performance of the process. The start up data of the runs performed with the pilot scale reactor so far are used to assess and compare the predictive qualities of models.

3.2 Theory

The problem of bed construction has been dealt with in literature (Jeris and Regan 1973). Publications generally formulate guidelines for the optimal values of moisture content and FAS, i.e. those values that yield the highest activity (oxygen uptake) per kg of organic matter. The focus of this research however is not to obtain maximum activity in the bed, but to construct a bed that will generate enough activity to finish the composting process in three weeks. For this the relation between activity and FAS has to be known.

The inductive model

There are two models known in literature that describe the effect of FAS on composting activity. The first model, developed by Haug (1993), is an empirical or

inductive model. This means it is a function fitted to experimental results without an underlying theory to explain the function.

The starting point for this model is the experimental finding by Jeris and Regan (1973) that beds packed with the same material, but with different moisture contents, have a relatively constant solids packing, v_s, which is defined as the fraction of bed volume filled by the solid material. Under these experimental conditions the pores in the bed can accommodate moisture or gas, but these cannot be optimised separately, as the fractional solids volume is fixed. Any increase in water volume automatically decreases FAS, and vice versa.

When different materials were studied, it was found that the optimum level for moisture was variable, but all optimum FAS values were found at around 33%. The optimum conditions are defined as those conditions where the OUR of the feed material was at its maximum. This led Haug to the development of a model, which considers the effect of FAS to be negligible when FAS >30% while for values of FAS lower than 30% a strong activity limitation is proposed. This limitation is expressed as a restriction factor F, defined as:

$$OUR(v_g) = F(v_g).OUR_{max,c} \qquad 1$$

Wherein

$$F(v_g) = \frac{1}{e^{(-23.675*v_g+3.4945)}+1} \qquad 2$$

$$v_g = \frac{FAS}{100} \qquad 3$$

v_g	Relative volume of gas	[-]
FAS	Free air space.	[%]
F	Restriction factor of the inductive model.	[-]
$OUR_{max,c}$	Maximum Oxygen Uptake Rate (OUR) of the feed material, for a given v_s.	[mmol kg_{VS}^{-1} h^{-1}]

The parameter $OUR_{max,c}$, expresses that all process factors other than FAS are considered to remain constant, or vary such that the oxygen uptake rate is not influenced. $F(v_g)$ is a fitted function to the data published by Jeris and Regan (1973). To our knowledge, this is still the only data available concerning the limitation caused by low FAS.

The mechanistic model

Recently, Hamelers and Richard (Hamelers and Richard 2001) presented a mechanistic model that describes the relation between gas, liquid, and solid volumes and microbial activity. Because the sum of fractional volumes is by definition 1, the input of the model is equivalent to the input of the model by Haug for any given value of v_S: Any increase in water volume automatically decreases FAS, and vice versa.

The mechanistic activity model is based on a theory describing the processes during composting at particle level (Hamelers 1993). The particles are aggregates, formed by solids connected by surrounding water. The aggregate boundary is formed by gas filled pores. If the material that is composted is rich in substrate, i.e. easily degradable, oxygen consuming micro-organisms will grow fastest on the aggregate surface where oxygen is constantly supplied from the gas phase. The surface of the aggregate becomes overgrown with a biofilm that consumes oxygen so quickly that little can diffuse into the aggregate.

The oxygen consumption of a bed is then dependent on the surface area of the aggregates. The consumption is bound to a maximum as oxygen has to dissolve before it is available to the biomass. The process changes once substrate is no longer plentiful, but during start up the surface area of the aggregates dictates the activity of the bed.

This particle model has been extended to take into account the aggregate size distribution. The starting point is a pile of dry solid particles with a fractional volume v_s. Either water or gas fills the pores between the solid particles, with water filling the smaller pores first. Water logged parts (without gas filled pores) form aggregates that are defined as waste particles. On theoretical grounds, the waste particle size distribution can be described by the gamma-distribution (Hamelers 2001). During start up it can then be assumed that the oxygen uptake rate of the compost bed is described by:

$$OUR(t) = \sqrt{\frac{1}{1 + e^{-\mu_{eff}(t-\Omega)}}}\,\frac{OUR_{m,\lambda}}{\gamma_c - 1} \qquad 4$$

$OUR_{m,\lambda}$	Maximum OUR of the bed, scaled to VS content	[mmol kg_{VS}^{-1} h^{-1}]
γ_c	Shape parameter of the gamma distribution	[-]
μ_{eff}	Effective biomass growth rate	[h^{-1}]
Ω	Lag time for biomass growth	[h]
t	Time	[h]

As can be seen in equation 4, the mechanistic model gives not only an expected OUR, but also the time course of the expected OUR. For our purpose the formula can be simplified. The term under the square root can be omitted, as this is the biomass growth term that calculates the time needed to obtain maximum oxygen consumption at the interface. Start-up times are relatively long, and pig manure solids very active, so the biofilm will be fully developed for most of the start up time.

The particle bed model also contains a number of parameters that specify the composting kinetics for a certain waste under certain conditions that are not visible in equation 4. A complete description can be found in Hamelers (2001). In equation 4 these parameters are hidden in $OUR_{m,\lambda}$.

By analysing the effect of moisture on the parameters underlying the parameter $OUR_{m,\lambda}$, Hamelers and Richard (2001) derived a relation for compost bed physical structure and activity. They concluded that during start-up, the main waste parameter describing process rate is the OUR_{max}, the maximal respiration of the material under ideal conditions. These are conditions where enough water and air are present. An OUR smaller than OUR_{max} is due to limitations caused by the physical structure of the bed. They constructed equations 5 through 7 to calculate the effect of these physical conditions.

$$OUR(\theta_w, v_s) = G(\theta_w, v_s).OUR_{max,c} \quad (5)$$

$$G(\theta_w) = \frac{f(\theta_w)}{f(\theta_w)_{max}} \quad (6)$$

$$f(\theta_w) = \left(\frac{1 - v_s.(1+\theta_w)}{\theta_w.(1-v_s)}\right)^n . \left(\frac{\theta_w}{1+\theta_w}\right)^m \quad (7)$$

G	Restriction factor of the mechanistic model	[-]
θ_w	Particle water volume; Volume of water per volume of solids ($v_w\ v_s^{-1}$)	[-]
v_s	Relative volume of solids.	[-]
v_w	Relative volume of water.	[-]
n	Parameter of the mechanistic model	[-]
m	Parameter of the mechanistic model	[-]

For the sake of comparison, equation 5 is written in a similar way as the model of Haug. In this relation a restriction factor G is calculated on the basis of particle water volume and the fractional volume of solids. These are the parameters used

by Hamelers and Richard (2001). Together they completely define the volume distribution between the three phases, solid, liquid and gas. The ability of the mechanistic model to calculate the dependency of bed activity on solid, water and gas volumes makes the model appropriate to investigate bed effects on start up.

The mechanistic FAS model implicitly assumes a constant v_s. If v_s changes, the γ_c describing the solid particle distribution will also change. The γ_c is dependent on the spatial distribution of the solids, which is expected to be for a large part defined by the type of material, and for a lesser part by the packing density. Changes in γ_c can be expected to be small over a range of solid packing densities. The model is therefore treated as applicable for changes in any of the relative volumes.

By using the volume fractions of the phases, equation 7 can be rewritten so that the effect of changes in the volumetric fractions of the phases on compost bed activity is clearer. This is done in equation 8.

$$f(\theta_w) = \left(\frac{v_g}{1-v_g}\right)^n \left(\frac{v_s}{1-v_s}\right)^n \left(\frac{v_w}{v_s+v_w}\right)^{m-n} \qquad 8$$

In equation 8, the last factor is a property of the mixture used to make the bed. The other two factors, depending on v_g and v_s respectively, give the influence of the packing density. Equations 8 is only applicable over a range of fractional solids volumes. It can be derived from the equation that the highest activity is predicted for $v_s = 0$, which is physically impossible to achieve. It is however assumed that over the range of fractional solids volume that can be achieved with a certain material, the n and m are constant.

Before applying the mechanistic model, it should be validated, i.e. checked against data. The mechanistic model was only validated in a qualitative way with respect to the effect of moisture content on activity. The probable range of values for the model parameters n (0.2-1) and m (1.25-3.25) given by Hamelers and Richard (2001) is based on literature values for the basic processes. The model has not yet been tested or validated with respect to the effect of FAS on activity. As the inductive model by Haug is a summation of past research identifying practical values for n and m from this model seems a plausible first attempt.

It is quite easy to fit equation 5 to equation 2 for different solid volume fractions, using equation 8, to determine n and m. However, this only proves that the functions have similar shapes. Therefore a different approach was used.

Comparison of models

Although Haug was perfectly aware of the dependence between FAS and DM, the inductive model considers FAS and DM independently. The mechanistic model treats the solids volume fraction and the particle water volume as independent variables. As a result of this, the mechanistic model predicts a FAS optimum, that is dependent on the solids volumetric fraction whereas the inductive model has an optimum independent of the solids volumetric fraction. Data on the effect of FAS on compost bed activity are relatively scarce, and there is insufficient empirical basis to decide if the optimum value of FAS depends on the volume of solids.

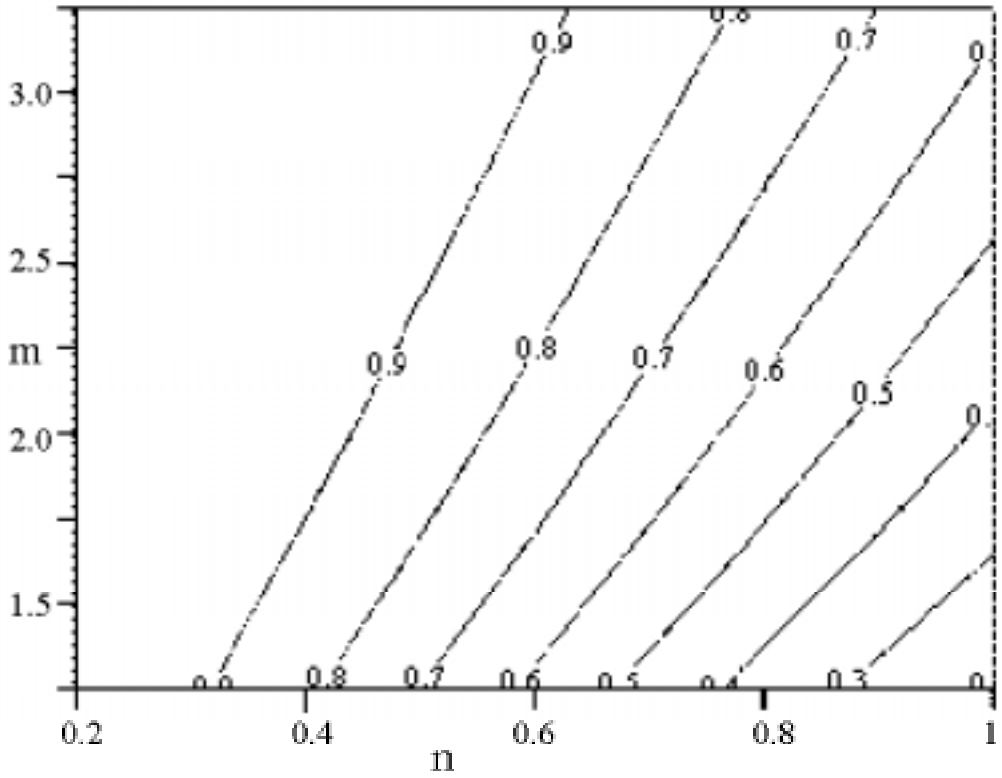

Figure 1 Contour plot of the calculated G at a relative solid volume fraction of 0.2 and a FAS of 0.3 for different values of n (X-axis) and m (Y-axis)

As the inductive model of Haug is based on the observation of the existence of a limited FAS range that can sustain high activities in the optimal moisture range, it will be investigated whether there are reasonable values for the mechanistic models parameters n and m that also predict this FAS range (0.2-0.4). Therefore, for each combination n, m within the earlier mentioned range given by Hamelers and Richard (2001), the G at a given v_s of 0.2 and v_g of 0.3 was determined. Values have

been calculated for 900 combinations equally spaced in the n, m range. The results are shown in figure 1 and show G as a function of n and m.

In figure 1 it can be seen that there are values of n and m for which indeed an optimum FAS in the range 0.2-0.4 is found. In the graph it is the section to the left of the line indicating a G of 0.9. Analysing similar graphs for other values of v_s, similar results were found. In general, lowering v_s will show high values for G at lower values for n. This shows that realistic parameter combinations exist where the mechanistic model predicts similar optimal FAS values to the inductive model.

3.3 Materials and method

Pilot scale composting experiments

The composting was done according to the protocol described in chapter 2. Bed temperatures were raised at relatively high oxygen concentrations. Thereafter the composting took place at different oxygen levels.

Description of the pilot scale composting reactor

The composting vessel is an insulated cupboard with interior dimensions of 1.0* 1.0* 1.8 meter. A scheme is given in figure 2. The bottom of the reactor has two openings. One, to remove percolate, is closed by a valve. The second, for air supply, is covered with a fine grid to prevent it from clogging. At the top of the reactor there are two openings in the back to let out used air. One is for waste gas that leaves the system via a ventilation pipe, the other, for recirculation, is led over a cooling unit and back to the bottom of the composting vessel. Recirculated and fresh air are blown into the vessel by the same fan. Two connected valves in the supply pipes, which are set to have a combined opening of 100%, control the ratio of the two flows. The cooling unit is a heat transfer unit with cooling elements perpendicular to the gas flow. Tap water is used as a heat sink, and the flow of water is controlled to regulate the recirculation gas temperature.

Inside the reactor, eight thermometers are used to measure temperature and humidity (using the wet bulb method) during the composting process. Four temperature probes are long metal poles that can be stuck into the bed through holes in the side of the cupboard. The other four are used as two pairs, one at the top and the other at the bottom of the reactor. Each pair gives both temperature and an indication to the relative humidity at the top and bottom of the reactor. Two oxygen sensors are attached to the side of the unit. Air is respectively withdrawn from the top or the bottom of the reactor, cooled in a water lock and measured. A control unit at the side of the cupboard electronically monitors all temperatures. This unit controls the two air valves, fan speed, and the water flow to the recirculation-cooling unit.

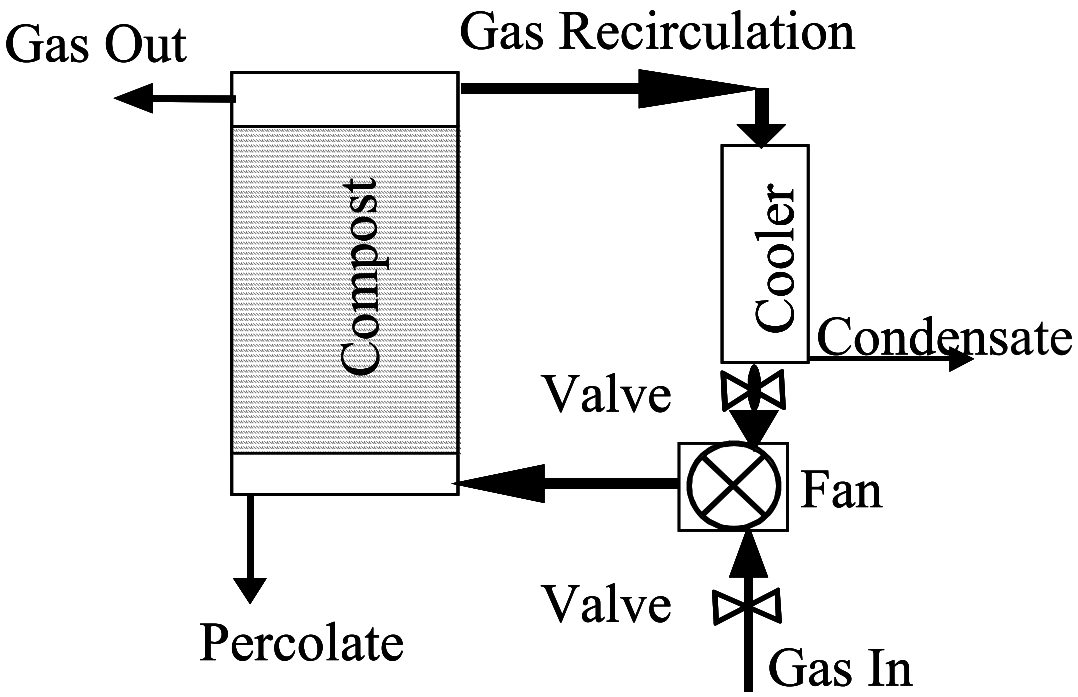

Figure 2 Flow scheme of the pilot scale compost reactor.

Description of the pilot scale composting experiments

The composition of the load material of the five runs is given in table 1. The composting material of all runs consisted of a mixture of separated pig manure and wheat straw as described in chapter 2. The manure was separated from the urine on a convex conveyer belt (Kroodsma et al. 1998) and collected over a few days. Thereafter it was kept in cold storage (4°C) until used. The straw was cut into twenty cm lengths.

Table 1 Composition of load material in the composting runs.

Run		I	II	III	IV	V
Manure	[kg]	1004.8	1361.7	1361.4	1153.7	1395.0
Straw	[kg]	53.4	28.0	47.2	30.0	28.8
Dry Matter (DM)	[kg kg^{-1}]	0.24	0.29	0.30	0.28	0.24
Organic Matter (OM)	[kg kg^{-1}]	0.84	0.84	0.84	0.84	0.82

The feed was fed into the reactor with help of a conveyor belt. Two rotating axles mixed the manure and the straw on the conveyer belt before it was surface fed into the reactor. The axles were set with transverse pins or with blades so as to have more grip on the material. It was found that the mixing action of the axles caused the manure to be divided in small particles and the straw to be orientated randomly. The contact between manure and straw however was very poor.

During start up, the controls were set to raise bed temperature. Therefore, no cooling water was used, fan speed was increased until the mean temperature rise of the bed was 1.5ºC h^{-1} and oxygen at the top of the reactor was kept over 10%(v v^{-1}). Start-up regime was used until the mean compost temperature reached 55°C. None of the runs reached a temperature rise of 1.5ºC h^{-1}.

After the compost had reached 55ºC different, control regimes were used. The end product therefore shows variations that may not be due to the differing loads. In general, the material composted well. During the individual runs, which lasted 2 to 4 weeks, approximately 25% of the organic material was degraded and dry matter content increased from 25% to 60%

Data treatment

The installation was not equipped with an accurate flow measurement device, so to determine the OUR a heat balance was set up over the composting bed. From literature it is known that the heat (enthalpy) generated (released) by aerobic biological systems, H_{O_2}, is 460 kJ $mol_{O_2}^{-1}$, regardless of substrate (Heijnen 1999). This means that the heat generated by the bed can be used to estimate the OUR. The generated heat is determined from a heat balance with three elements:

1 The fresh air flow is heated and saturated with water vapour during the passage through the compost reactor system.

The heat extracted from the compost bed in this way can be calculated according to:

$$J_Q = Q_{air} * \left(H_w * f(T) + \Delta T * C_{p,air}\right) \qquad 9$$

J_Q	Flux of heat removed by the aeration	[W]
Q_{air}	Flow of fresh air entering the reactor	[kg s^{-1}]
H_w	Enthalpy needed to evaporate water	[J kg^{-1}]
f(T)	Function that calculates the change in H_w with temperature, as well as the (change in) water saturation concentration of the gas	[kg_{H_2O} kg_{air}]
ΔT	Temperature difference between the inside and the surroundings of the compost reactor	[K]
$C_{p,air}$	Enthalpy needed to heat a kilogram of air one degree Kelvin	[J kg^{-1} K^{-1}]

From an elemental balance it follows that Q_{air} is can be calculated from the OUR and the off gas oxygen content. Equation 9 can then be written as:

$$J_Q = \frac{M_{air}}{1000} * \frac{\alpha * OUR}{0.21 - \{O_2\}_{out}} * \frac{M_{OM}}{3600} * \left(H_{w,l\rightarrow g} * f(T) + \Delta T * C_{p,air}\right) \qquad 10$$

M_{OM}	Initial mass of organic matter in the compost bed	[kg]
M_{air}	Average molar mass of ambient air	[g]
$\{O_2\}_{out}$	Molar oxygen fraction in the dry off gas	[-]
α	Respiration Quotient	[mol_{CO_2} $mol_{O_2}^{-1}$]

2 The heat loss through conduction via the wall and piping.

To calculate this loss the following formula can be used:

$$J_{wall} = \Delta T * R_w * A_r \qquad 11$$

J_{wall}	Enthalpy flux through the compost reactor wall.	[W]
R_w	Heat transport coefficient of the compost reactor wall.	[W K^{-1} m^{-2}]
A_r	Surface area of the compost reactor.	[m^2]

According to the manufacturer of this reactor R_w = 0.265 W m^{-2} K^{-1} and the surface approximately 15 m^2

3 The heat required to warm the compost bed.

To calculate the heat retained as temperature increase in the compost bed the following formula can be used:

$$\frac{dH}{dt} = \frac{d(T_C)}{dt} * C_{p,tot} * M_{tot} \qquad 12$$

H	Enthalpy of the compost bed.	[J]
t	Time variable	[s]
T_C	Compost temperature	[°C]
$C_{p,tot}$	Heat capacity of the initial feed material	[J K^{-1} kg^{-1}]

To calculate this the heat capacity of the bed was estimated by assuming a liquid fraction of the compost bed equal to the water content and the ash with a heat capacity of 3.9 [= C_p of seawater and milk (NVON 1977)] and a solid fraction with a heat capacity of 1.8 [= C_p of flour and wood (Janssen and Warmoeskerken 1997)] kJ kg^{-1} K^{-1}. The calculation method is given in equation 13. The given heat capacities multiplied with the respective weights give the heat capacity of the compost beds.

$$C_{p,tot} = \frac{(M_w + M_{Ash}) * 3.9 + M_{OM} * 1.8}{M_{tot}} \quad 13$$

M_w	Initial mass of water in the compost bed	[kg]
M_{Ash}	Initial mass of non-volatile solids in the compost bed	[kg]
M_{tot}	Initial mass of water and solids in the compost bed	[kg]

From the equations 10 through 13 an estimate for the OUR can be calculated as follows:

First the enthalpy provided by the oxygen consumption is calculated according to Heijnen (1999):

$$R_H = \frac{M_{OM} * H_{O_2}}{3600} * OUR \quad 14$$

R_H	Enthalpy production rate due to compost reactions	[W]
H_{O_2}	Enthalpy released per mole of oxygen when reacting with organic matter.	[J mol^{-1}]

Then the enthalpy needed for the temperature rise is calculated:

$$\frac{dH}{dt} = R_H - J_Q - J_{wall} \quad 15$$

It is assumed that the terms in equation 15 give a complete enthalpy balance of the compost bed, and that therefore:

$$M_{OM} * OUR = \frac{3600 * \left(\frac{dH}{dt} + J_{wall}\right)}{H_{O_2} - \frac{M_{air}}{1000} * \frac{\left(H_w * f(T) + \Delta T * C_{p,air}\right)}{0.21 - \{O_2\}_{out}}} \quad 16$$

Equation 16 is a function of the compost bed temperature and ambient temperature. All other parameters are constants. The ambient temperature was not recorded permanently, but there is some data from when the reactor was empty. The temperatures recorded are fairly constant, so it was assumed that ambient temperatures were constant at 17ºC. The reactor was located inside an insulated shed sharing a non insulated wall and the roof with the pig stable where the temperature was controlled. Therefore the assumption is plausible.

To calculate the volume of the three phase fractions in the bed the following densities were assumed: water 1, organic matter 1.5, and ash 2.6 kg L^{-1} (Ginkel

Van et al. 1999). These volumes were then subtracted from the total bed volume, assumed constant for all runs, of 1450 litre. Because the door hindered a complete use of reactor space, this is the normal volume for a full reactor. The amount of heat used for temperature increase is estimated from the temperature rise over a period of time centred around the moment where the bed reaches a certain average temperature. The estimation was done by regressing a line through 18 temperature measurements, covering 4.5 hours, and using the slope.

Parameter estimation

The OUR values calculated from the temperature data are used to compare the compost activity predictions of the FAS activity models. The inductive and the mechanistic compost activity models both have a similar structure for the prediction of the OUR, namely as the product of a restriction factor F or G and the $OUR_{max,c}$. This latter parameter needs to be estimated for each temperature, as $OUR_{max,c}$ is a function of temperature. This was done as follows:

A plot of the measured OUR versus G or F (G/F) should yield a straight line through the origin. The value of G/F was calculated for all beds, and for each temperature a linear regression with the OUR data was performed. The value of the regression line at G/F=1, yields an estimate for the $OUR_{max,c}$. The linearity of the dataset, expressed as R^2, with the model restriction factors is considered an indication for the predictive value of the model via interpolation. The value predicted at G/F=0 is a measure for the reliability of extrapolating the relation found to values outside the range covered by the experiments.

Before the restriction factor G can be calculated from the data, the value of the parameters n and m has to be known. As no values for n and m are known beforehand the linear regression was used to obtain the n and m which gave the best prediction. The Residual Sum of Squared Errors of the five separate linear regressions for all measurements made at mesophilic temperatures were calculated over the whole n, m range. To correct for the difference in slope between the various temperatures, these sums were divided by the variance in measured OUR at that temperature. For each combination of n and m the so obtained values were summated, and plotted in a contour plot. The probable value of n and m was expected to coincide with the minimum sum found.

3.4 Results

In table 2 the amounts of water, OM, and ash in the beds are given. Also stated are the specific heats calculated with equation 13, and the relative volumes

Table 2 Measured and calculated values for the compost beds.

Run		I	II	III	IV	V
Ash	[kg]	40.0	65.2	65.9	53.4	59.5
Organic Matter	[kg]	213.3	336.9	355.3	282.1	279.4
Water	[kg]	804.9	987.6	987.4	848.2	1084.9
Specific heat	[kJ kg^{-1} K^{-1}]	3.48	3.39	3.37	3.40	3.49
v_w	[-]	0.56	0.68	0.68	0.58	0.75
v_s	[-]	0.11	0.17	0.18	0.14	0.14
v_g	[-]	0.34	0.15	0.14	0.27	0.11

The oxygen uptake rates calculated with equation 19 are given in table 3.

Table 3 OUR of the five runs at given temperatures.

Temperature [ºC]	Estimated OUR [$mmol_{O_2}$ h^{-1} kg_{OM}^{-1}]				
Run	I	II	III	IV	V
20	41	23	21	33	24
25	46	36	27	37	23
30	53	37	25	37	18
35	58	38	22	39	11
40	56	23	21	29	8
45	41	22	22	15	7
50	32	30	27	21	10

Figure 3 gives the sum of squared errors divided by the variance in OUR of the restriction factor G with the data from 20 to 40°C for a range of n and m. It is remarkable that the best correlation found coincides with the n and m values that predicted the same optimum value of FAS as the inductive model (figure 1). The best fit is found on the line m=6.7*n. For n=0.4 and m=2.7, the fit statistics are given in table 5.

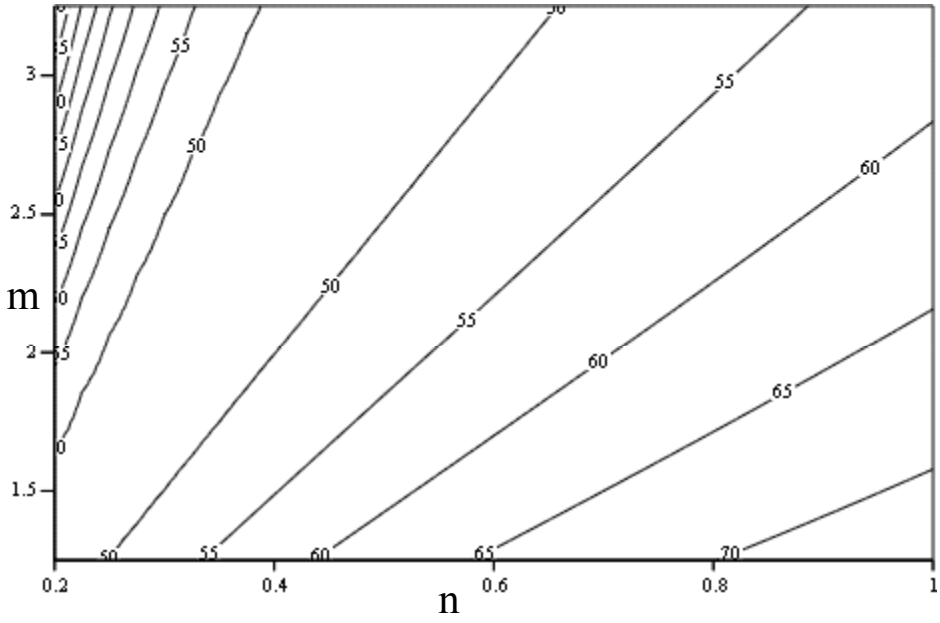

Figure 3 Contour plot of the sum of squared errors rated to variance in OUR, between measured OUR values, of all five runs over T is 20 through 40 °C, and mechanistic model predictions using different values of n (X-axis) and m (Y-axis)

The value of the intercept at G/F=0 proved to be very dependent on the assumptions made for total bed volume while calculating G. Data on bed volumes is not available (the experiments were used in retrospect) and as a result the intercepts cannot be calculated reliably from the dataset. The given values are for the assumed value of 1450 litre.

In table 4 the values of F and G are given. G was calculated for the optimal values of n and m determined. The factor G was scaled by assuming the minimal v_s to be 0.1, and therefore $f(\theta_w)_{max}$ to be 0.25. In table 5 the correlation between the restriction factor F/G and the regressed line of the form OUR=a*F/G+b are given.

Table 4 F and G values for the compost beds. Calculated with: n=0.4, m=2.7, and $f(\theta_w)_{max}$ = 0.25

Run		I	II	III	IV	V
F	[-]	0.99	0.49	0.44	0.95	0.28
G	[-]	0.87	0.63	0.61	0.78	0.56

Table 5 Correlation between OUR and the restriction factor G/F for a line a*G/F+b.

T	F	F	F	G	G	G
	R^2	one tailed F	one tailed T	R^2	one tailed F	one tailed T
[°C]	[-]	p	p	[-]	p	p
20	0.81	< 0.05	< 0.025	0.91	< 0.025	< 0.01
25	0.77	< 0.05	< 0.025	0.83	< 0.05	< 0.025
30	0.73	< 0.1	< 0.025	0.82	< 0.05	< 0.025
35	0.76	< 0.1	< 0.025	0.82	< 0.05	< 0.025
40	0.73	< 0.1	< 0.025	0.86	< 0.025	< 0.025
45	0.37	> 0.1	> 0.1	0.52	> 0.1	< 0.1
50	0.23	> 0.1	> 0.1	0.26	> 0.1	> 0.1

3.5 Discussion

The comparison of the inductive and the mechanistic model shows that for the mechanistic model there exist reasonable parameter values that predict the same behaviour as the inductive model. When the best correlation with the dataset is used, the same values for n and m are found. This is reassuring, as it indicates that the basis of the mechanistic model is sound.

It is surprising that the mechanistic model needs only two parameters to model both the effect of moisture and FAS, while the empirical model needs two to model only the FAS. This is in line with the general finding in systems science that well developed mechanistic models (i.e. those that reflect the underlying structure of reality) have less parameters than inductive models. (Ljung and Glad 1994). The reason for this is that no parameters are required to model known relations.

Validity of the models at higher temperatures

Both models do not explain the difference in OUR at thermophilic temperatures, as presented in table 3. This bad estimation of activity for high temperatures could have various causes. As the models are simplified to calculate the effect of the volumes distribution only, changing, or less than optimum conditions for any of the other process factors will give a deviation between model and measurements.

- **The first factor is the availability of substrate. As the composting process progresses the easily available substrate may be consumed, after which the OUR is limited by the hydrolysis of the remainder of the OM (Hamelers 1993; Rudrum et al. 2000). The total amount of oxygen consumed during start-up is less than 2 mol kg_{OM}^{-1} for all runs, except for run V which took eleven days to**

reach 55°C. This value is so low that no substrate limitation is expected during the whole start-up period.

- The second factor could be a lack of moisture as a result of the evaporation of water. Considering the low initial DM of the material and the amount of oxygen consumed this seems improbable.
- Thirdly, as the temperature rises, there is a transition in the bacterial population from mesophiles to thermophiles. The way the data are treated is, in the case of the deductive model, only possible if the logistic term in the model (see equation 4, the square root), is near 1. During the shift from a mesophilic to a thermophilic population, this assumption might no longer be valid.
- The last factor is the change in the FAS. As there is always evaporation of water, the volumes of liquid will decrease and the volume of gas in the bed will increase in time. On the other hand, subsidence of the bed might increase the solids volume fraction and thus reduce the FAS. In the experiments the amount of energy used for start-up, and thus evaporation, will not affect FAS noticeably. This leaves subsidence which would, generally, lower the OUR.

We observed both increases and decreases in OUR with temperature. See for example table 3 runs II and V where the development of the activity is completely reversed. Both have comparable values for v_w, v_s and v_g, resulting in similar values for G (see table 4) in the area where n and m give the minimal sum of squared errors. This coincides with their initial identical OUR. But whilst Run II can overcome initial problems and increases activity, in Run V activity slowly drops. The difference is in the DM content of the feed. In Run II the initial DM is 0.29 (Table 1), whereas in Run V has an initial DM of 0.24 which means that a lot more water has to be evaporated before a similar stability of the bed is obtained. Therefore, Run V is more vulnerable to subsidence of the compost bed. Subsidence was concluded to be the main cause for the very long start up periods.

This shows a limitation of the model. Activity can be estimated for a certain distribution of the three phases in space, but no prediction for stability of this distribution is incorporated. With respect to the amount of moisture, such information can be directly calculated from the aeration regime employed. A change in the solids volume fraction is harder to model, as changes in the physical load on the material, the strength of the material and the size of the solid particles need all to be modelled.

The reason as to why the OUR in run V is poor has a profound influence on the interpretation of the composting process. Whilst from the inductive model it is, justifiably, concluded that a compost bed like that of run V will not show much

activity, from the mechanistic model the interpretation would be that such a bed should only be made from wet substrates with a high mechanical strength. If the loss in FAS does occur, then the inductive model predicted the low OUR due to this loss of stability accurately. As bed stability is more a function of the material used than of the packing density, this is not something that can be relied on when composting different materials.

Starting at a high v_s would be a much more efficient use of reactor space than starting at an optimal FAS. During composting the substrate dries, allowing the activity to go up. Therefore, it makes sense to strive for the minimal initial activity that will yield the desired compost. From equations 10 through 15 it can be derived that compost beds can heat up effectively if the OUR is more than 10 $mmol_{O_2}\ h^{-1}\ kg_{wet\ mass}$. The stability of such a bed will have to be derived from an other measurement.

3.6 Conclusions

To make the start up period shorter the FAS should be better controlled. Although, in general, the addition of straw improves the FAS more insight is needed on the factors determining the physical stability and compaction of the composting bed.

Both the inductive and the mechanistic models can adequately describe effects of FAS on composting activity. From this, it may be concluded that the FAS is the limiting factor during start up of the composting of wet manure.

Comparison of the mechanistic model by Hamelers and Richard with the inductive model by Haug, and the results of the parameter identification, indicate that the mechanistic model provides a simpler and more effective tool to predict activity in relationship to FAS. Predictions are not significantly better than those made by the inductive model, but the fact that fewer parameters are used, only one simple equation is needed and that the model provides insight into the composting process justifies ongoing research into the values for n and m and verification of predictions.

From the data it is concluded that the FAS at the packing density may not be the cause for the overly long start-up observed. Following the mechanistic model it could be that the bed collapses at higher temperature. It is therefore recommended that the stability of the bed as a function of temperature is researched.

3.7 References

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4

Modelling mass transfer in stability measurements

4.1 Introduction

Composting manure reduces the water content and improves the stability. Therefore, the end product is more easily transported, stored and handled. To obtain a good product quality, it is essential that the compost is both sufficiently dry and stable. The energy necessary to evaporate water comes from microbiological conversion of organic matter (chapter 2). To provide sufficient heat, it can be necessary to boost the energy content by adding easily biodegradable amendments. Too high an energy content causes the compost to dry out before sufficient stabilisation has been achieved. In that case water must be added. Therefore, it is necessary to control the energy content in relation to the moisture content to obtain compost with the desired moisture content and stability.

An appropriate manure-amendment mix cannot be established on knowledge of the amount of organic matter alone. The chemical composition and the biodegradability of the organic matter are also important factors to consider. The composting experiments described in chapter 3, using a mixture of pig manure solids and straw, showed big differences in the amount of water evaporated per kilogram of organic mass lost, indicating differences in the energy content and, therefore, the chemical composition of the organic matter (unpublished data). In addition, there were also large variations in the percentage of organic matter degraded. More detailed knowledge of the organic matter is necessary to construct an appropriate feed.

The aerobic growth of micro-organisms is the source of heat during composting. The micro-organisms consume oxygen and dissolved organic substrate. This dissolved substrate is replenished by the hydrolysis of polymeric organic substrates, mostly cellulose. It is generally assumed that hydrolysis is the rate limiting process in the composting process (Haug 1993). This, in turn, is assumed to mean that the oxygen uptake rate (OUR) is proportional to the rate of hydrolysis. Further, it is the standard assumption in composting respiration research that all dissolved substrate is directly transformed into active biomass, water and carbon dioxide (Hamelers 2001). The heat produced per mol oxygen consumed is approximately constant (Heijnen 1999). Oxygen consumption, heat production and biodegradation are therefore all eventually determined by the rate of hydrolysis.

Stabilisation of particulate organic matter

Hydrolysis is generally considered to be a first order process (Sanders et al. 2000). This means the rate of substrate formation is proportional to the mass of solid organic matter. However, during composting the stability of the remaining organic solids increases. Therefore, the reaction rate constant of the hydrolysis decreases during the composting process, and the overall degradation during composting is

determined by the initial value and subsequent change of the hydrolysis rate. If this relation is known, the stability of the compost can also be predicted.

Changes in hydrolysis rate are usually slow. Experimental determination of the change in hydrolysis rate in time would take as long as the composting process. There is no room or time on a farm to store manure for several weeks before composting. Therefore, in the Hercules system, the change in hydrolysis rate has to be estimated from manure properties using a model. Ideally an estimate would require only parameters that can be measured on farm and within a few days.

There are two types of models that are used to predict the degraded fraction of organic matter in time. The first uses the fraction of organic matter degraded after a (long) time, and assumes an exponential change in the degraded fraction during the degradation time (Keener et al. 1993). These are the models generally used in composting. These models require the amount of degradable organic matter as an input parameter. The measurement of this parameter will take too long, and the manure is too variable to provide an adequate estimate from previous compost batches. Therefore, another model must be used.

The second type of model is used in soil science (Janssen 1984; Yang and Janssen 2000). It assumes degradation follows a certain pattern, equal for all materials. If the remaining fraction of organic matter at one point during degradation is known, the change in degradation rate up to that time and for a long time after can be estimated. The model can be shown to be consistent with the assumption of a particle size distribution and a particle surface area related degradation rate. Janssen (1986) developed the model for organic matter amended to soil, but in a composting environment this approach should also give good results. No such models are known for composting systems.

Instead of the degraded fraction at some time during degradation, also the initial rate of degradation can be used as input for the second type of model. Information on the initial rate of organic matter hydrolysis could thus be used to predict the amount of heat that would be produced, the amount of water that would be evaporated and the stability of the compost. Considering the variability in material properties observed for pig manure, this information has to be obtained for each batch to be composted. This requires an easy, cheap and fast measurement of the initial hydrolysis rate.

This chapter and chapter 5 deal with the development of an accurate measurement of the initial hydrolysis rate by respiration measurements. In this chapter the accurate measurement of oxygen uptake rates will be discussed. Chapter 5 will deal with the relation between the oxygen uptake due to micro-biological

degradation of hydrolysis products and the hydrolysis of the solid organic matter. It is expected that an accurate measurement of the initial hydrolysis could be a valuable tool to construct better feed mixtures that will reach stability and the desired water content simultaneously.

Oxygen uptake rate measurements

Oxygen consumption is generally indicated as the oxygen uptake rate (OUR), which is an important parameter in a wide range of biological fields, composting included. It is not surprising that many different methods have been developed to measure and quantify oxygen uptake rates. For measuring the OUR of composts and feedstock two possibilities can be distinguished: 1: measuring in solid bed systems, and 2: measuring in aqueous suspensions. The advantage of measuring in aqueous suspensions is that, if an experiment is conducted well, no limitations due to lack of nutrients, accessibility of the substrate or mass transfer exist.

In the optimised process the rate of hydrolysis is the factor limiting respiration. The rate of oxygen uptake of an aqueous suspension is thought to represent the maximum rate attainable at that temperature, as the conditions, except for substrate, are optimum. The oxygen uptake rate, or respiration, may then be assumed to be a material property indicating the highest possible biodegradation rate of the material under investigation.

Many different systems to measure OUR using suspended samples have been described, and many of these are available commercially. Unfortunately, OUR measurements in liquid suspension are costly and limited in their capacity to simultaneously measure a variety of materials at various temperatures. To assess the need for amendments in constructing a compost bed the OxiTop system was chosen because it is cheap, simple and can be used to measure many samples at various temperatures simultaneously.

Mass transfer limitations to the measurement

The OxiTop system is based on the closed volume pressure change method, in which a sample is degraded within a closed system containing a known gas volume, in part consisting of oxygen. The oxygen consumed by the sample is derived from the change in pressure. Dissolved oxygen is neglected, and carbon dioxide is removed from the gas phase.

Our purpose is to measure the OUR resulting from the biodegradation of organic matter. For suspended samples, oxygen is consumed in the liquid phase. To sustain the aerobic biodegradation oxygen must be transported from the gas to the liquid, and through the liquid to the biomass. By intensive mixing the limitation for

mass transfer of oxygen within the liquid is eliminated, leaving the gas to liquid transfer as the rate limiting step.

If the OUR resulting from the biodegradation of organic matter is faster than the transfer of oxygen from the gas phase, oxygen in the liquid phase will be depleted. Eventually the OUR will decrease as a result of the limiting oxygen level in the liquid phase. The OUR measured in this situation is not related to the rate of the hydrolysis reaction. Therefore, knowledge of oxygen transfer rates is needed to assess the reliability of measurements of hydrolysis limited respiration.

With the OxiTop, the OUR is derived from the pressure change. Other gases can be formed or consumed during biodegradation and can also influence the pressure, as can changes in temperature. Carbon dioxide is captured in a caustic absorbent in contact with the gas phase. These factors affecting pressure will also be investigated for their influence on the reliability of the OUR measurement.

Goal

In this chapter, the OxiTop system is investigated as a potential device to measure the OUR of compostable materials. As compostable materials by necessity have a high degradation rate, high oxygen uptake rates have to be measured, as sample sizes cannot be reduced indefinitely. Above a threshold value, the OUR measured is expected to become limited by mass transfer effects. It is the objective of the presented work to quantify effects of these limitations and to assess the reliability of the OUR measurements with respect to mass transfer limitations in the OxiTop system. If necessary modifications to the OxiTop design will be proposed, and their influence on reliability of OUR measurements investigated.

4.2 Description of the OxiTop system

Measurements with the OxiTop are performed in bottles fitted with a screw-on cap containing carbon dioxide absorbent, a pressure sensor and a data collection unit. A more detailed presentation of the OxiTop is given in figure 1. The bottles can be moved and handled, without disturbing the measurement function, provided they are kept upright. During measurements, the bottles have to be kept at the desired -constant- temperature, preferably in an incubator. Shaking or stirring is necessary to prevent mass transfer limitations in the liquid phase. The liquid phase contains the sample, nutrients and a buffer to control pH. N-allylthiourea is added to suppress nitrification. The gas phase initially consists of ambient air.

The OxiTop head consists of two parts (figure 1). The upper part, sitting on top of the bottle, is the electronic part containing the pressure sensor and data logger. The lower part hangs down into the bottle and consists of an outer Teflon cup with an inner rubber cup, both with aeration holes. The rubber cup is filled with a

caustic substance to absorb carbon dioxide; the Teflon cup prevents any of the absorbent falling into the liquid phase and changing the pH of the sample suspension. The top of the rubber container also functions as a sealing ring between the Teflon container and the pressure sensor.

Every OxiTop is programmed for gas phase pressure data collection by entering a time period for data collection. Pressure measurements are made 360 times (evenly distributed) in the data collection period. Data consists of the difference between the pressure at the logged time and the starting pressure. Data can be extracted from the head with a hand held controller at any time during or after the run. This is done via infrared communication. From the controller the data can be uploaded to a computer where it can be analysed using any spreadsheet or data analysing program. The controller is also used for programming the data collection period.

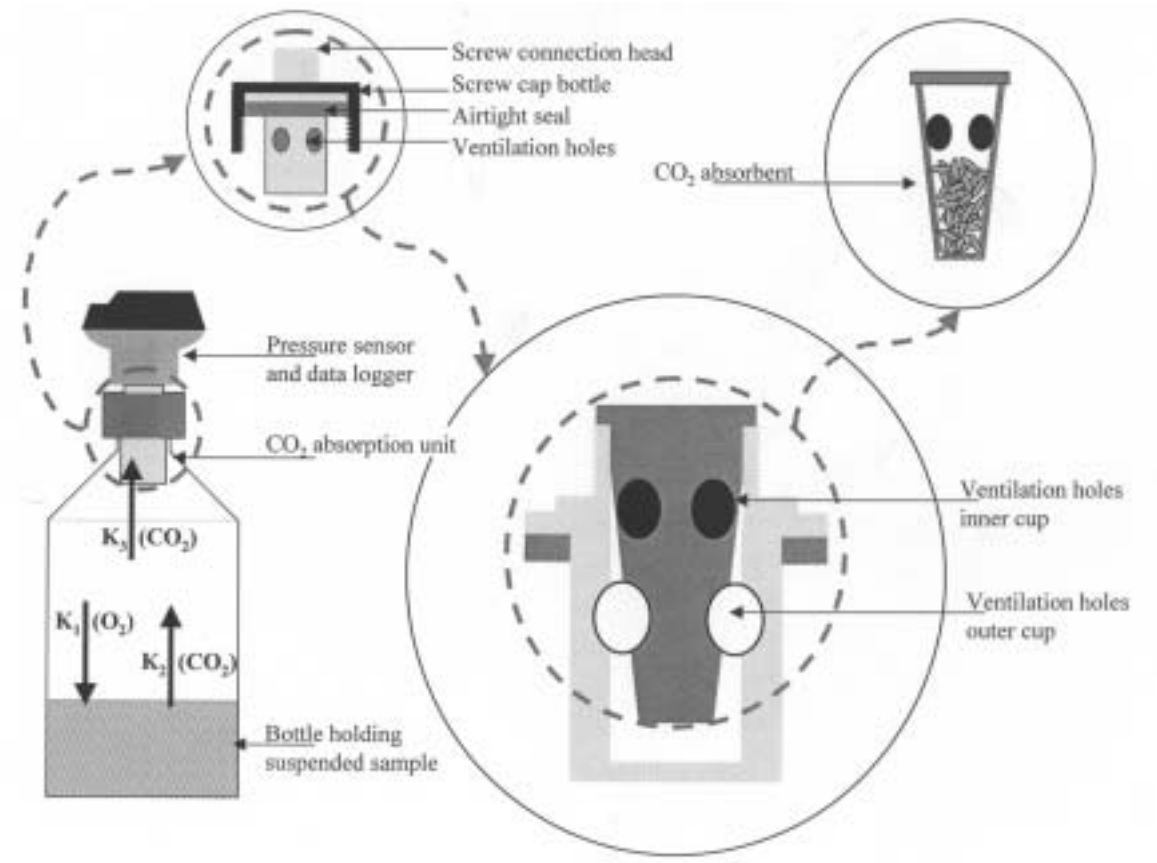

Figure 1 Schematic presentation of the OxiTop system. Not shown is the hand held controller with which the data loggers are programmed and the data are collected from the data loggers.

Principle of the OxiTop OUR measurement

The OxiTop system has a constant volume, pressure change is measured. A sample of a substrate to be investigated, suspended in water, is enclosed in a known gas

volume. Oxygen is transferred to the liquid phase and consumed by the biomass, usually naturally present in the sample The gas phase is much larger than the liquid phase, and the small quantity of dissolved oxygen is neglected. Changes in the oxygen partial pressure are therefore linearly related to oxygen consumption as expressed in equation 1. By using the universal gas constant the oxygen consumption in mmol can be calculated.

$$\frac{d[O_2]_g}{dt} * V_g = \frac{V_g}{RT} * \frac{dP_{O_2}}{dt} \qquad 1$$

$[O_2]_g$	Oxygen concentration in the gas phase	[mmol L^{-1}]
V_g	Gas phase volume	[L]
P_{O_2}	Partial oxygen pressure in the gas phase	[Pa]
T	Gas temperature	[K]
t	Time variable	[h]
R	Universal gas constant	[L Pa $mmol^{-1}$ K^{-1}]

In OxiTop measurements the pressure change has to equal the change in the partial pressure of oxygen. The total pressure change however, is the sum of changes in partial pressure, as is expressed in equation 2.

$$\frac{dP}{dt} = \frac{dP_{O_2}}{dt} + \frac{dP_{CO_2}}{dt} + \frac{dP_{N_2}}{dt} + \frac{dP_{H_2O}}{dt} + \frac{dP_{Rest}}{dt} \qquad 2$$

P	Total pressure	[Pa]
P_{CO_2}	Partial carbon dioxide pressure	[Pa]
P_{H_2O}	Partial water vapour pressure	[Pa]
P_{N_2}	Partial pressure of natural inert gasses, mainly nitrogen, but also argon, neon, helium, xenon, and krypton	[Pa]
P_{Rest}	Partial pressure of other biological gasses.	[Pa]

In general, partial pressures may change because of a change in volume or temperature of the gas phase, or concentrations in the gas phase. The volume of the bottle is constant, and the change in liquid volume and carbon dioxide absorbent volume is neglected, so gas phase volumes do not change during experiments. The temperature during measurements is kept constant as even small fluctuations can give rise to big pressure changes that are not easily corrected for. Therefore, only changes in the number of molecules can change the partial pressure of a gas.

Nitrogen gas will be present in a constant quantity, and therefore the partial pressure will be constant. Measurements are performed while the oxygen

concentration in the suspension is relatively high, preventing denitrification. For simplicity, all noble gasses are included in the term for nitrogen. No change in concentration of any of these gasses is expected.

Water vapour pressure can be assumed to be in equilibrium with the suspension. Temperature is constant, so the equilibrium water partial gas pressure is constant too. However, water may be absorbed by the carbon dioxide absorbent, influencing water vapour pressure. It is known from experience that during an experiment lasting several days hardly any water is transferred to the absorbent. Therefore, the influence of the absorbent on water partial pressures can be neglected during equilibrium.

In a lab temperature control is easily done, and therefore temperature is not regarded a variable. However, initial temperatures are normally lower than operating temperatures so that the heating time has to be quantified. During these first hours of a measurement water vapour increases due to the temperature rise, and during this phase water absorption by the carbon dioxide absorbent may influence the partial water pressure. Initial absorption may be much higher than subsequent absorption, due to saturation of the absorbent. However, experiments showed no difference between the pressure increase in experiments with and without adsorbent, and the pressure reached equilibrium values in less than two hours. Changes in water vapour pressure are therefore neglected.

Many volatile substances other than oxygen or carbon dioxide can be depleted or formed during measurements. These are captured in the term P_{Rest}. During the degradation of organic matter ammonia can be formed, and many samples contain volatile fatty acids and other volatile organic substances that can be degraded or formed. However, for most natural materials, it is safe to assume that changes in quantities of these substances are too slow and quantities in the gas phase too low to affect the measurement. Measurements are performed while oxygen levels in the suspension are high, preventing methane formation. Therefore the pressure of these substances is neglected.

Carbon dioxide is usually formed in equal molar quantities to the oxygen that is consumed. Therefore, lye is present during measurements to absorb carbon dioxide. It is vital that this carbon dioxide absorption is quick and complete. The faster the oxygen is depleted, the better the absorption needs to be. The pH of the liquid phase also affects the partial carbon dioxide pressure, because the solubility of carbon dioxide increases with pH. Initial carbon dioxide present in air can be neglected because of the low concentration, but the samples being measured can contain high levels of carbon dioxide. Both the initial carbon dioxide from the

sample and the carbon dioxide formed by respiration during an experiment have to be considered as a possible source of error.

4.3 The influence of mass transfer on OUR measurements

From the discussion of equation 2 it follows that two gasses, oxygen and carbon dioxide, could cause pressure changes the OxiTop can measure. These gasses have to cross phase boundaries before any pressure change occurs. The systems accuracy is therefore dependent on several mass transfer steps. In figure 2 these are schematically shown and indicated with the mass transfer coefficient used in the text. To quantify the relation between mass transfer coefficients and system limitations a model of the OxiTop was used. To assess the limitations to OUR measurements in an OxiTop the mass transfer rates were measured, and the model used to identify critical factors and limitations of the system.

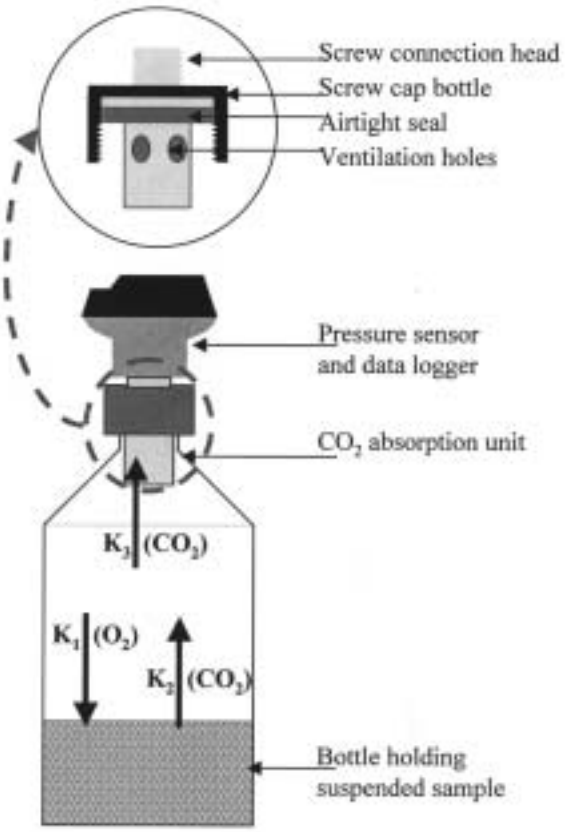

Figure 2 Schematic presentation of the OxiTop, showing the three most essential mass transfer steps, indicated by the mass transfer coefficients: oxygen, K_1 (gas to liquid); carbon dioxide, K_2 (liquid to gas), and K_3 (gas to absorbent).

Oxygen is the central substance of the measurement. The basic assumption is that the oxygen depletion, as measured by the pressure drop, is proportional to the hydrolysis rate of the sample. This means mass-transfer of oxygen gas to the liquid

(characterised by the mass transfer coefficient K_1 in figure 2) has to be fast enough to maintain a sufficient oxygen concentration in the liquid phase, so that the OUR is not limited by a shortage of oxygen.

Carbon dioxide is formed as oxygen is consumed. Dissolved carbon dioxide is not a problem. However, transfer of carbon dioxide from the liquid to the gas will occur (characterised by the mass transfer coefficient K_2 in figure 2), thus influencing the measured pressure. To minimise this effect, an absorbent is placed at the top of the bottle. Transfer from the gas phase to the absorbent (characterised by the mass transfer coefficient K_3 in figure 2) has to be fast, so that the partial pressure of carbon dioxide remains low.

Model

As described in the introduction, the objective of this research is to determine under which conditions 1) the pressure drop in the OxiTop can be considered equal to the change in oxygen partial pressure, and 2) the liquid phase oxygen concentration remains high enough not to limit activity of the micro-organisms. To that aim a model of the OUR measurement system was developed. In this model all mass transfer processes that were identified as important are combined, so that interactions may be studied.

The experiment is started (t=0) when the sample is put in the liquid, and the OxiTop is closed. It is assumed that there is no concentration gradient in either the liquid phase or the gas phase. Both are considered ideally mixed. All mass transfer processes are assumed to be first order processes. All equations are expressed in mmol, in line with units normally used in measurements.

All oxygen is brought into the system via the gas, and has to be dissolved in the liquid before it can be consumed. Gas to liquid oxygen transfer is determined by the mass transfer coefficient, and the oxygen deficit of the gas phase in relation to the liquid phase. The oxygen deficit is the difference between the oxygen concentration in the gas phase that would be in equilibrium with the concentration in the liquid phase and the actual gas phase concentration. The change in oxygen concentration in the gas phase with time is then given by:

$$\frac{d[O_2]_g}{dt} V_g = K_1 * ([O_2]_l m_{O_2} - [O_2]_g) * V_g \qquad 3$$

K_1	Gas to liquid oxygen mass transfer coefficient	[h^{-1}]
$[O_2]_l$	Oxygen concentration in the liquid phase	[mmol L^{-1}]
m_{O_2}	Equilibrium ratio oxygen concentration gas/liquid	[-]

In the liquid phase, oxygen is used for respiration. The oxygen leaving the gas phase enters the liquid phase. The change of the amount of oxygen in the liquid phase is then given by equation 4:

$$\frac{d[O_2]_l}{dt} V_l = -K_1 * ([O_2]_l m_{O_2} - [O_2]_g) * V_g - OUR_l * V_l \qquad 4$$

V_l	Liquid volume, including sample	[L]
OUR_l	Oxygen uptake rate of the liquid phase	[mmol L^{-1} s^{-1}]

The OUR_l, denoting respiration in the model, is volume based. This limits the number of parameters needed. In the text OUR will often be used. This refers to the OUR in an OxiTop (unit $bottle^{-1}$).

The gas phase carbon dioxide concentration is changing because of absorption to the absorbent and release of carbon dioxide from the liquid. Because the absorbent is considered a strong absorbent for carbon dioxide, it is assumed that the equilibrium concentration of the absorbent is zero. The change of the amount of carbon dioxide in the gas is given by the equation 5:

$$\frac{d[CO_2]_g}{dt} V_g = K_2 * ([CO_2]_l * f_{H_2CO_3} * m_{CO_2} - [CO_2]_g) * V_g - K_3 * [CO_2]_g * V_g \qquad 5$$

$[CO_2]_l$	Carbon dioxide concentration in the liquid phase, including carbonate and bi-carbonate	[mmol L^{-1}]
$[CO_2]_g$	Carbon dioxide concentration in the gas phase	[mmol L^{-1}]
K_2	Gas to liquid carbon dioxide mass transfer coefficient	[h^{-1}]
$f_{H_2CO_3}$	Fraction of carbon dioxide species in the liquid present as H_2CO_3	[-]
m_{CO_2}	Equilibrium ratio carbon dioxide concentration gas/liquid	[-]
K_3	Gas to solid carbon dioxide mass transfer coefficient	[h^{-1}]

Carbon dioxide release from the liquid is dependent on the mass transfer coefficient and the carbon dioxide deficiency of the gas phase in relation to the liquid phase. The gas to liquid mass transfer coefficient of carbon dioxide is assumed to be proportional to the gas to liquid mass transfer coefficient of oxygen. The fraction undissociated dissolved carbon dioxide is calculated in an independent procedure, using temperature and pH as input, and can be considered constant. The procedure uses the equations given by (Edwards et al. 1975).

In the liquid phase, carbon dioxide is formed as a waste product of respiration, and it is transferred to the gas phase. The change of the amount of carbon dioxide in the liquid phase is given by the equation:

$$\frac{d[CO_2]_l}{dt} V_l = -K_2 * ([CO_2]_l * f_{H_2CO_3} * m_{CO_2} - [CO_2]_g) * V_g + \alpha * OUR_l * V_l \qquad 6$$

α Respiration quotient [mol_{CO_2} $mol_{O_2}^{-1}$]

The respiration quotient α gives moles of carbon dioxide formed from one mole of oxygen consumed. As nitrification is suppressed, the respiration quotient α will be approximately one.

The influence of oxygen transfer on the OUR measurement

It is assumed that the oxygen transfer rate is a first order process. In that case the liquid phase oxygen concentration is a function of gas phase oxygen concentration and the gas phase oxygen depletion rate. By rearranging equation 3, the liquid phase oxygen concentration can be calculated by equation 7.

$$[O_2]_l\, m_{O_2} = \frac{d[O_2]_g}{dt} * \frac{1}{K_1} + [O_2]_g \qquad 7$$

This provides the amount of oxygen in mmol L^{-1}. To convert gas phase concentrations to pressure, the equation is multiplied by R*T.

The activity of micro-organisms can be limited by a low liquid phase oxygen concentration. Once the oxygen concentration in the liquid phase drops below this level, the OUR measurement is no longer reliable. The calculated liquid phase oxygen concentration will be used to evaluate the measurement with respect to oxygen limitations.

As can be seen from equation 7, with increasing gas phase oxygen depletion rates the liquid phase oxygen concentration associated with a particular gas phase oxygen concentration decreases. Therefore an OUR measurement with a large sample will have limiting liquid phase oxygen concentrations at a higher gas phase oxygen concentration than an OUR measurement with a smaller sample, as the gas phase oxygen concentration decreases faster. It can also be seen that as the oxygen mass transfer coefficient, K_1, decreases, limiting liquid phase oxygen concentrations are reached at a higher gas phase oxygen concentration. This implies that knowledge of the gas phase oxygen concentration is insufficient to determine when oxygen limitation occurs.

The influence of carbon dioxide transfer on the OUR measurement

From the evaluation of the terms of equation 2 it can be assumed that the pressure change during an OxiTop experiment is given by equation 8:

$$\frac{dP}{dt} = \frac{dP_{O_2}}{dt} + \frac{dP_{CO_2}}{dt} \qquad 8$$

The rate of oxygen depletion is the quantity to be measured from the pressure change. Therefore, the change in gas phase carbon dioxide levels has to be small in relation to the change in gas phase oxygen concentrations. It was stated earlier that there are two separate sources of carbon dioxide in the system. There can be carbon dioxide present in the sample or the gas at the beginning of an OUR measurement. The depletion of this quantity takes a certain amount of time, after which it no longer influences the pressure. There is also a continuous formation of carbon dioxide, proportional to the OUR.

The mass transfer rate of carbon dioxide will be studied in more detail to determine under which conditions OUR measurements might be influenced by changes in gas phase carbon dioxide concentrations. This effect is seen clearest when the carbon dioxide production rate is constant. The carbon dioxide production rate is linearly related to the OUR. Therefore the effect of a changing carbon dioxide concentration on OUR measurements will be discussed first for a constant OUR, after which the effect of a changing OUR on the given analysis will be discussed.

The carbon dioxide concentration of the gas phase changes according to equation 5. The change in carbon dioxide gas concentration is determined by two mass transfer coefficients simultaneously. Carbon dioxide is exchanged with the liquid phase, and carbon dioxide is transferred to the absorbent. The equilibrium concentration in the gas phase at the absorbents surface is constant, so that a change in gas phase concentration is only influenced by the liquid phase concentration.

It is obvious that if the carbon dioxide absorption is fast enough (K_3 is big) the gas phase concentration of carbon dioxide will be low, and carbon dioxide will not affect the OUR measurement, as the range in pressure is smaller than the resolution of the pressure measurement. It is therefore expected that once K_3 reaches a certain value, gas phase carbon dioxide levels are kept so low that an accurate measurement can be obtained irrespective of K_2. This is because both the production of carbon dioxide and the initial concentration have a maximum.

If K_3 is somewhat smaller only fast changes in liquid phase carbon dioxide concentration will lead to a noticeable change in the gas phase carbon dioxide concentration. For these fast changes, K_2 has to be large, as otherwise the rate at which the liquid concentration can change due to absorption of gas phase carbon dioxide is limited (relative change). Therefore, the smaller K_2, the smaller K_3 can be without carbon dioxide interfering with the OUR measurement. From this it is

concluded that the minimal K_3 needed if K_2 is infinite would also be sufficient if K_2 is smaller. In the following section the minimal K_3 will be derived using this assumption. The relation for the minimal K_3 required, will depend on initial carbon dioxide and the carbon dioxide formation rate. In reality, because K_2 has a finite value, K_3 can be smaller and still provide accurate measurements. Thereafter the effect of changes in the OUR on the accuracy of the measurement will be discussed.

Limitations to measuring the OUR due to initial carbon dioxide concentrations

The carbon dioxide error in the OUR measurement is determined by the change in gas phase carbon dioxide concentration in relation to the OUR. To obtain this the carbon dioxide concentration as a function of time needs to be solved. By combining equations 5 and 6 the change in total carbon dioxide in the gas and liquid phase combined can be calculated:

$$\frac{d[CO_2]_l}{dt} V_l + \frac{d[CO_2]_g}{dt} V_g = \alpha * OUR_l * V_l - K_3 * [CO_2]_g * V_g \qquad 9$$

To investigate whether the gas phase carbon dioxide concentration change influences the OUR measurement equation 9 will be solved for a constant OUR_l. We assumed K_2 to be infinite, so that the gas and liquid phase will always be in equilibrium. Using this assumption equation 9 can then be written:

$$\left(\frac{V_l}{V_g * f_{H_2CO_3} * m_{CO_2}} + 1 \right) \frac{d[CO_2]_g}{dt} V_g = -K_3 * [CO_2]_g * V_g + \alpha * OUR_l * V_l \qquad 10$$

From equation 10 it can be derived that the gas phase carbon dioxide concentration as a function of time is given by:

$$[CO_2]_g(t) * V_g = \left([CO_2]_g(0) * V_g - \frac{\alpha * OUR_l * V_l}{K_3} \right) * e^{-\frac{K_3 * t}{\Lambda}} + \frac{\alpha * OUR_l * V_l}{K_3} \qquad 11$$

Where:

$$\Lambda = \frac{V_l}{V_g * f_{H_2CO_3} * m_{CO_2}} + 1$$

The carbon dioxide distribution in the system
Total amount divided by the amount in the gas phase. [-]

$[CO_2]_g(t)$ $[CO_2]_g$ as a function of time [mmol L^{-1}]

$[CO_2]_g(0)$ $[CO_2]_g$ at t = 0 [mmol L^{-1}]

From equation 11 it can be seen that as the OUR is constant the value for the carbon dioxide concentration after a sufficient measuring time is given by:

$$[CO_2]_g^{\#} = \frac{1}{K_3}\alpha * OUR_l * \frac{V_l}{V_g} \qquad 12$$

#	Superscript used for steady state conditions	[-]

Equation 12 gives a steady state for the carbon dioxide concentration where inflow and outflow of carbon dioxide in both the gas and in the liquid phase are balanced. Equation 11 can now be written as:

$$[CO_2]_g(t) = \left([CO_2]_g(0) - [CO_2]_g^{\#} \right) * e^{-\frac{K_3 * t}{\Lambda}} + [CO_2]_g^{\#} \qquad 13$$

In appendix 1 this relation is derived as a special case of the exact solution, when K_2 is more than five times K_3. Taking the first derivative to time of equation 13 gives the rate of change in the carbon dioxide gas concentration:

$$\frac{d[CO_2]_g(t)}{dt} = -\frac{K_3}{\Lambda}\left([CO_2]_g(0) - [CO_2]_g^{\#} \right) * e^{-\frac{K_3 * t}{\Lambda}} \qquad 14$$

The rate of change in the gas phase carbon dioxide concentration can now be related to the rate of oxygen depletion in the gas phase, which is to be measured. As the rate of change in carbon dioxide concentration decreases exponentially, mathematically it will never become zero. Therefore, an acceptable error has to be used to find a value for the time needed before accurate OUR measurements can be done. This error is defined as:

$$\left| \frac{d[O_2]_g}{dt} * Er \right| \geq \frac{K_3}{\Lambda} \left| [CO_2]_g(0) - [CO_2]_g^{\#} \right| * e^{-\frac{K_3 * t}{\Lambda}} \qquad 15$$

Er	Error from changing carbon dioxide concentrations that is considered acceptable; fraction	[-]

As the amount of oxygen present in the liquid phase can be neglected, the change in gas phase oxygen concentration is linearly related to the OUR by:

$$\frac{d[O_2]_g}{dt} * V_g = -OUR_l * V_l \qquad 16$$

Substitution of equation 16 in equation 12 gives:

$$\frac{d[O_2]_g}{dt} = -[CO_2]_g^{\#} * \frac{K_3}{\alpha} \qquad 17$$

Combining equations 15 and 17 results in:

$$e^{\frac{K_3 * t}{\Lambda}} \geq \frac{\alpha}{\Lambda * Er} * \left| \frac{[CO_2]_g(0)}{[CO_2]_g^{\#}} - 1 \right| \qquad 18$$

By solving equation 18 the time needed to obtain a gas phase carbon dioxide concentration, that is close enough to the steady state concentration so that changes do not bias the OUR measurement, can be obtained:

$$t \geq \frac{\Lambda}{K_3}\left(\ln\left| \frac{[CO_2]_g(0)}{[CO_2]_g^{\#}} - 1 \right| + \ln(\alpha) - \ln(\Lambda) - \ln(Er) \right) \qquad 19$$

Various parameters influence this minimal time needed.

- The carbon dioxide distribution in the system, Λ.
  Equation 19 is subject to the condition that the concentrations of carbon dioxide in the gas and liquid phases are in equilibrium, so that the carbon dioxide content of the system can be calculated from either of these concentrations if the distribution coefficient Λ is known.
  Larger values of Λ mean a greater fraction of the carbon dioxide is in the liquid phase. The more carbon dioxide is kept in solution, the longer it takes to reach steady state. This is represented by the linear relation between time needed and Λ. But the more carbon dioxide is kept in solution, the smaller the rate of change in gas phase carbon dioxide concentration. This is represented by the factor ln(Λ). From equation 19 it is clear that an increase in Λ will mean longer waiting times before accurate measurement of the OUR is possible.
- The initial carbon dioxide concentration, $[CO_2]_g(0)$.
  It takes time to absorb (or form) the gas and to reach the steady state concentration. Note that it is not the absolute value of the concentration, but the ratio with the steady state concentration that determines the time needed. Because practically all carbon dioxide in the system originates

from the sample, and the OUR_l for a particular sample is proportional to the amount of sample used, varying sample sizes will not change this ratio. That means changing sample sizes is not an option to reduce the error. Also note that there can be too little initial carbon dioxide, just as well as there can be too much. Flushing out the initially present carbon dioxide will not eliminate the error from initial conditions either.

- The gas to solid carbon dioxide mass transfer coefficient, K_3.
  The steady state gas phase carbon dioxide concentration also depends on this coefficient, so that K_3 influences two sections of equation 15. Changing K_3 will change the steady state concentration, which drops with increasing K_3. Therefore, the effect of an increase in K_3 on the logarithmic factor is a slower absorption. Even with a high initial carbon dioxide concentration the effect on the logarithmic factor does not balance the linear factor that predicts shorter waiting times as K_3 increases.
- The desired accuracy of the measurement, Er.
  Notice that the maximal error allowed can very easily be changed. As the error is a fraction and therefore smaller than one, decreasing the error will increase the time needed for an accurate measurement.
- The respiration quotient, α.
  This is caused by defining the carbon dioxide formation rate in terms of oxygen uptake. The respiration quotient is then needed as a conversion factor. Normal values of α for compost systems, which usually contain mostly carbohydrates, are around one, so that the influence of this factor will be small.

This analysis is subject to the restrictions used. These are that K_2 is much larger than K_3 and that the OUR is a constant. It was shown that the minimal K_3 for a very large K_2 is also applicable for smaller K_2's (appendix 1). The only restriction is then that the OUR is constant. The calculated time can therefore be seen as the time needed to deplete initial carbon dioxide, or, if no carbon dioxide is present initially, to form enough carbon dioxide to satisfy the steady state concentration demand.

Limitations to measuring a changing OUR.

During unimpaired growth micro-organisms increase exponentially. The first order increase in OUR as a function of the OUR would under these circumstances equal the growth rate, μ, of the micro-organisms. Assuming a first order change in the OUR, the relative error found is a constant in time. This error depends on system parameters and the OUR rate change coefficient. In appendix 1 the systematic error due to changes in the gas phase carbon dioxide concentration when there is a first order change in the OUR is derived. The result is given in equation 20.

$$\frac{d[CO_2]_g}{d[O_2]_g} = \alpha\mu \frac{1}{K_3 + \mu\left(\Lambda + (\Lambda - 1)\frac{K_3 + \mu}{K_2}\right)} \qquad 20$$

μ First order rate coefficient for the change in OUR. During the growth phase this is the growth rate [h^{-1}]

In the standard OxiTop tests used in this research Λ is approximately two. From equation 20 it then follows that if α is assumed to be one, an exponential change in OUR can be measured without problem as long as K_3 is more than 18 times the growth rate of the micro-organisms (μ). The error is then less than 5%.

To measure faster changes in OUR, K_2 has to be smaller than K_3, or the system has to be changed so that Λ becomes larger. Unfortunately, increasing Λ would increase the waiting time for initial deviations in the carbon dioxide content to be equalised. To measure a normal (mixed culture) growth rate of 0.12 h^{-1} (Heijnen 1999) a K_3 of 2.2 h^{-1} is required. Measuring the growth rate of e-coli would require a much better carbon dioxide adsorption, because this species has reported growth rates of 0.5 h^{-1} or higher (Stanier et al. 1977; Schlegel 1981; Madigan et al. 2000) which would require a K_3 value of 10 h^{-1} or higher.

Equation 20 is valid only if the system is in semi-steady state. This is after the initial excess or shortage of carbon dioxide has been equalised by the system. From the analysis in appendix 1 it follows that the time needed to establish this "equilibrium" is more or less equivalent to the time required when OUR is constant, provided the growth rate is much smaller than K_3. From the above it is concluded that this must be the case to obtain a reliable measurement, so that equation 19 can be used for all measurements.

4.4 Materials & Methods

General aspects of measurements with the OxiTop System

Method

After filling the bottles (Schott, 1L) with the appropriate chemicals and samples, the bottles were sealed by screwing the caps (OxiTop, WTW) on, and the data collection period was set and started. Then the bottles were placed in a temperature controlled incubator (Innova 4000 or Gallenkamp orbital shaker), and shaken at 120 rpm.

The volume of the bottles averaged 1130 ml. Care was taken that during experiments the gas phase was always larger than 800 ml, and thus much larger than the solid and liquid phases. Gas phase volumes for the separate measurements were determined by subtracting added volumes of sample, water,

buffer, absorbent and other chemicals from the average bottle volume. Added volumes were calculated from added weights and analyses by using the following conversion factors: liquids 1000 ml kg^{-1}, volatile solids 1400 ml kg^{-1}, and ash 2300 ml kg^{-1}. It was assumed that the volume of the liquid phase equals the separate volumes of liquids and solids added to that phase.

Water transfer rate measurements

Oxygen uptake rate measurements usually take place at temperatures different to the filling conditions. To assess the time it takes the system to warm up and for water vapour to reach equilibrium, pressure data from blanc OUR measurements was used. As discussed earlier, the initial absorption of water by the carbon dioxide absorbent may hinder OUR measurements.

The measured pressure change is the sum of pressure increase of the gas phase because of temperature increase and increase in equilibrium water vapour pressure. The rate at which the new equilibrium is reached depends on various mass and heat transfer coefficients. These experiments were not aimed at determining and measuring these separate coefficients, but at quantifying the time the system needs to obtain equilibrium after an increase in temperature. During this time OUR measurements may be influenced by changes in temperature and water vapour pressure. Thereafter it is assumed that partial pressures of all substances except oxygen and carbon dioxide are constant.

Method

Bottles were filled with 200 ml of demi water, and sealed with an OxiTop cap filled with a carbon dioxide absorbent (Soda lime with indicator, Merck). The measurement was started, and the bottle transferred to one of the incubators and shaken at 120 rpm. Ambient starting temperature, as well as incubation temperature were recorded.

Oxygen Transfer rate measurements

The oxygen used by micro-organisms in the liquid phase has to be supplied from the gas phase. The rate at which oxygen is transferred depends on the mass transfer coefficient. In these experiments the mass transfer coefficient is measured. Experiments were conducted according to Dankwerts (1970).

Method

Sodium sulphite (Merck) was weighed and dissolved in water to provide a 0.1 – 0.5M solution. The solution was transferred to a glass flask which was tightly sealed. The flask was kept in a shaker-incubator at 30°C for several hours to days. Schott bottles (1L), loosely fitted with an OxiTop cap without carbon dioxide absorbent, were acclimatised in a shaker-incubator for several hours at 30°C. A

quantity of a pre-heated sulphite solution, with a sulphite amount corresponding to two to five times the molar oxygen content of the gas phase, was poured into the pre-heated bottles. The exact amount was determined by weight. Half a ml of a 0.02M cobalt chloride (Merck) solution was added to catalyse the oxidation of the sulphite to sulphate. The bottles were sealed with the OxiTop cap, and the pressure measurement was started. Care was taken to minimise the time between filling the bottles and returning them to the shaker.

Determining transfer rates

The pressure data were analysed using MathCAD. The first fifteen minutes were discarded to allow for temperature adjustment. K_2 was measured from the pressure data by fitting a first order curve to the decrease in pressure over time using Mathcad. This was done by varying both the initial oxygen concentration and the oxygen mass transfer coefficient, K_2, used in the calculation. The initial oxygen concentration found was checked. Initial values lower than 21% were expected, due to absorption before the measurement could be started, but the difference had to be plausible in relation to the measured K_2.

Carbon dioxide transfer rate measurements

During an OUR measurement, change in gas phase carbon dioxide concentrations can influence results. The mass transfer coefficient for carbon dioxide absorption by the absorbent (K_3) determines the importance of changes in partial pressure of carbon dioxide for changes in total pressure. In these experiments this mass transfer coefficient was measured for various absorbents and conditions. These measurements were done without shaking or stirring, to minimise the interaction with the liquid.

Method

The bottles were thoroughly flushed with the CO_2/N_2 gas mixture (Indugas). During flushing parafilm was placed over the top to act as a one way valve to prevent back flow of surrounding air once the flushing was stopped. The flushed bottles were then fitted with an OxiTop cap containing absorbent by pushing it through the parafilm, making sure all of the ventilation holes in the lye container remained open.

Transfer rates were measured using Schott bottles (1L) containing 200 ml acidified water. During both flushing and incubation the bottles were kept at rest and on that basis it was assumed that the release of dissolved carbon dioxide during the pressure measurement was negligible. If in equilibrium, carbon dioxide concentrations in the acidified water would be twenty percent of the carbon dioxide present in the system.

Runs without acidified water were done to check whether the presence of water or water vapour significantly affects the results.

Determining transfer rates

The pressure data were analysed using MathCAD. The first hour was discarded to allow for temperature adjustment. K_3 was measured from the pressure data by fitting first order curve to the decrease in pressure over time using Mathcad. This was done by varying both the initial carbon dioxide concentration and the carbon dioxide mass transfer coefficient, K_3, used in the calculation. The initial carbon dioxide concentration was checked to see whether it did not exceed the concentration in the gas mixture used. Lower initial concentrations found by the fit were expected, due to absorption before the measurement could be started, but the difference had to be plausible in relation to the measured K_3. In addition, depletion rates were fitted on part of the data to check for continuity of the first order process.

Experimental

Carbon dioxide mass transfer coefficients were determined changing the following parameters:

- Temperature
  Rates were determined at two temperatures, 20 and 40°C.
- Absorbent
  Six different absorbents were tested, all technical grade Merck chemicals, the solutions made with demi-water:
  * KOH solutions in different strengths
  * NaOH solutions in different strengths
  * KOH pellets
  * NaOH pellets
  * NaOH on a carrier
  * Soda lime with indicator
- The container holding the absorbent
  Four different set ups were tried for holding the absorbents, as is depicted in figure 3.
  cup 1 The system as provided by OxiTop.
  cup 2 The system as provided by OxiTop but replacing the rubber container with a sealing ring and placing the absorbents directly in the Teflon container.
  cup 3 A custom made Teflon container (Technische dienst, Wageningen University) with larger ventilation holes and hanging deeper into the bottle was used in combination with the sealing ring.

cup 4 **A custom made Teflon container as before, but with larger holes along its sides, almost down to the bottom, and covered with gauze preventing the pellets falling out. This container cannot hold liquids.**

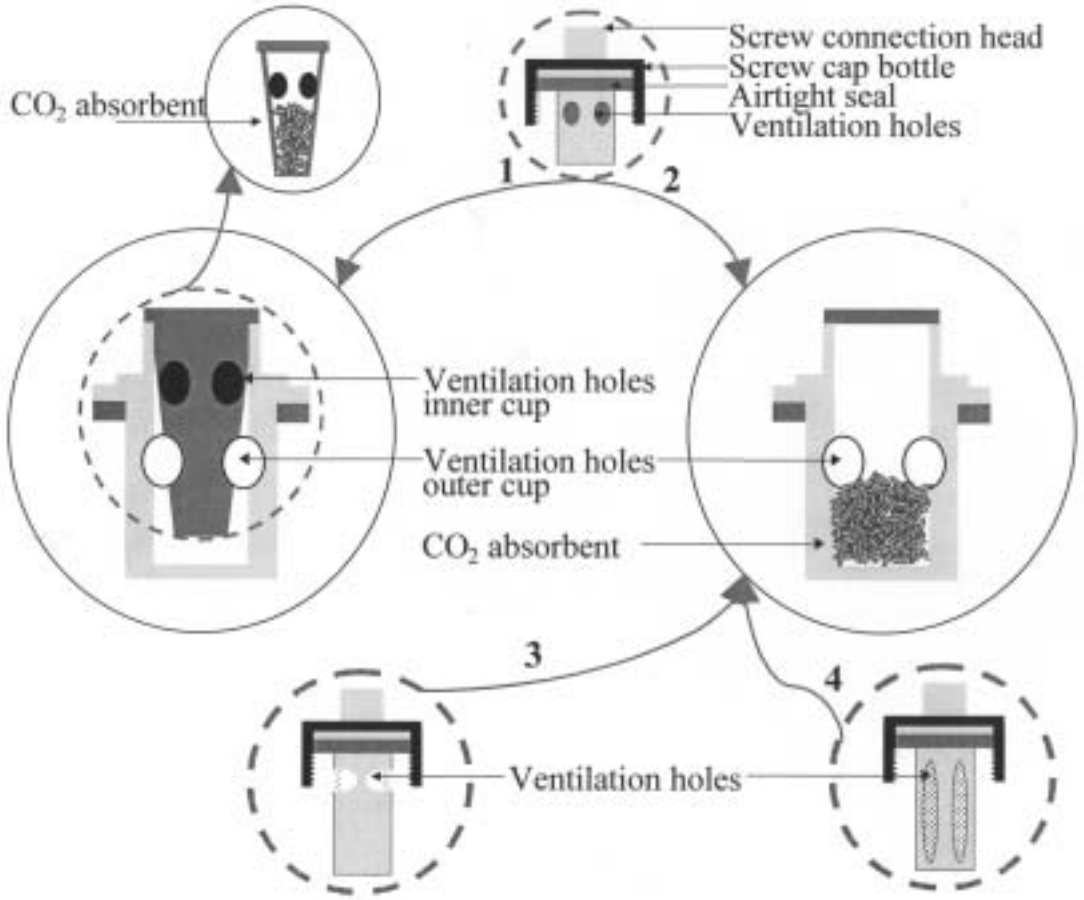

Figure 3 The cups used to hold the carbon dioxide absorbent

4.5 Results and discussion

Water Vapour Transfer Rates

These measurements were done by placing OxiTops at ambient temperature into an incubator with a higher temperature. Pressure changes measured are therefore the result of more processes than water vapour transfer alone. It was however concluded earlier that water vapour transfer would be the only process that might influence measurements over a longer period.

A typical graph depicting pressure change against time is shown in figure 4. The measurement was performed in duplicate. As can be seen pressure change becomes negligible in less than one hour. In this experiment the temperature increase was 18°C.

Before the oxygen uptake rate can be measured, the system has to adjust itself to the measuring conditions. The pressure change in water vapour is only one of these adjustments. The carbon dioxide concentrations have to become near steady state concentrations, and the micro-organisms have to adjust to the new temperature. The data lost by a temperature adjustment period of one hour will not affect the accuracy of the OUR measurement in any way.

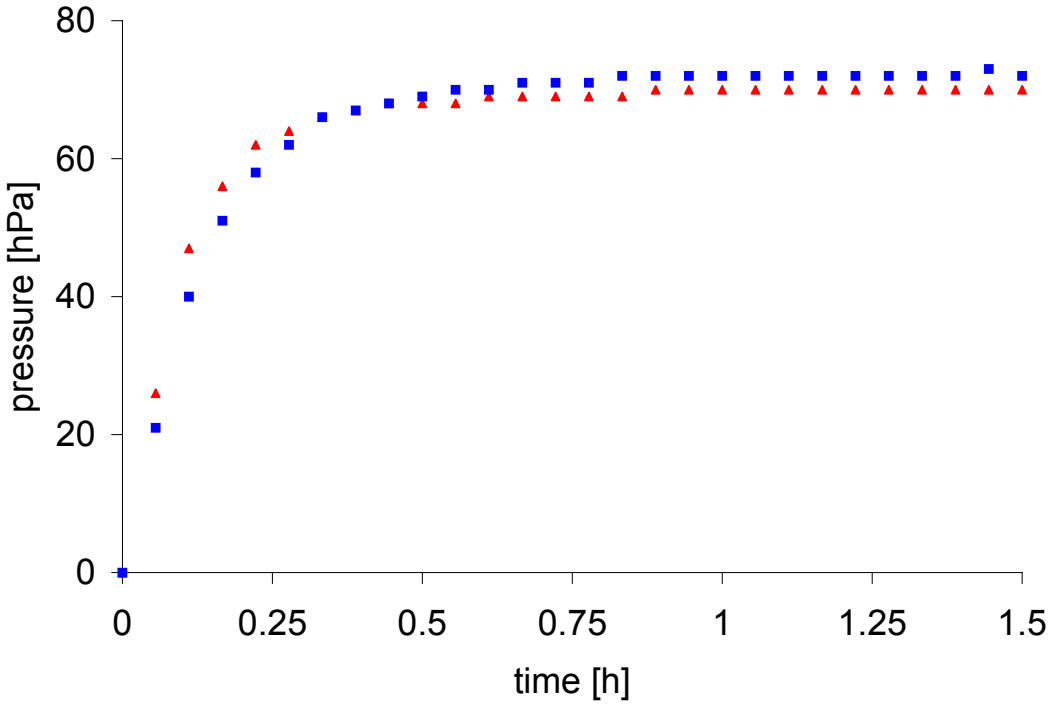

Figure 4 Pressure increase in a blank OxiTop measurement, measured in duplicate. The ambient filling temperature was 22°C and the incubation temperature 40°C.

Oxygen Transfer Rates

The gas to liquid oxygen mass transfer coefficient (K_2) was measured to check whether the microbial activity is not hindered by low oxygen concentrations in the liquid phase. When the oxygen transfer coefficient and the oxygen uptake rate are known, the oxygen concentration in the liquid phase can be calculated from the oxygen concentration in the gas phase. This relation can be used to link measured rates to a minimal gas phase oxygen concentration. Below this concentration the microbial activity will be limited by low oxygen concentrations in the liquid phase.

The oxygen mass transfer coefficients were measured by following the pressure decrease in an OxiTop filled with ambient air and sulphite present in the water phase. A typical graph of the pressure drop versus time during oxygen uptake experiments is shown in figure 5. As can be seen, the bulk of the oxygen was transferred to the liquid phase within one hour. This means measurements must

start as soon as possible after adding the sulphite, as the reliability of the measurement increases if a greater pressure drop is measured. Therefore the OxiTops and chemicals were kept at incubation temperature for some time before a measurement. Handling time to start a measurement was minimised.

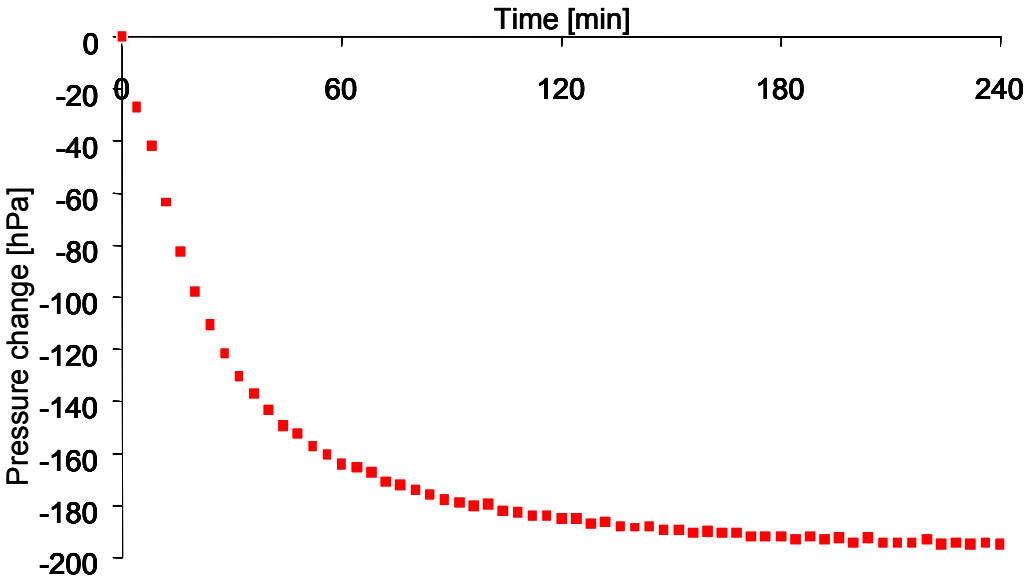

Figure 5 Pressure change in an OxiTop filled with 28.5 mmol of Na_2SO_3 in 114 ml water. Temperature was kept constant at 30°C.

The pressure data were analysed assuming a first order transfer process. The average K_2 measured was 2.0 h^{-1}. A mass transfer rate coefficient of 2.0 h^{-1} can be compromised by reactions in the interface, which would mean an overestimation of the oxygen transfer (Danckwerts 1970). However, the depletion fits a first order process (indicating a reliable measurement) much better than it fits a one and a half order process (which would indicate a compromised measurement) (Danckwerts 1970). From this, it was concluded that the overestimation, if present, was small.

To calculate the relation between gas phase oxygen concentrations and liquid phase oxygen concentrations equation 7 was used. The relation is dependent on the gas phase oxygen concentration and the change in gas phase oxygen concentration. The change in gas phase oxygen concentration is linearly related to OUR_l as can be seen from equations 3 and 4 (the liquid phase oxygen content is assumed to stay negligible). Therefore, from equation 7 it can be seen that a higher OUR_l will mean lower liquid phase oxygen concentrations at a particular gas phase oxygen concentration.

Measurements in which the oxygen is depleted fast will have limiting liquid phase oxygen concentrations at a higher gas phase oxygen concentration than measurements with a smaller depletion rate. It can be seen from equation 7, that if a limiting liquid phase oxygen concentration is defined, the associated gas phase concentration increases with the OUR. This increase is independent of both the gas and the liquid phase oxygen concentration. Therefore the decrease in the lower limit gas phase oxygen concentration that can be used for an OxiTop measurement can be calculated from equation 7.

A very high oxygen depletion rate of 0.35 mmol h^{-1} was used to quantify the influence of oxygen mass transfer. The fast depletion rate and the measured oxygen transfer coefficient were substituted in equation 7, and it was calculated that the lower limit gas phase oxygen concentration decreased by 0.17 mmol L^{-1}. At 30°C this concentration equals a partial pressure of 0.5 kPa. The OxiTop measures pressures with a resolution of 0.1 kPa. To obtain an accurate measurement a pressure drop of several kPa is necessary. Decreasing the oxygen partial pressure range in which accurate measurements can be performed by 0.5 kPa will therefore not affect the applicability of the system.

It was concluded that the rate of oxygen transfer was more than sufficient for accurate OUR measurements. As the system is virtually in equilibrium improving oxygen mass transfer will not raise liquid phase oxygen concentrations.

Carbon Dioxide Transfer Rates

Carbon Dioxide Absorbents

Changing carbon dioxide concentrations in the gas phase can make OUR measurements unreliable. To assess the impact of likely changes the carbon dioxide absorption rate constant (K_3) was measured.

The first experiments were done using the standard OxiTop system, and were focussed on obtaining the best absorbent to maintain a low carbon dioxide concentration. The absorption rates found were very slow. This means that it takes a long time to reach steady state concentrations. The continuous change in carbon dioxide concentration in the gas phase has a negative influence on OUR measurements.

There were however differences observed between the materials tested. It was found that saturated solutions are unreliable because of a crust forming on top of the solution. The crust hindered the absorption process considerably. Dilute solutions showed a much better performance, as did solid absorbents. The measured mass transfer coefficients for carbon dioxide absorption of the tested materials are given in table 1. The transfer coefficient is determined by assuming a

first order mass transfer process in gas phase concentration, and fitting an exponential decline to the measured data. This proved impossible for the saturated lye solutions, which were therefore omitted.

Table 1 Carbon dioxide mass transfer coefficients, K_3, of several absorbents at different temperatures, using the standard OxiTop absorption system. Measurements performed in the presence of an acidified water phase.

	KOH solution	NaOH solution	KOH pellets	NaOH pellets	Soda lime pellets	NaOH carier
K_3 20°C [h^{-1}]	0.15	0.12	0.12	0.17	0.13	0.15
K_3 40°C [h^{-1}]	0.12	0.12	0.14	0.11	0.13	0.16

As can be seen in table 1, the transfer coefficients measured are more or less the same for all measured materials. It was therefore concluded that the design of the absorbent container was the principle factor determining absorption rates. All numbers are single measurements. Because solids are much more convenient to work with the liquids were not further tested.

On closer inspection of the data it was found that the sodium and potassium hydroxide pellets' carbon dioxide depletion rate did not fit a first order process very well. The absorption transfer coefficient decreases with time. The transfer coefficient for sodium hydroxide on a carrier also decreases, but less. Therefore the K_3 given for these materials in table 1 has limited meaning as the value depends on the duration of the measurement. The values are given for comparison only. The non-saturated solutions and the soda lime pellets did show a first order decrease in carbon dioxide.

Visually it was observed that the structure and texture of the hydroxide pellets changed during the experiment. With water present, the pellets dissolved for a major part, and in dry experiments, a crust formed on the pure sodium and potassium hydroxide pellets. It was thought that these phenomena could explain the decreasing absorption rate, by introducing a physical barrier between the absorbent and the gas. However, this physical barrier was less hindering than the barrier observed with saturated lye solutions.

In figure 6 an example of the pressure change in time observed during carbon dioxide absorption experiments is given. The experiment was done at 20°C with the standard OxiTop set-up, and with water present in the system. Data analysis showed that only the transfer coefficient for the soda lime was constant during the experiment. The other three absorbents show a decreasing transfer coefficient.

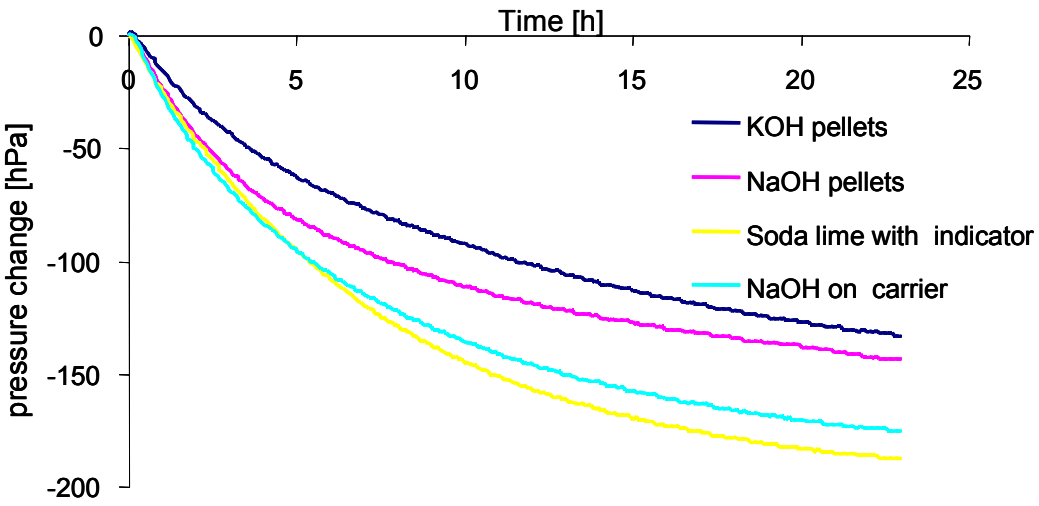

Figure 6 Pressure change in OxiTop due to carbon dioxide absorption at 20°C, using the standard set-up.

As the soda lime was the only material that had a constant transfer coefficient, it was concluded that this was the most suitable carbon dioxide absorbent tested. The soda lime pellets do not dissolve in absorbed water, and the colour indicator present in the pellets shows whether the pellet still has absorption capacity left. Because of these advantages further experiments were performed solely with this material.

Containers holding the absorbent

The second set of experiments was aimed at improving the design of the absorbent container. Earlier it was shown (section 4.3) that a K_3 of 2.2 h^{-1} or higher would be needed to measure growth rates in mixed cultures. Three different cups were tested (see figure 3):

Cup 2 was the standard outer OxiTop container replacing the inner rubber container with a ring. This had a positive, but insufficient, effect on the mass transfer coefficient (table 2), which remained constant during experiments.

Cup 3 was custom made. The carbon dioxide transfer coefficient measured was higher than for cup 2. The transfer coefficient remained constant during experiments. The increase in the carbon dioxide transfer coefficient was sufficient to measure the OUR reliably if the OUR remains constant for several hours. This was concluded from calculations done with equation 19. However, it was also concluded from the analysis of equation 20 that the absorption was insufficiently fast to measure exponential growth rates of mixed cultures.

Table 2 Carbon dioxide mass transfer coefficients, K_3 [h^{-1}]. Measurements performed used soda lime pellets in the standard OxiTop, and in modified set-ups using only Teflon absorbent containers, both standard and custom made. Numbers correspond to figure 3. Measurements performed in the presence of an acidified water phase, and at 40°C.

	Cup 1	Cup 2	Cup 3	Cup 4
K_3	0.13	0.26	0.39	2.9

Cup 4 was also custom made. The carbon dioxide transfer coefficient measured was higher than for cup 3. The transfer coefficient remained constant during experiments. The design of this container was based on the experience that the soda-lime pellets remained dry (visually) even after prolonged periods in the OxiTop at temperatures up to 40°C. This makes the fluid retaining properties of the containers redundant. The new model container was designed to give the gas maximum access to the absorbent, without worrying about the possible formation of a caustic solution that could drip into the sample suspension and change the pH. This design increased the carbon dioxide transfer coefficient above the minimum value calculated from equation 20 (table 2).

Initial Carbon Dioxide Absorption

The capacity of the different containers to measure the OUR uninfluenced by initial carbon dioxide levels was investigated using equation 19. The analysis was done by choosing a constant OUR, and plotting the time needed to obtain steady state against initial gas phase carbon dioxide concentrations assuming constant equilibrium between gas and liquid phase. The result for an OUR of 0.17 mmol h^{-1} $bottle^{-1}$ is presented in figures 7 and 8. This rate depletes the oxygen in 2 days.

Equation 19 was derived assuming that $K_2 >> K_3$. This is not the case for high values of K_3 (e.g. cup 4). However, an approximate analysis, using the formulas presented in appendix 1, yielded an equivalent outcome. Only if the initial carbon dioxide content is raised to very high concentrations does the finite value of K_2 increase the time needed to deplete the carbon dioxide to such an extent that equation 19 can no longer be used.

The graphs in figure 7 and 8 show two lines per cup. From the graphs the lag time before OUR measurements become reliable can be derived. In figure 7 the grey area indicates the combinations of initial gas phase carbon dioxide concentration and time passed since the start of the measurement that will not give an accurate measurement of the OUR because of carbon dioxide concentration interference for K_3 = 0.39 (cup 3). The region where the calculated time is zero, is due to the allowed error of 10%. Somewhere in this region lies the steady state carbon dioxide concentration. Small deviations from steady state show acceptable errors.

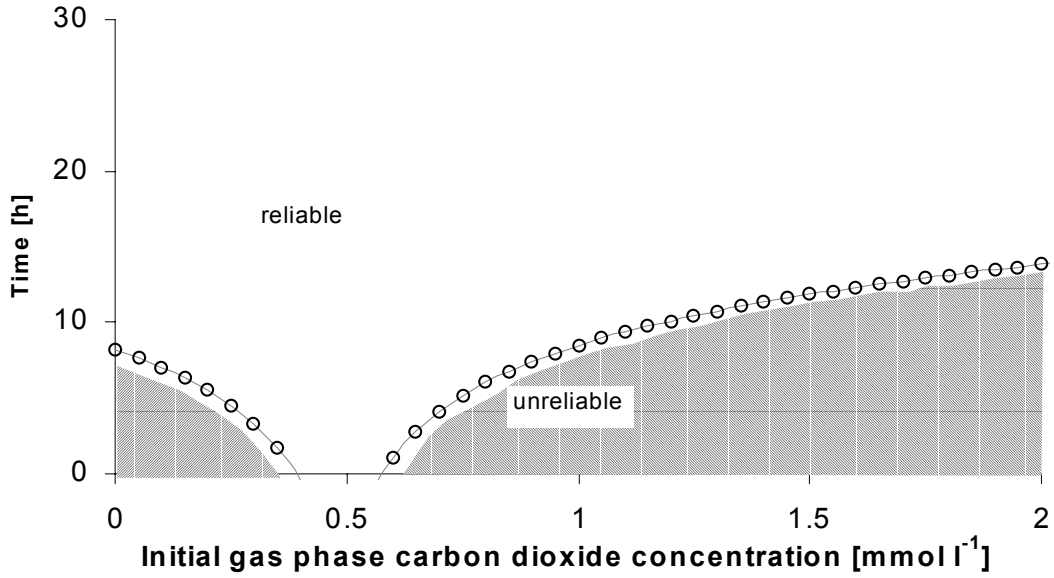

Figure 7 Time needed to obtain carbon dioxide concentrations close enough to steady state concentrations for any change to have negligible influence on the OUR measurement. Calculated for container 3 with equation 19. X-axis depicts initial gas phase carbon dioxide concentrations. Circles are calculated values, the grey area are incubation time - initial concentration combinations that would give a measurement error larger than 10%. K_3 = 0.39, OUR_l = 0.85 mmol h^{-1} l^{-1}, Λ = 2, α = 1, Er = 0.1.

As can be seen in figures 7 and 8 the time to reach equilibrium improved dramatically by changing the absorbent container. The plot for cup 3 in figure 7 shows that measuring times of under ten hours at constant OUR_l would produce reliable measurements with regard to carbon dioxide disturbance, even with big initial deviations from steady state concentrations. It was assumed that this would enable reliable OUR measurements of the hydrolysis rate.

It can be seen in figure 8 that the equilibrium carbon dioxide concentration drops for better absorption systems. With equation 12 it can be calculated that, as the OxiTop contains approximately one litre of gas phase, the equilibrium carbon dioxide content is quite high in relation to the OUR. For cup 1 the equilibrium carbon dioxide content equals twice the hourly production from respiration. For cup 4 the equilibrium carbon dioxide content still equals the production during ten minutes of respiration. Even with good carbon dioxide absorption the concentration does not become negligible.

The OUR_l used to calculate the graphs in figures 7 and 8 would deplete the oxygen in two days, and, at 30°C is approximately equivalent to an oxygen partial pressure drop of 0.5 kPa h^{-1}. If the OUR_l is halved, it can be shown using equation 19 that this increases the lag time for carbon dioxide interference to become negligible. It

can be calculated that halving the OUR_l adds $ln(2)*\Lambda / K_3$ to the lag time For K_3 = 0.13, this is 10 hours extra, for K_3 = 2.9 it is half an hour extra.

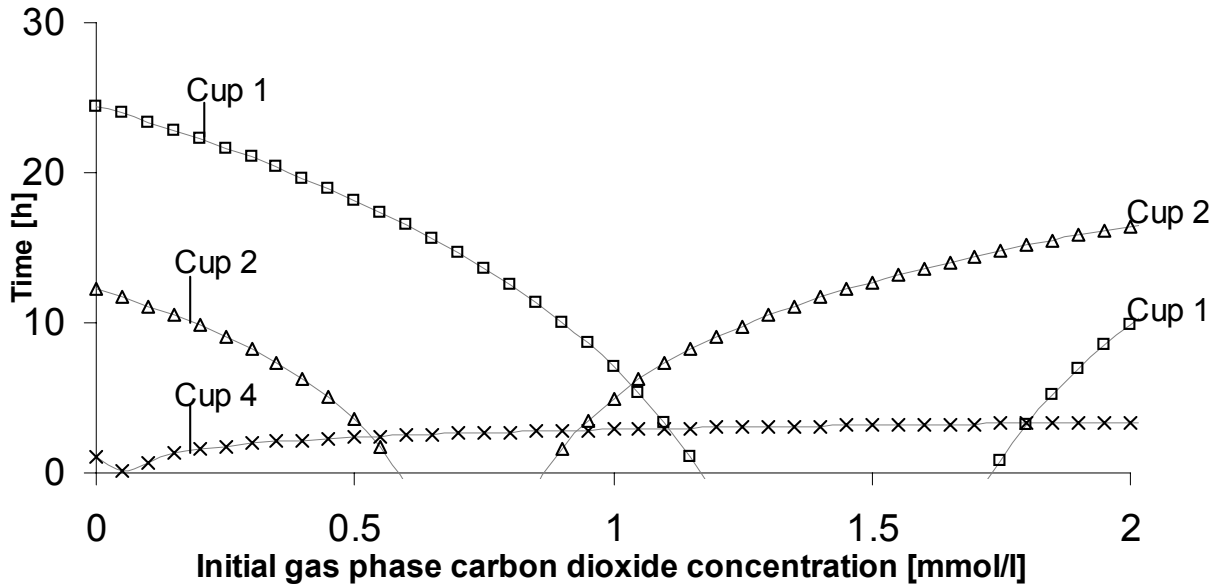

Figure 8 Time needed for reliable OUR measurement using measured K_3 values, assuming equilibrium between gas and liquid phase carbon dioxide concentrations. OUR_l = 0.85 mmol h^{-1} l^{-1}, Λ = 2, α = 1, Er = 0.1.

Accurate measurements can be obtained with any cup, provided the measurement of the OUR takes place after several days of incubation. Measurements during the first day can only be done with cup 4. Cup 3 has a K_3 that would allow measurements during the second day, even for samples with a very high carbon dioxide content. For models one and two, measurements would have to wait two or one and a half days respectively.

Changing Carbon Dioxide Concentrations

Initial carbon dioxide levels are adjusted by the system to steady state concentration if the OUR is constant. Once the oxygen becomes limiting the OUR could decrease very fast, leaving a residual carbon dioxide concentration that needs time to adapt to the new situation. Pressure drop in the OxiTop could continue after all oxygen has been depleted. To see what the impact of these factors is on the pressure decrease observed the mass transfer model of the OxiTop was used. To illustrate the effect, a high, constant, OUR_l was chosen. This does not influence the relative error, but makes it possible to show more clearly how the system pressure continues to change after oxygen is completely consumed. The results of the calculation using an initial carbon dioxide content of zero are given in figure 9.

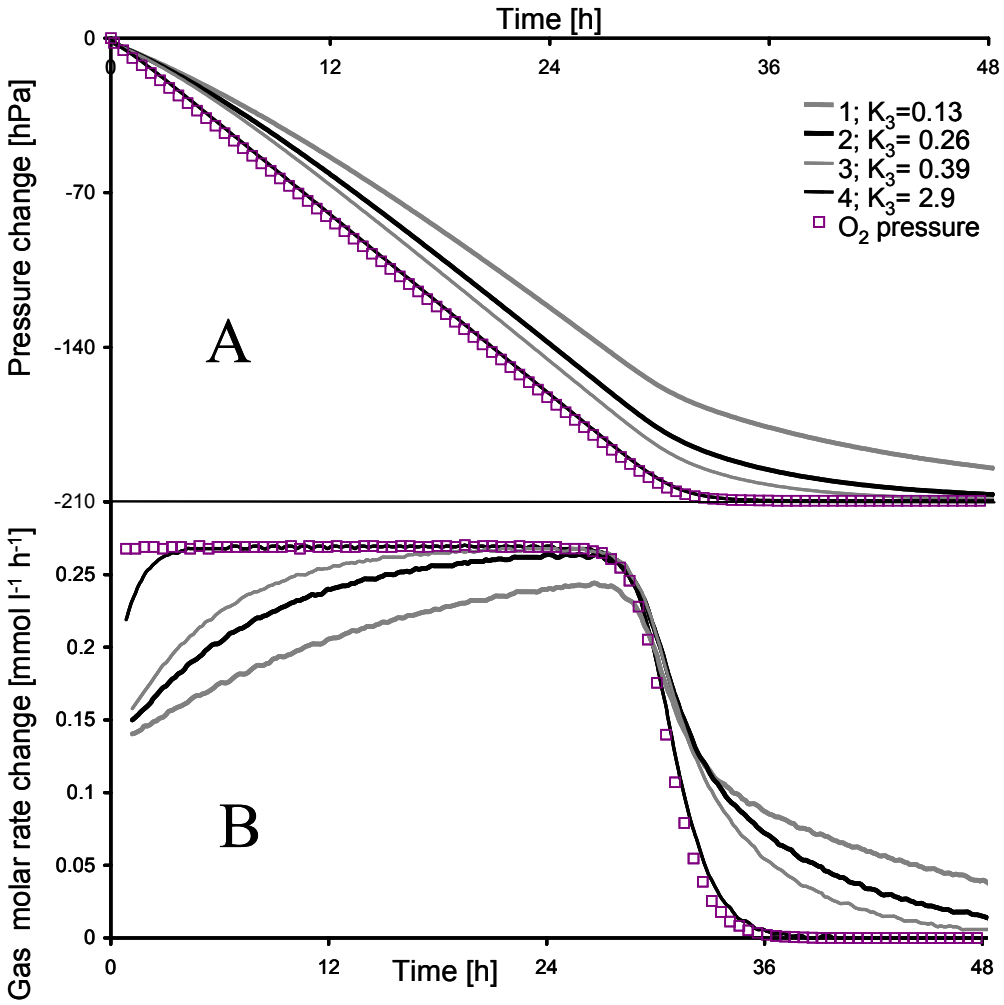

Figure 9 Expected pressure change in the OxiTop (A) and the derivative to time (B). Calculations used the measured K values and a constant OUR_l of 0.28 $mmol_{O_2}$ h^{-1}. This OUR_l depletes the oxygen in 30 hours.

As can be seen in figure 9A, with the best absorbent container, cup 4, the simulated pressure drop accurately represents oxygen pressure given by the squares. The other three cups systematically under- or over-estimate the oxygen depletion. In figure 9B it can be seen that after some time cups 2 and 3 accurately represent the OUR. From the simulation it follows that when using the standard system, cup 1,no relevant information can be extracted from the pressure drop during the simulated time.

The continuation of the pressure drop after complete oxygen depletion is negligible for cup 4. For the three other cups the pressure continues to change for a few hours. All show a distinct change in the measured rate, which could be recognised by a knowledgeable analyst. However, an unsuspecting observer might interpret the observed pressure change as a change in OUR.

In the presented case the oxygen is depleted fast. If oxygen were present during a longer time, all the cups would show the correct pressure drop rate during a limited time period. However, because in the measurements of real substrates it is not known how much carbon dioxide is present, and it is also not known whether the OUR_l is indeed constant during the measurement, or whether oxygen limitation will influence the activity, the interpretation of the pressure drop becomes impossible, as there are multiple explanations for the observed curve. The slow response time of the system to the measured variable, the OUR_l, means that fast rate used cannot be measured with cups number 1, 2 and 3. Cup number 4 can be used without problem.

Cup 1, 2 and 3 could be used if the system has the time to equalise carbon dioxide levels and the OUR_l thereafter is (almost) constant. Cup number 3 can be used to measure hydrolysis rates, because it is almost certain that after 24 hours the system has equalised carbon dioxide concentrations. If however the pressure drop after 24 hours is not constant, interpretation should be done very carefully.

4.6 Conclusions

The mass transfer model of the OxiTop presented in this chapter gives a clear insight in factors influencing the accuracy of an OUR measurement. It was shown that in the OxiTop carbon dioxide absorption is far more critical than oxygen transfer. Relations with which the limits to the measurement can be calculated have been derived, both for a constant and for an exponentially changing OUR. On the basis of this analysis improvements to the OxiTop have been made.

The standard OxiTop system must be modified for measuring the oxygen uptake rate of suspended solid samples. The absorption of carbon dioxide is a critical factor. For short incubation times of two days, or less, the standard carbon dioxide absorption system provided is inadequate. The modification with cups 3 and 4 suggested in this chapter can provide the absorption rate necessary. Both cups can be used to measure a constant OUR, which is expected during the hydrolytic phase.

The increase in absorption capacity attained by modified adsorbent containers proves that diffusion into the containers is the limiting process. The results show that the standard system inhibits absorption considerably, and that adjustments to the standard containers are less effective than replacing these containers with an improved model. The best container, cup 4, with completely open sides, has by far the fastest carbon dioxide absorption. Because these vessels cannot contain liquid, they are only suitable for non-hygroscopic carbon dioxide absorbents. Soda lime pellets are the only absorbent we found that meets this requirement.

The highest K_3 of 2.9 h^{-1} we obtained for the best container/absorbent combination (cup 4 and soda lime pellets) is sufficient to measure dynamic changes in OUR (i.e. growth rates) normally found in mixed cultures. It is however still too low to measure the growth rate of fast growing bacteria.

The OUR measurements with an adjusted OxiTop are simple, and could be performed by operators on location provided certain conditions are fulfilled. Complete oxygen depletion should take at least 36 hours, limiting the sample size that can be measured. Use of a good incubator is necessary to keep the bottles at a constant temperature.

The oxygen transfer in the system is very good. Measurement errors due to slow oxygen transfer rates are not expected. Oxygen transfer in a Schott bottle (1 L) shaken on an orbital shaker at 120 rpm is fast enough to sustain oxygen concentrations in the liquid close to equilibrium values. Even at a high oxygen uptake rate of 1 kPa h^{-1} the oxygen concentration in the liquid phase is the equilibrium concentration of an oxygen partial pressure that differs only 0.5 kPa from the actual oxygen partial pressure. If oxygen limitation does occur, this can only be solved by enriching the systems oxygen content.

Appendix Exact solution for the carbon dioxide in an OxiTop

The gas phase carbon dioxide content in the OxiTop was solved in equation 19 under the assumption that the gas and liquid phase are in constant equilibrium. In this appendix the exact solution of the equations 5 and 6 will be derived, and it will be shown that this exact solution can, under the assumed condition of equilibrium, be simplified to equation 19. Further the exact solution will be used to derive equation 20, describing the accuracy of measuring a changing OUR.

The exact solution

The gas phase carbon dioxide concentration in the OxiTop is described by equations 5 and 6. This system of differential equations can be solved exactly by using the characteristic equation method (Walas 1991). For this a linear system of three autonomous differential equations was derived from equations 5 and 6. To simplify the procedure, a few substitutions were used:

$$[CO_2]_g = y_1 \qquad 21$$

$$[CO_2]_l \frac{V_l}{V_g} = y_2 \qquad 22$$

$$\alpha * OUR_l \frac{V_l}{V_g} = y_3 \qquad 23$$

$$\frac{f_{H_2CO_3} m_{CO_2} V_g}{V_l} = F \quad \Rightarrow \quad \Lambda = \frac{F+1}{F} \qquad 24$$

In the standard OxiTop experiments used at the sub-department of Environmental Technology of Wageningen University, in part based on this research, F is approximately 1. In these measurements the temperature is kept at 30°C, the pH is 7 and the ratio of V_g : V_l = 4.5. The pH has a big influence on the value of F, it can be calculated that at pH 6 F = 4.4, and at pH 8 F = 0.13. Within practical boundaries the temperature and the ratio of gas and liquid volumes have a smaller effect on F.

To obtain a system of equations that can be solved the growth rate (or death rate depending on the growth phase of the batch culture) μ is used for the derivative of y_3 (equation 27). If the change in the OUR is not actually a first order process, usually a good fit can be obtained for a limited time span with an exponential function, so that the solution is valid for most instances where the OUR changes.

The set of differential equations that can be derived from equations 5 and 6 then becomes:

$$\frac{dy_1}{dt} = -(K_2 + K_3) * y_1 + K_2F * y_2 \qquad 25$$

$$\frac{dy_2}{dt} = K_2 * y_1 - K_2F * y_2 + y_3 \qquad 26$$

$$\frac{dy_3}{dt} = \mu y_3 \qquad 27$$

This set of equations can be solved (Walas 1991). The solution consists of a vector of Eigenvalues and a matrix Y(0) giving the initial values. The Eigenvalues give the time constant for an exponential change in value of y_1, y_2 and y_3, given a certain ratio between the y's, that remains constant. The vector of Eigenvalues is:

$$\begin{pmatrix} \mu \\ -\frac{1}{2}\left(K_2(F+1)+K_3+\sqrt{K_2^2(F+1)^2-2K_2K_3(F-1)+K_3^2}\right) \\ -\frac{1}{2}\left(K_2(F+1)+K_3-\sqrt{K_2^2(F+1)^2-2K_2K_3(F-1)+K_3^2}\right) \end{pmatrix} = \begin{pmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \end{pmatrix} \qquad 28$$

The ratios belonging to a solution are given as the columns of Y(0), one for each Eigenvalue. The sum of the columns in matrix Y(0) give the initial values of y_1, y_2 and y_3 as a vector, a row for every y. Y(0), the matrix of initial values is given as equation 29:

$$Y(0) = \begin{vmatrix} \frac{K_2F}{\mu(K_2(F+1)+K_3+\mu)+K_2FK_3}y_3(0) & \frac{\lambda_2+K_2F}{K_2}\gamma & \frac{\lambda_3+K_2F}{K_2}\beta \\ \frac{K_2+K_3+\mu}{\mu(K_2(F+1)+K_3+\mu)+K_2FK_3}y_3(0) & \gamma & \beta \\ y_3(0) & 0 & 0 \end{vmatrix} \qquad 29$$

Every Eigenvalue gives a solution of the system for a certain ratio of the initial values of y_1, y_2 and y_3. These ratios stay constant in time, only the weight attributed to the solution changes exponentially by e^{λ}. For a given set of initial conditions the $y_1(0)$, $y_2(0)$ and $y_3(0)$ are distributed over the columns in Y(0) by virtual values in

such a way that the sum of a row gives the initial value, and the ratio of values within a column does not change. By linearly combining solutions, a solution for any initial value of y_1, y_2 and y_3 can be found:

$$y_n = Y_{n,1}(0) * e^{\lambda_1 t} + Y_{n,2}(0) * e^{\lambda_2 t} + Y_{n,3}(0) * e^{\lambda_3 t} \qquad 30$$

In Y(0) the fist column is linked to λ_1, the second to λ_2 and the third to λ_3. The sum of every row gives the initial value $y_1(0)$, $y_2(0)$ and $y_3(0)$ respectively, and the matrix combined with the Eigenvalues remains a valid solution (of the system of equations, but with different initial values) if a whole column is multiplied by a constant. The different values in Y(0) do not have to represent real fractions of the concentration. A negative value is also correct, as long as the sum of the row gives the right initial value. The γ and β are the factors that can be chosen in Y(0) to obtain the initial carbon dioxide concentration in the system.

Measuring a changing OUR

As can be seen, the first column depends on the value of $y_3(0)$, μ, F and the mass transfer coefficients. The initial carbon dioxide levels (y_1 and y_2) do not influence this factor. The first column gives the "steady state" concentrations towards which the system converges. The other two columns are for initial deviations from this concentration, and decrease exponentially with time. Hereby λ_2 describes a fast adaptation of the CO_2 in the gas phase, and λ_3 a slower absorption of CO_2 from the liquid phase, via the gas phase, on the absorbent.

If the deviation from the "steady state" is negligible, either from the start or by waiting long enough so that the system has stabilised, the change in carbon dioxide concentration is:

$$\frac{d[CO_2]_g}{dt} = \frac{dy_1}{dt} = \frac{K_2 F}{\mu\left(K_2(F+1) + K_3 + \mu\right) + K_2 F K_3} y_3(0) * \mu e^{\mu t} + 0 + 0 \qquad 31$$

The change in gas phase oxygen is given by equation 32. Three different representations for y_3 are given. These were obtained from equations 23, 3 & 4, and 30 respectively.

$$y_3 = \alpha * OUR_l \frac{V_l}{V_g} = \alpha \frac{d[O_2]_g}{dt} = y_3(0) * e^{\mu t} \qquad 32$$

The systematic relative error in deriving the OUR from the pressure change in the system is the difference between the measured pressure and the change in the

oxygen partial pressure divided by the oxygen partial pressure. The change in pressure is linearly related to the change in concentration. Substitution of equations 31, 32 and 24 gives equation 33. This is equation 20 and is discussed there.

$$\frac{dP - dP_{O_2}}{dP_{O_2}} = \frac{d[O_2]_g + d[CO_2]_g - d[O_2]_g}{d[O_2]_g} = \frac{\alpha\mu K_2 F}{\mu(K_2(F+1) + K_3 + \mu) + K_2 F K_3} =$$

$$\frac{d[CO_2]_g}{d[O_2]_g} = \alpha\mu \frac{1}{K_3 + \mu\left(\frac{F+1}{F} + \frac{K_3 + \mu}{K_2 F}\right)} = \alpha\mu \frac{1}{K_3 + \mu\left(\Lambda + (\Lambda - 1)\frac{K_3 + \mu}{K_2}\right)} \qquad 33$$

The solution when $K_2 >> K_3$

If K_2 and K_3 are not of the same order of magnitude, the Eigenvalues can be simplified. From the Eigenvalues and Eigenvectors also the effect of initial deviations of the carbon dioxide concentration from the "steady state" can be obtained. Clearly there is no difference in effect whether the OUR is constant ($\mu = 0$) or changes exponentially as both the second and third Eigenvalue and the associated eigenvectors are independent of μ. Only the systems initial carbon dioxide concentrations ($Y_{1,n}(0)$ and $Y_{2,n}(0)$) are influenced by μ, but as it follows from equation 20 that an accurate measurement requires a μ that is much smaller than K_3, and therefore very much smaller than K_2, this change in values in Y(0) is small.

Even though the absolute concentration effect is the same, the relative effect on the measured OUR can differ, as the OUR changes in time. However, if μ is smaller than λ_3, the slower of the two Eigenvalues describing the elimination of initial deviations in carbon dioxide concentration, the time needed until an accurate measurement can be obtained will not differ much from the time calculated for a constant OUR. Therefore a constant OUR is used in this analysis. Under the condition that $K_2 >> K_3$ the Eigenvalues become:

$$\begin{pmatrix} 0 \\ -\frac{1}{2}\left(K_2(F+1)+K_3+\sqrt{K_2^2(F+1)^2-2K_2K_3(F-1)+K_3^2}\right) \\ -\frac{1}{2}\left(K_2(F+1)+K_3-\sqrt{K_2^2(F+1)^2-2K_2K_3(F-1)+K_3^2}\right) \end{pmatrix} \approx \begin{pmatrix} 0 \\ -K_2(F+1) \\ -\frac{K_3}{2}? \end{pmatrix} \qquad 34$$

The approximation, whereby al terms containing K_3 are neglected when adding to terms not containing K_3, is not exact enough. The square root almost equals $K_2(F+1)$, but the factor consequently left as the new λ_3, K_3, was to be very small, so that a small deviation can lead to big errors in the result. Therefore, a more accurate approximation was used, in which the negligible term of K_3^2 was multiplied with a factor that has a range from 0 to 1. By using this factor the square root can be solved:

$$\lambda_3 = -\frac{1}{2}\left(K_2+K_3+K_2F-\sqrt{K_2^2(F+1)^2-2K_2K_3(F-1)+K_3^2\frac{(F-1)^2}{(F+1)^2}}\right) =$$
$$= -\frac{K_3}{2}\left(1+\frac{F-1}{F+1}\right) =$$
$$= -\frac{K_3F}{F+1} = -\frac{K_3}{\Lambda} \qquad 35$$

For F = 1 the approximation is equal to the one used earlier. For any other value of F, the introduced factor is between 0 and 1, making this approximation more accurate. Not only is the third term of the square root not completely neglected, the whole second term is preserved. The exponential change found by this method equals the one found in equation 11.

Filling in the approximate λ_2 and λ_3, and simplifying by omitting negligible terms, the matrix Y(0) becomes:

$$Y(0) = \begin{vmatrix} \frac{1}{K_3} & y_3(0) & -\gamma & F\beta \\ \frac{1}{FK_3} & y_3(0) & \gamma & \beta \\ & y_3(0) & 0 & 0 \end{vmatrix} \qquad 36$$

From the approximate Eigenvalues and Y(0) it follows that:

$$y_1(0) = y_1(\infty) - \gamma + \beta F \qquad 37$$

$$y_1(t) = y_1(\infty) - \gamma e^{\lambda_2 t} + \beta F e^{\lambda_3 t} \qquad 38$$

When it is assumed that the process characterised by λ_2 is very fast (it is certainly much faster than the process characterised λ_3), then γ can be assumed to be zero. Notice that a non-zero value of γ only redistributes carbon dioxide between the gas and liquid phase and gives no net contribution to system carbon dioxide levels. The change in carbon dioxide in the gas and liquid phase combined is therefore described by λ_3. Hence the assumption that a fast process justifies the approximation that γ equals zero. This is equivalent to assuming constant equilibrium in carbon dioxide concentrations between the liquid and the gas phase as was done in chapter 4. The equation for gas phase carbon dioxide (y_1) can under this assumption be rearranged to:

$$y_1(t) = \left(y_1(0) - y_1(\infty)\right) e^{-\frac{K_3 t}{\Lambda}} + y_1(\infty) \qquad 39$$

This is equation 13.

4.7 References

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5

Measuring hydrolysis using the OxiTop system

5.1 Introduction

In composting research one of the key issues is predicting the speed at which the feed material will be turned into compost. To do this one must know how fast the material can degrade. The most used parameters to quantify degradation rates are activity measurements. Activity is defined as either the oxygen uptake or the carbon dioxide evolution per mass of volatile solids (VS, sum of particulate and dissolved organic matter) in the material under aerobic conditions, and under anaerobic conditions as the methane production per mass of volatile solids in the material. The measured quantity is usually referred to as the activity, always specifying the gas measured and measurement conditions. For composting aerobic conditions are used, as the composting process is aerobic.

The definition for activity originates from biological wastewater treatment, where it is used to evaluate the bacterial sludge used. It gives an indication of how much waste the sludge can degrade, and because the bulk of bacterial sludge consists of bacteria, it is an indication of the viability of the bacteria in the sludge. In composting the bulk of the material consists of particulate organic solids, most of which is dead matter. Therefore, the definition of activity means that a measure of bacterial activity is attributed to dead matter. This is done because use of the definition of activity entails the implicit assumption that the substrate contained in the particles can only be biodegraded at a certain rate. This rate is considered a property of these particles. It is generally accepted that hydrolysis is the rate-limiting step in the degradation of solid particles by micro-organisms.

Recognising hydrolysis as the limiting factor, hydrolysis theory can be used in optimising composting processes. The theory predicts that the amount of organic matter biodegraded during a standard (± three week) composting run is for a large part dependent on the hydrolysis of the solid material. It can be assumed that any free substrate, present initially, is degraded completely within the three weeks. Even then, most degradation of organic matter has to be related to hydrolysis (Hendriks 1992; Haug 1993; Hamelers and Richard 2001; Sanders 2001).

From literature it is also known that the hydrolysis rate of a given organic solid is influenced mainly by particle size (Sanders et al. 2000; Sanders 2001), temperature (Veeken and Hamelers 1999) and concentrations of hydrolysis products (Veeken et al. 2000). Temperature relations of the hydrolysis rate of various materials are known (Hendriks 1992; Veeken and Hamelers 1999; Sanders 2001) allowing for predictions of the degradation process. Therefore, in a composting reactor with temperature control, knowledge of the hydrolysis rate can be used to predict compost respiration rate, or to evaluate the performance of a compost bed. A

composting bed performs at the maximum degradation rate if the oxygen uptake rate (OUR; activity based on oxygen consumption) equals the hydrolysis rate.

For anaerobic systems the activity (expressed as the amount of methane formed per kg VS per hour) of systems containing solid material is, under certain circumstances, assumed to be the hydrolysis rate of the material (Sanders 2001). For a reliable estimate of the hydrolysis rate from a biological activity measurement, the activity of the biomass has to be substrate limited. In this chapter the term substrate refers exclusively to biodegradable organic compounds in solution.

Under aerobic conditions a major part of the substrate taken up (after solubilisation through hydrolysis) is used to increase biomass. The substrate taken up by the bacteria is then not completely oxidized, and therefore, the oxygen uptake rate measured cannot be directly linked to the hydrolysis rate. The objective of this chapter is to analyse the relation between the hydrolysis rate and the OUR. The goal is to develop a protocol to measure the hydrolysis rate aerobically. It is expected that this additional information will enable better control and operating of a composting process.

Measuring OUR in suspension

Substrate concentration is only one of many factors influencing respiration in a compost bed. The proportions of water, solids, and air, and their spatial distribution, are key parameters. Within a compost bed, control of these parameters is poor, so the OUR of a compost bed is unlikely to accurately reflect hydrolysis. Measurements in a more controlled environment are needed to make an accurate assessment of potential composting performances possible.

Suspending a sample in liquid, and measuring the OUR eliminates the uncertainty caused by some of the factors influencing respiration in compost beds (see chapter 4). The spatial distribution of the three phases, gas water and solids, is known, and concentration variations in the water and gas phase are eliminated. In addition, suspending the organic matter in water makes it less likely that hydrolysis is influenced by product inhibition or by the action of toxins as both these substances are diluted. Further, all bacteria have access to required nutrients, and the pH is buffered to an appropriate value.

The hydrolysis rate under these optimised conditions can be assumed to be the maximum for the solids at that temperature. The advantage of working with the maximum hydrolysis rate is that it is a constant independent of the type of aerobic biodegradation system. Therefore, the OUR measured under conditions of

maximum hydrolysis can be used to evaluate the performance of a compost bed objectively, or to compare different biodegredation processes.

There are many systems for measuring OUR in suspension. In this research the OxiTop was chosen because of its ease, as discussed in chapter 4. In this chapter (5) the OUR measurement of hydrolysing solid material with an OxiTop will be investigated in detail, focussing on the possibility to measure the hydrolysis rate. A model is presented that can simulate an OxiTop measurement using known relations from literature.

In chapter 4 it was shown that with appropriate modification, the OxiTop can accurately measure the oxygen depletion of the gas phase. A correct measurement of the oxygen uptake rate (OUR) does not necessarily provide an accurate estimate of the hydrolysis rate. This chapter will focus on the interactions of the oxygen, substrate and micro-organisms during a measurement, and how liquid phase concentrations of these components influence the oxygen uptake of a suspended batch of degrading solid matter. The result will be used to formulate conditions under which the hydrolysis rate can be measured.

5.2 Biomass growth Model

Substrate can either be oxidized to provide energy or be used for biomass increase. Therefore, the OUR is not a direct measurement of the hydrolysis rate. To use the OUR to assess the rate of hydrolysis , the relation between the hydrolysis rate and the OUR has to be understood. It is known that bacteria growing under substrate-limited conditions consume more substrate per amount of biomass produced than under unlimited conditions (Heijnen 1999). Therefore the biomass needs more oxygen per amount of substrate consumed than under unlimited conditions. To obtain a value for the hydrolysis rate, it is necessary to analyse this relation in more detail using a microbial growth model. For a batch system with a declining oxygen concentration and a steady substrate production from hydrolysis, no model linking substrate uptake to oxygen uptake could be found in literature. Therefore, a model was first constructed, using relations found in other bacterial growth systems.

Assumptions used in the model

The widely held assumption of the aerobic hydrolysis measurement is that there is a constant respiration plateau caused by substrate limited respiration, and that the OUR measured at this plateau gives information on the hydrolysis rate of the solid components. This assumes that the rate at which the substrate is becoming available through hydrolysis is determining the microbial activity, and that this hydrolysis rate has to be constant for the duration of the measurement. Following

this line, in the model the hydrolysis rate per kilogram volatile solids is a material property, independent of biomass concentrations or sample size, and during a measurement the hydrolysing volatile solids concentration is constant in time.

In a Closed Volume Pressure Change (CVPC) system, like the OxiTop, the oxygen concentration drops as it is consumed. Therefore at some point in time oxygen limitation will occur in the system. The growth model is used to define conditions where the oxygen limitation is absent or negligible. Because this evaluation was based on theoretical considerations, the worst case was evaluated to allow for deviations of assumed values from the actual values of the system.

It is assumed that the substrate uptake of the biomass can be described by the Monod relation, that substrate uptake on a COD (chemical oxygen demand: oxygen needed to fully oxidize the substrate) basis is independent of the type of substrate, and that the micro-organisms do not produce any substances they cannot break down again. As this means all substrate consumed for maintenance is completely oxidized, the maintenance requirements for oxygen and substrate, in COD units, are the same.

Standard relations for bacterial growth and activity limitations

To assess how bacterial growth influences measurements a growth model was derived. Because the focus is on the respiration under measurement conditions with substrate limitation, but without oxygen limitation, the model to be developed has to include both substrate limitation and oxygen limitation. It also has to incorporate requirements for maintenance, as these are not negligible under limited conditions. The basis of the model (equations 1 through 4) was based on the standard equations for biomass growing on a single substrate (Heijnen 1999). As long as the kinetic parameters of the various hydrolysis products are of similar value, these equations are also applicable for biomass growing on a mixture of substrates (Kovářová-Kovar and Egli 1998).

The equations given in this section are based on substrate. For oxygen the same equations apply, only with different subscripts to the parameters, or in some cases a different symbol, but denoting an analogue process.

Equations 1 through 3 are definitions of parameters widely used for bacterial growth. The specific growth rate μ is the amount of biomass produced per unit biomass per hour, the specific substrate uptake q defines the substrate uptake of a unit biomass per hour, and the yield Y_S defines the amount of biomass that is produced per unit of substrate consumed by the biomass.

$$\frac{d[X]_l}{dt} = \mu[X]_l \qquad 1$$

$[X]_l$	Biomass concentration in the liquid	[$mmol_{CODX}$ L^{-1}]
μ	Specific growth rate	[h^{-1}]

$$R_l = -q[X]_l \qquad 2$$

R_l	Substrate uptake rate by biomass per unit volume of the liquid phase.	[$mmol_{COD}$ L^{-1} h^{-1}]
q	Specific substrate uptake rate	[COD L^{-1} h^{-1} $CODX^{-1}$]

$$Y_S = -\frac{d[X]_l}{dt}\frac{1}{R_l} = \frac{\mu}{q} \qquad 3$$

Y_S	Biomass yield on substrate	[CODX COD^{-1}]

Equation 4 gives the change in yield as a function of the specific growth rate. This equation is called the Herbert-Pirt relation (Loosdrecht and Henze 1999). It assumes cells need to constantly respire and replace part of their mass to remain active. This is referred to as maintenance, as it produces no extra biomass. It further assumes that any extra substrate is built into new biomass with a constant composition, and that the amount of energy required for the conversion of substrate into biomass is constant.

$$\frac{1}{Y_S} = \frac{1}{Y_{max,S}} + \frac{m_S}{\mu} \qquad 4$$

m_S	Maintenance substrate requirement of the biomass	[COD $CODX^{-1}$ h^{-1}]
$Y_{max,S}$	Theoretical maximum of the biomass yield on substrate	[CODX COD^{-1}]

From equations 2, 3 and 4 it can be derived that the substrate uptake rate by the biomass is given by:

$$R_l = -\left(\frac{\mu}{Y_{max,S}} + m_S\right)[X]_l \qquad 5$$

In this equation the distinction between the two uses of substrate, either for growth or for maintenance, can be clearly seen.

From equations 3 and 4 it can be derived:

$$\mu = Y_{max,S}\ (q - m_S) \qquad 6$$

Equation 7 gives the rate of uptake of substrate by the biomass as a function of the substrate concentration. This equation is the well-known Michaelis Menten equation, also called the Monod relation when used for microbial growth. It is based on the assumption that bacteria have a limited and constant number of enzymes to transport substrate into the cell, and that the cells are far enough apart to avoid interaction. When no limitation is present, the rate of uptake of substrate is at its maximum, q_{max}. This maximum is determined by the fact that only a limited amount of enzymes is present in the organism. The relation further contains a limitation factor that gives the fraction of the maximum that is achieved as a function of the substrate concentration. Despite the simplification of the uptake process, the equation is widely used and provides an adequate estimate of activity.

$$q = q_{max} * \frac{[S]_l}{K_{M,S} + [S]_l} \qquad 7$$

q_{max}	Maximum specific substrate uptake rate	[COD L^{-1} h^{-1} $CODX^{-1}$]
$[S]_l$	Substrate concentration in the liquid	[$mmol_{COD}$ L^{-1}]
$K_{M,S}$	Affinity constant of the biomass for the substrate. Equivalent to the substrate concentration at which the activity is half the maximum activity	[$mmol_{COD}$ L^{-1}]

For our purpose substrate has to be a limiting factor for the respiration. As the oxygen concentration drops during a measurement, at some point oxygen will become limiting too. Therefore the growth model used has to incorporate both limitations. It is assumed that a Monod relation can describe both limitations.

When a second limitation is brought into the model this gives rise to a classic problem. If a culture is limited by two compounds, are the effects on the activity multiplicative, or is activity determined by the most limiting factor? Data on this subject is limited and inconclusive (Kovářová-Kovar and Egli 1998). The approach of the limiting substance, as used by Liebich (in:Wit De 1992), is an example of the latter, whereas the serial Monod model used here in equation 8 is a multiplicative model. The multiplicative model was chosen because intuitively it represents the worst-case scenario. It seems unlikely that in an otherwise unlimited system where $[S]_l$ is $K_{M,S}$, and $[O_2]_l$ is K_{M,O_2} the activity is less than a quarter of the maximum.

$$q = q_{max} * \frac{[S]_l}{K_{M,S} + [S]_l} * \frac{[O_2]_l}{K_{M,O_2} + [O_2]_l} \qquad 8$$

$[O_2]_l$	Oxygen concentration in the liquid	[mmol L^{-1}]

K_{M,O_2}	Affinity constant of the biomass for oxygen. Equivalent to the oxygen concentration at which the activity is half the maximum activity	[mmol L^{-1}]

Model for the pressure change due to batch growth in the OxiTop

From the equations 1 through 8, together with the mass transfer relations from chapter 4 (equations 3 through 6) a system of equations describing all relevant processes occurring during measurements in the OxiTop is obtained. The model simulates the pressure drop as a function of time during a measurement, given the specifications of the material and the experimental set-up. To keep formulas compact and understandable, all concentrations are expressed as mmol per unit volume (liquid or gas phase), or, for biomass and substrate, mmol COD per unit volume, which eliminates the need for conversion factors. The subscripts l for liquid and g for gas are used to indicate the relevant phase of the parameter, even in obvious cases. Hereby l denotes the liquid phase in which the solids are suspended, and g the overlying gas phase.

A number of conversion rates have to be distinguished for a good understanding of the model. Rates referring to substrate are denoted by an R, rates referring to oxygen are denoted by OUR. The purpose of the model to simulate the measurement of the hydrolysis rate of a material. Therefore, the oxygen uptake rate and the hydrolysis rate are also used on a mass basis. These rates can be recognized by the absence of an l or g. The particle based rate is the material property that is measured, whereas the liquid volume based rates change with sample size and liquid volume, and are only used to make calculations easier. A good measurement system will give the same value for the particle based hydrolysis rate over a range of liquid based rates.

R_{hydr}	Hydrolysis rate of the solids per mass of volatile solids (VS) in the sample.	[$mmol_{COD}$ kg_{VS}^{-1} h^{-1}]
$R_{hydr,l}$	Hydrolysis rate of the solids per unit volume of the liquid phase.	[$mmol_{COD}$ L^{-1} h^{-1}]
$R_{l,max}$	Maximum substrate uptake rate by the biomass per unit volume of the liquid phase.	[$mmol_{COD}$ L^{-1} h^{-1}]
$R_{l,maint}$	Maintenance substrate uptake rate by the biomass per unit volume of the liquid phase.	[$mmol_{COD}$ L^{-1} h^{-1}]
OUR	Oxygen uptake rate of the biomass per mass of VS in sample.	[mmol kg_{VS}^{-1} h^{-1}]
OUR_l	Oxygen uptake rate of the biomass per unit volume of the liquid phase.	[mmol L^{-1} h^{-1}]
$OUR_{l,max}$	Maximum OUR of the biomass per unit volume of the liquid phase.	[mmol L^{-1} h^{-1}]

$R_{hydr,l}$ is an input parameter that is calculated from the hydrolysis rate of the volatile solids R_{hydr}, the liquid volume V_l, and the mass of volatile solids M_{SM}:

$$R_{hydr,l} = \frac{M_{SM} * R_{hydr}}{V_l} \qquad 9$$

To calculate the maximum rate of uptake of substrate and the rate required for maintenance per unit volume, equations 10 and 11 are used. To use these equations, the biomass concentration and the biomass parameters q_{max} and m_S have to be known. The biomass parameters q_{max} and m_S are input parameters, the biomass concentration is an input variable of the model. The biomass concentration change during the measurement is simulated. The biomass parameters are considered constants.

$$R_{l,max} = q_{max} * [X]_l \qquad 10$$

$$R_{l,maint} = m_S * [X]_l \qquad 11$$

The rate of uptake of substrate by the biomass per unit volume is calculated with equation 12, which is equivalent to equation 8. The K_M values are input parameters obtained from literature:

$$R_l = R_{l,max} * \frac{[O_2]_l}{K_{M,O_2} + [O_2]_l} * \frac{[S]_l}{K_{M,S} + [S]_l} \qquad 12$$

The increase in biomass concentration can be obtained by combining equations 1 and 6. $Y_{max,S}$ is an input parameter:

$$\frac{d[X]_l}{dt} = (R_l - R_{maint,l}) * Y_{max,S} \qquad 13$$

When there is no uptake of substrate, the biomass decreases in weight according to the maintenance requirement. This is why maintenance is also referred to as the decay rate of the biomass.

It was assumed that the biomass does not produce any substances it cannot break down. Therefore, dead biomass is consumed immediately by the remaining bacteria. Under this assumption equation 14 must hold to satisfy the COD balance:

$$OUR_l = R_l * (1 - Y_S) \qquad 14$$

The change in substrate concentrations is the difference between substrate formed by hydrolysis, and that consumed by micro-organisms:

$$\frac{d[S]_l}{dt} = R_{hydr,l} - R_l \qquad 15$$

The change in gas and liquid phase oxygen and carbon dioxide concentrations is determined by the mass transfer relations as discussed in chapter 4. The change in gas phase oxygen concentration, given by equation 16, is calculated from the rate of oxygen uptake by the liquid phase. Uptake takes place because the liquid concentration is not in equilibrium with the gas concentration. The mass transfer coefficient K_1 for oxygen transfer from the gas phase to the liquid phase was obtained from measurements described in chapter 4. The equilibrium ratio m_{O_2} was obtained from literature:

$$\frac{d[O_2]_g}{dt} = -K_1 * ([O_2]_g - [O_2]_l m_{O_2}) \qquad 16$$

$[O_2]_g$	Oxygen concentration in the gas	[mmol L^{-1}]
K_1	Gas to liquid oxygen mass transfer coefficient	[h^{-1}]
m_{O_2}	Equilibrium ratio oxygen concentration gas/liquid	[-]

All oxygen disappearing from the gas phase goes into the liquid, so the amount of oxygen entering the liquid has to be the same amount that leaves the gas phase. The oxygen uptake rate by the biomass in the liquid phase, OUR_l, is calculated by equation 14. The difference between oxygen uptake rate by the biomass and oxygen transfer rate from the gas phase gives the change in oxygen concentration of the liquid:

$$\frac{d[O_2]_l}{dt} = K_1 * ([O_2]_g - [O_2]_l m_{O_2}) * \frac{V_g}{V_l} - OUR_l \qquad 17$$

One of the products formed from the aerobic biodegradation of substrate is carbon dioxide. The amount of carbon dioxide produced, is related to the amount of oxygen used in this oxidation process, via the respiration quotient α. For most biological materials α is approximately one, and can be considered a constant. This is the assumption used in this model. If α has a different value, the value of α will change with the yield, as the oxidation level of the substrate is then different to that of the biomass. The oxidation level of assimilated substrate has to be adapted

to that of the biomass. This adaptation will either consume oxygen, or produce carbon dioxide, so that α is not constant when the yield changes.

Dissolved, undissociated carbon dioxide in the liquid phase is transferred to or supplied from the gas phase if carbon dioxide concentrations in the gas and liquid phase are not in equilibrium. To be able to calculate both the fraction of carbon dioxide that is undissociated, $f_{H_2CO_3}$, and the equilibrium concentration ratio, m_{CO_2}, relations given by Edwards (1975) were used. The change in carbon dioxide concentration in the liquid phase is given by equation 18:

$$\frac{d[CO_2]_l}{dt} = K_2 * ([CO_2]_g - [CO_2]_l * f_{H_2CO_3} * m_{CO_2}) * \frac{V_g}{V_l} + \alpha * OUR_l \qquad 18$$

$[CO_2]_l$	Carbon dioxide concentration in the liquid	[mmol L^{-1}]
$[CO_2]_g$	Carbon dioxide concentration in the gas	[mmol L^{-1}]
K_2	Gas to liquid carbon dioxide mass transfer coefficient	[h^{-1}]
$f_{H_2CO_3}$	Fraction of carbon dioxide species in the liquid present as H_2CO_3	[-]
m_{CO_2}	Equilibrium ratio carbon dioxide concentration gas/liquid	[-]
α	Respiration quotient	[mol_{CO_2} $mol_{O_2}^{-1}$]

The amount of carbon dioxide entering the gas phase is the same as leaves the liquid. Carbon dioxide gas is absorbed by an absorbent. The change in carbon dioxide concentration can therefore be calculated by equation 19:

$$\frac{d[CO_2]_g}{dt} = -K_2 * ([CO_2]_g - [CO_2]_l * f_{H_2CO_3} * m_{CO_2}) - K_3 * [CO_2]_g \qquad 19$$

K_3	Gas to absorbent carbon dioxide mass transfer coefficient	[h^{-1}]

In a CVPC system OUR is derived from measured changes in pressure. The pressure drop in an OxiTop is given by ΔP, and can be calculated by equation 20:

$$\Delta P = \left([CO_2]_g + [O_2]_g - [CO_2]_g(0) - [O_2]_g(0)\right) * RT \qquad 20$$

ΔP	Change in OxiTop gas pressure since start of the experiment	[Pa]
R	Gas constant	[L Pa $mmol^{-1}$ K^{-1}]
T	Absolute temperature	[K]
(0)	Initial condition	[-]

Only carbon dioxide and oxygen are considered. In chapter 4 it was concluded that these are the only gasses of consequence to pressure changes measured with the

OxiTop. The shift in pressure due to an initial temperature adjustment is not accounted for in the model.

5.3 Determining the hydrolysis rate by measuring the OUR

In this section the model will be used to evaluate the possibility for measuring the hydrolysis rate from the oxygen uptake rate (OUR). To measure the OUR from a drop in pressure, constant volume pressure change systems like the OxiTop rely on a significant change in oxygen partial pressure. If gas phase oxygen concentrations are lowered, liquid phase oxygen concentrations will be lowered as well. It is known that low liquid phase oxygen concentrations can limit aerobic activity. Once the OUR becomes a function of the liquid phase oxygen concentration, rather than of properties of the sample, the measurement loses its value.

It is vital to quantify those conditions where OUR measurements are not affected by the oxygen concentration. From equation 14 it can be clearly seen that the OUR depends on the substrate uptake rate (R_l) and the yield (Y_S). Of these factors R_l changes when the oxygen concentration in the OxiTop changes (equation 12). Therefore, first the relation between oxygen concentration and R_l will be analysed. Thereafter the relation between R_l and Y_S will be analysed.

Error in estimating hydrolysis from substrate uptake

Rewriting equation 15 it can be derived that the hydrolysis rate of the solids equals the sum of the substrate uptake rate by the biomass and the rate of change in substrate concentration in the liquid phase:

$$R_{hydr,l} = R_l + \frac{d[S]_l}{dt} \qquad 21$$

If the biomass consumes less (or more) substrate than is produced by hydrolysis this will give an error in the hydrolysis estimates based on biomass activity:

$$error(R_l) = \frac{R_l - R_{hydr,l}}{R_{hydr,l}} = -\frac{1}{R_{hydr,l}}\frac{d[S]_l}{dt} \qquad 22$$

Equation 12 is used to express the effect of substrate and oxygen limitation on substrate uptake rate. By substituting equation 12 in the second part of equation 22 the error due to insufficient substrate uptake by the biomass can be calculated according to equation 23.

$$error(R_l) = \left(\frac{R_{l,max}}{R_{hydr,l}}\right) * \left[\frac{[O_2]_l}{K_{M,O_2} + [O_2]_l}\right] * \frac{[S]_l}{K_{M,S} + [S]_l} - 1 \qquad 23$$

The Monod limitation factors for oxygen and for substrate, are both smaller than one, consequently, the first term in equation 23 has to be larger than one. Because this ratio between maximum substrate uptake rate and substrate production rate by hydrolysis is so important, it is given a symbol, C, and called the capacity ratio. The definition is given in equation 24:

$$C = \frac{R_{l,max}}{R_{hydr,l}} \qquad 24$$

The interaction between activity and substrate concentration as described by the Monod relation, equation 7, tends to go to a steady state, whereby the substrate level remains constant. If the uptake rate is higher, the substrate concentration drops, limiting the uptake rate, and if the uptake rate is lower, the substrate concentration rises, enabling an increase in uptake rate. If the system would have no oxygen limitation, this would give equation 23 without the oxygen limitation term (in square brackets). As long as C is large enough, there would be no error due to a difference between substrate formation rate by hydrolysis and substrate uptake rate by the biomass.

In the OxiTop there could also be an oxygen limitation, and equation 23 applies. In analogy it can be seen that oxygen inhibition does not bias measurements, as long as the product of the two terms in brackets is larger than one. If this product is smaller than one the measurement can never be accurate. However, if the product is larger than one, the measurement is no longer necessarily accurate. The substrate concentration will naturally change towards steady state conditions where the error is zero (see above). The oxygen concentration is however decreasing, which in itself creates an error, as it increases the substrate concentration at which the rate of hydrolysis equals the rate of uptake of substrate by the micro-organisms.

The potential consequences of this inherent error are discussed below.

Relation between oxygen concentration and substrate uptake rate

From equation 23 it is predicted that in a CVPC measurement under substrate limited conditions, and a large enough capacity ratio, the substrate concentration increases. This increase in substrate concentration compensates the falling oxygen concentration, keeping the rate of substrate consumption constant. This

may just be an artefact, but even then it is important to quantify the effect for limitations in the models use.

It can be derived from equation 12 that the substrate concentration at which its rate of uptake equals its rate of formation by hydrolysis, at a given oxygen concentration in the liquid phase, is given by:

$$[S]_l^{\#} = K_{M,S} * \frac{[O_2]_l + K_{M,O_2}}{[O_2]_l * (C-1) - K_{M,O_2}} \qquad 25$$

$[S]_l^{\#}$ Substrate concentration in the liquid at which rate of substrate consumption equals the rate of hydrolysis. [$mmol_{COD}\ l^{-1}$]

To assess the potential importance of this source of error, it is necessary to estimate its size. We assume that the concentration of substrate in the liquid phase derived from equation 25 is valid so that the change in substrate concentration with a change in oxygen concentration represents the size of the error. This assumption is only valid as long as the error found in this way is small.

To estimate the error in a hydrolysis measurement caused by an increase in substrate concentrations we have to relate them together. Therefore, equation 25 has to be changed to a rate equation. Equation 25 can be differentiated to equation 26, where the rate of the change in substrate concentration in relation to the concentration of oxygen in the liquid phase is given:

$$\frac{d[S]_l^{\#}}{d[O_2]_l} = K_{M,S} * \frac{-K_{M,O_2} * C}{\left([O_2]_l * (C-1) - K_{M,O_2}\right)^2} \qquad 26$$

Equation 26 gives the change in substrate concentration with the oxygen concentration, but not the error in a hydrolysis measurement, or the relation of R_l to $R_{hydr,l}$. To do that, the rate of change in the liquid phase oxygen concentration has to be related to the OUR. In chapter 4 it was shown that liquid phase oxygen concentrations are close to the equilibrium concentration as long as the OUR remains less than 1 kPa h^{-1}. Typical values of OUR in OxiTop hydrolysis measurements are 0.1-0.8 kPa h^{-1}. Therefore it is assumed that there is continuous equilibrium in the oxygen concentrations. The liquid phase oxygen concentration can then be calculated from the gas phase concentration as is given in equation 27.

$$[O_2]_l = \frac{[O_2]_g}{m_{O_2}} \qquad 27$$

Using equation 27, equation 28 can be derived. Here the change in substrate concentration is given as a function of gas phase oxygen concentration:

$$\frac{d[S]_l^{\#}}{d[O_2]_g} = \frac{d[S]_l^{\#}}{d[O_2]_l} * \frac{1}{m_{O_2}} \qquad 28$$

As more than 99% of the oxygen present in an OxiTop is in the gas phase, the change in gas phase oxygen concentration is directly related to the OUR_l:

$$\frac{d[O_2]_g}{dt} = -OUR_l * \frac{V_l}{V_g} \qquad 29$$

The first time derivative of the substrate concentration can be calculated from:

$$\frac{d[S]_l^{\#}}{dt} = \frac{d[S]_l^{\#}}{d[O_2]_g} * \frac{d[O_2]_g}{dt} \qquad 30$$

By substituting equations 26, 27, 28 and 29 in 30 it can be derived:

$$\frac{d[S]_l^{\#}}{dt} = \frac{K_{M,S} * K_{M,O_2} * C}{\left(\frac{[O_2]_g}{m_{O_2}} * (C-1) - K_{M,O_2}\right)^2} * OUR_l * \frac{V_l}{m_{O_2} * V_g} \qquad 31$$

If the change in the amount of substrate in solution is very small compared to the amount produced by hydrolysis then it can be assumed that the actual substrate concentration follows equation 31.

Combining equations 14 and 21 the ratio of substrate produced by hydrolysis and consumed by the biomass can be found:

$$\frac{R_{hydr,l}}{R_l} = \frac{\frac{OUR_l}{1-Y_S} + \frac{d[S]_l}{dt}}{\frac{OUR_l}{1-Y_S}} \qquad 32$$

Substituting equation 31 in 32 gives equation 33. This can be used to define the conditions where the predicted rise in substrate concentrations has a negligible influence on the rate of substrate consumption:

$$\frac{R_{hydr,l}}{R_l} = 1 + \frac{K_{M,S} * K_{M,O_2} * \alpha}{\left(\frac{[O_2]_g}{m_{O_2}} * (C-1) - K_{M,O_2}\right)^2} * \frac{(1-Y_S) * V_l}{m_{O_2} * V_g} \qquad 33$$

In figure 1 the inverse of the ratio calculated by equation 33 is plotted as function of the partial oxygen pressure. As the yield is not known, the largest error with respect to the yield was assumed, i.e. a yield of zero was used. Oxygen concentrations were converted to pressure assuming temperature to be 30°C.

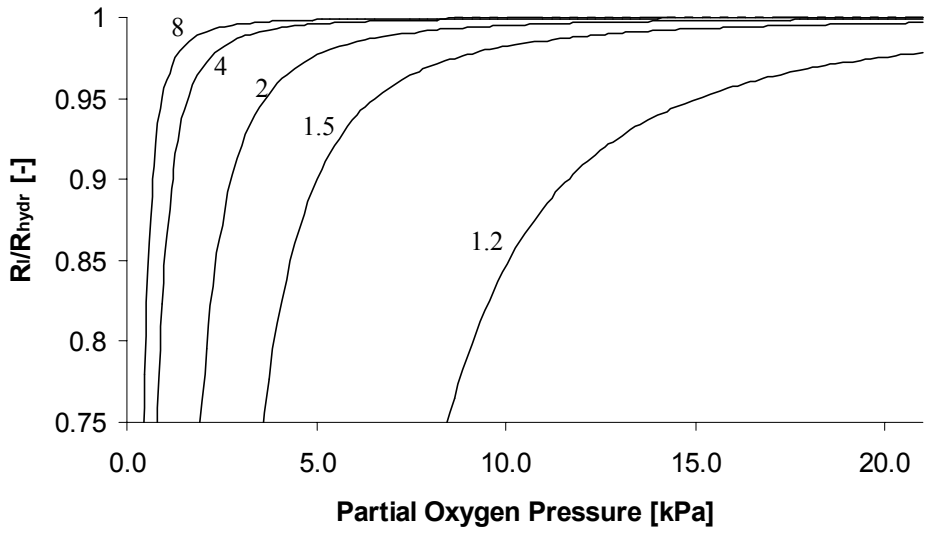

Figure 1 Predicted ratio of rate of uptake of substrate to rate of hydrolysis. Deviations from one are due to substrate concentration build up. Numbers indicate C, the capacity ratio. Oxygen concentrations at instantaneous equilibrium. $K_{M,S}$ =0.5, K_{M,O_2} =0.01, Y_S =0.

Figure 1 shows the model predicts that oxygen depletion is not a problem during measurements if C is larger than 2, meaning sufficient potential biomass activity is

present. Also, notice that if the capacity for the uptake of substrate is several times the rate of hydrolysis, then the rate of uptake of substrate is predicted to equal the rate of hydrolysis for gas phase oxygen pressures as low as three kPa and higher. Of course this limiting value should be increased with the extra oxygen pressure required to maintain the gas to liquid transfer as was calculated in chapter 4, adding 0.5 kPa for very active samples down to 0.0 kPa for samples with low activity.

From figure 1 and equation 33 it is concluded that if C is larger than 2, and the partial oxygen pressure larger than 5 kPa the substrate uptake by the biomass equals the substrate produced by hydrolysis. Therefore, typical changes in oxygen concentration during measurement of OUR will not introduce error in the estimation of hydrolysis, provided the capacity ratio is larger than 2. This conclusion is valid for all systems where the oxygen transfer is good enough to assume that the liquid phase oxygen concentration is near the equilibrium concentration.

Biomass growth under substrate limited conditions

In the previous section it was concluded that, if C is larger than 2, and the partial oxygen pressure larger than 5 kPa, declining oxygen levels do not limit the rate of uptake of substrate during substrate-limited activity. In this section the growth model will be used to assess the time needed for the biomass to grow to a capacity ratio of two or larger.

Once the rate of uptake of substrate exceeds its rate of formation (i.e. C>1) growth can become substrate limited. Once substrate limitation is reached, the rate of uptake of substrate by the biomass is presumed constant and equal to the rate of hydrolysis. This is expressed in equation 34:

$$\frac{d[X]_l}{dt} = (R_l - R_{maint})Y_{S,max} = (R_{hydr,l} - m_S[X]_l)Y_{S,max} \qquad |C \geq 1 \qquad 34$$

By integrating equation 34 the biomass growth can be calculated. As equation 34 is only valid if the biomass is substrate limited, a new timevariable has to be used. The moment the system becomes substrate limited is used as the initial value, instead of the start of the measurement:

$$[X]_l(t)_S = \frac{R_{hydr,l}}{m_S} - \left(\frac{R_{hydr,l}}{m_S} - [X]_l(0)_S\right)e^{-m_S Y_{S,max} t} \qquad |C \geq 1 \qquad 35$$

$(t)_S$ Time variable, set at 0 the moment respiration becomes substrate limited. [h]

Equation 35 relates the biomass concentration to the rate of hydrolysis. The capacity ratio C defines the potential biomass activity relative to the rate of hydrolysis. By multiplying both sides of equation 35 by q_{max}, dividing by $R_{hydr,l}$ and substituting equation 24, equation 36 is obtained which gives the change in the capacity ratio C in time:

$$C(t)_S = \frac{q_{max}}{m_S} - \left(\frac{q_{max}}{m_S} - C(0)_S \right) e^{-m_S Y_{S,max} t} \qquad |C \geq 1 \qquad 36$$

From equation 36 it can be seen that there is no direct influence of sample sizes and concentrations on the increase in C under substrate limited conditions.

In figure 2 the increase of C in time is given starting from $C(0)_S = 1$. After an initial phase of unlimited growth, C is necessarily greater than 1, as substrate uptake had to "catch up" with substrate formation and was oxygen limited during the exponential growth phase. Maximum substrate uptake rate, q_{max}, and maximal yield, $Y_{S,max}$, are based on published data (Heijnen 1999), but the q_{max} has been chosen small. Therefore figure 2 gives a worst-case estimate of the time needed to obtain enough biomass.

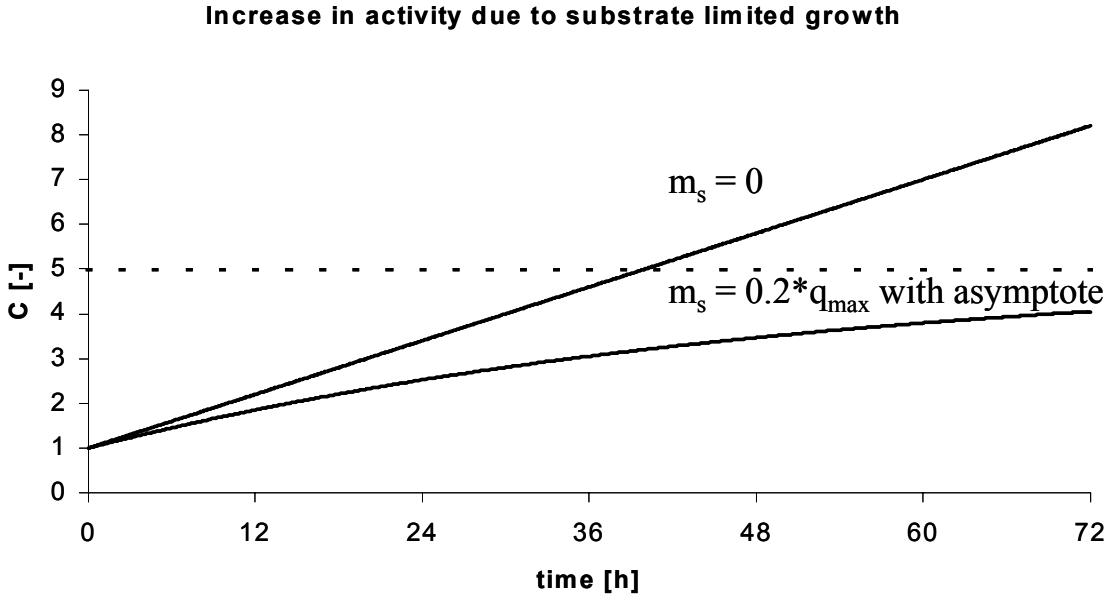

Figure 2 Biomass growth depicted as increase in potential substrate uptake rate, C. Calculated values using substrate limited growth of equation 36, neglecting the increase in substrate concentration. (q_{max}= 0.2 [h^{-1}], $Y_{S,max}$ = 0.5).

Figure 2 depicts the increase in biomass calculated with a very high maintenance requirement, and with no maintenance requirement. It can be seen that the

maintenance limits the increase in C to a maximum. In figure 2 the maximum is given by the dotted line. Whether a high or a low maintenance is assumed, the calculation predicts a capacity ratio, C, of two after fifteen hours. Bearing in mind that a value of $C(0)_S$ of 1, and a q_{max} of 0.2 were used, it can be concluded that a C of two would normally be obtained in a few hours. From this and figure 1 it was concluded that the rate of uptake of substrate by the biomass can be assumed to be the rate of hydrolysis during substrate limited growth.

The conclusion that the rate of uptake of substrate equals the rate of hydrolysis during substrate limited growth means the double limitation, of both oxygen and substrate, in the growth model only differs from the single limitation approach during the transition periods between the different growth phases. During the exponential growth phase, substrate is abundantly present, and growth is completely determined by the concentration of oxygen in the liquid phase. Once substrate becomes limiting, growth rates are determined by the rate of hydrolysis, the biomass concentration and its maintenance requirement, irrespective of the concentration of oxygen in the liquid phase.

The model was developed to depict a worst-case scenario. Even under these restrictions the model predicts that the rate of uptake of substrate equals its rate of formation, indicating that oxygen limitation of the biomass has no influence on the OUR measured during substrate limited respiration. During the exponential growth phase however, oxygen is the growth-determining factor and should be taken into account when performing measurements during this growth phase. Unlike the rate of hydrolysis, the oxygen limitation changes with time, consequently, interpretation of the OUR during the exponential growth phase will be more difficult.

The oxygen limitation due to its low concentration in the liquid phase should not be confused with the oxygen transfer, which remains an important factor to consider as it changes when the experimental setup is altered. The underlying assumption for all conclusions is the good oxygen transfer found for the OxiTop in chapter 4.

The effect of growth on OUR measurements

From chapter 4 it is concluded that the OUR measured, is the actual oxygen depletion in the OxiTop system, and from the previous paragraph that this is a function of the rate of hydrolysis. It is however also a function of the biomass concentration because of the change in yield. It will now be discussed whether, or under which conditions, the change in yield is of negligible influence, so that parameters can be defined under which the OUR measured can be used to estimate hydrolysis.

It was demonstrated that the rate of uptake of substrate is equal to the rate of hydrolysis. The OUR_l is given by equation 37, derived from equations 3 and 14.

$$OUR_l = R_{hydr,l} - \frac{d[X]_l}{dt} \qquad 37$$

The biomass growth under substrate-limited conditions is given in equation 34. Substitution of equation 34 and 35 in equation 37, using the definition for C and dividing by the hydrolysis rate gives:

$$\frac{OUR_l(t)_S}{R_{hydr,l}} = 1 - \left(1 - \frac{m_S}{q_{max}} * C(0)_S\right) e^{-m_S Y_{S,max} t} * Y_{S,max} \qquad |C \geq 1 \qquad 38$$

Equation 38 gives the expected change in the ratio of the OUR_l to the rate of hydrolysis during the substrate limited phase of an OxiTop measurement. The formula is plotted in figure 3 for three different values for $C(0)_S$, using standard values for q_{max} and m_S from wastewater treatment. The ratio of q_{max} to m_S limits C to a maximum of ten. With q_{max} 0.25, the maximum active biomass content that can be maintained during the substrate limited phase is forty times the hourly COD production from hydrolysis.

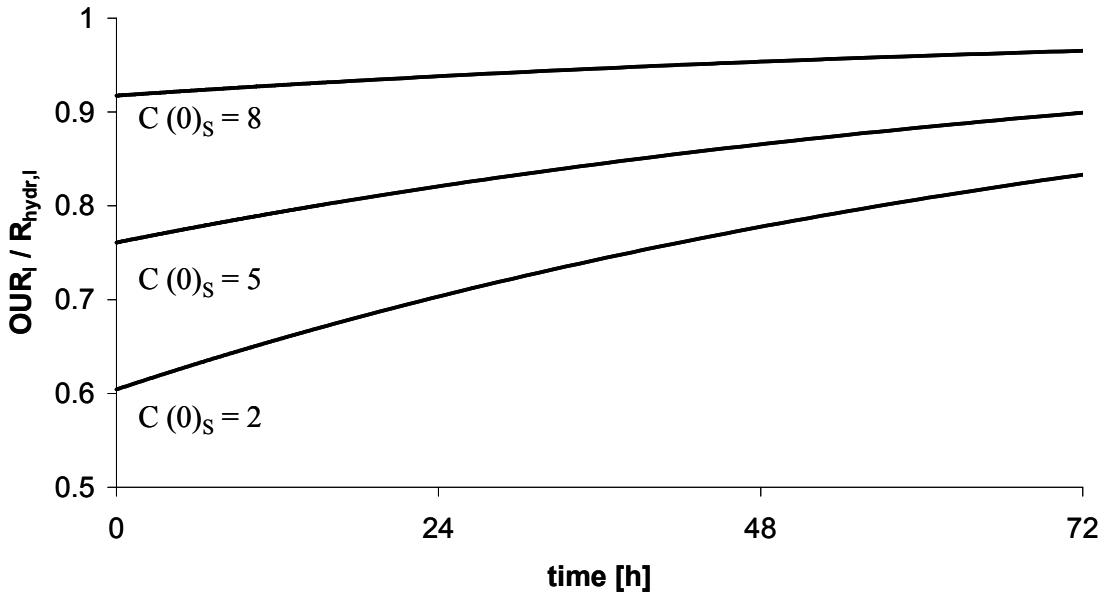

Figure 3 The ratio of oxygen uptake rate to the hydrolysis rate as a function of biomass and time. Biomass expressed as $C(0)_S$. (q_{max} = 0.25 [h^{-1}], m_S = 0.023 [h^{-1}], $Y_{S,max}$ = 0.5)

From figure 3 it can be seen that as expected the measured OUR depends on the capacity ratio C, as the OUR is linearly related to the OUR_l. The amount of biomass present determines the yield on substrate. Exact values depend on the characteristics of the biomass, but measured values of the OUR are predicted to be 60-95% of the rate of hydrolysis. It can also be seen that it is expected that the ratio of OUR to hydrolysis rate will increase somewhat during an experiment due to growth. As growth is much faster for a low capacity ratio than at a high ratio, the OUR to rate of hydrolysis ratio can be estimated to be 0.8 for most practical conditions.

Conclusions

The evaluation of the growth model showed that the growth model is in accordance with the working hypothesis that hydrolysis will determine the OUR during the substrate limited phase. Measurements in the OxiTop can be performed down to oxygen partial pressures of 5 kPa, and possibly even lower. For other systems this lower oxygen pressure value can depend on K_1, the gas to liquid oxygen transfer coefficient. If K_1 is large enough, as in the OxiTop, the lower limit is determined by the gas to liquid equilibrium concentration ratio of oxygen, m_{O_2}, and the efficiency with which the biomass can take up oxygen, K_{M,O_2}.

Table 1 Accuracy of the measured hydrolysis rate by measuring the OUR during substrate limited growth, using standard wastewater treatment values for q_{max} and m_S. $K_1 > 2\ h^{-1}$, $P_{O_2} > 5$ kPa.

C	OUR / $R_{hydr,l}$	Growth conditions
C > 2	0.6 – 0.95	The increase in substrate concentrations, relative to the rate of hydrolysis, is negligible. All hydrolysed substrate is taken up by the biomass and either incorporated in new biomass or oxidized to CO_2 and H_2O.
2 < C > 8	0.6 – 0.9	The OUR is a measure for the rate of hydrolysis, but biomass growth is not negligible. Because of change in the yield of biomass on substrate, the hydrolysis, in COD units, is between 1 and 1.5 times the OUR.
C > 8	> 0.9	The OUR is a direct measure for the rate of hydrolysis. Biomass growth is very slow, so the production of new cells is negligible. All hydrolysed substrate is taken up by the biomass and is oxidized to CO_2 and H_2O.

The results and conclusions are summarised in table 1. The key factor for measuring the hydrolysis rate is the capacity ratio C. The ratio has to be larger than 1, as otherwise the OUR cannot be substrate limited. To avoid interaction with a

possible limitation by low oxygen concentrations, a C of two is minimally required. Under these conditions an estimate for the hydrolysis can be given. There is an inherent inaccuracy because of the variance in yield. To eliminate this variance a capacity ratio of 8 is required.

5.4 Materials and Methods

Model calculations

The system of growth and mass transfer, given in equations 8 through 20 was programmed into a MathCAD procedure. This model was used to calculate the change in pressure in an OxiTop as a function of time depending on sample characteristics. The fall in pressure is used to derive the substrate limited OUR. This was done with the calculated pressure data, using the same method as is used for evaluating OxiTop measurements in our lab. In this method, the pressure data is plotted against time in a graph, and visually a linear portion of the graph is selected. From this selected data the OUR is calculated by linear regression of the pressure data, expressing the slope in mol oxygen per hour.

In the model the rate of hydrolysis is a parameter with a constant value. As the main objective of this research was to find a method to measure the rate of hydrolysis of sample materials, the "measured" OUR was divided by the rate of hydrolysis. From the results presented in the previous section, this ratio was expected to be 0.8 ± 0.1. The data obtained were plotted in a graph to give a normalized estimate of the influence of the parameter used for the x-axis, usually the sample size.

Oxygen Uptake Rate measurements

Experiments to measure OUR were conducted using the OxiTop as described in chapter 4. Carbon dioxide was captured using cup model 3. Samples were suspended in a growth medium, based on the standard BOD medium according to the (APHA 1992). Buffer capacity, nutrient concentrations and nitrification inhibitor concentrations were increased to compensate for the increased amount of volatile solids and activity per unit volume as described by Veeken (2003).

Method

Four solutions are prepared and kept in stock until use:

A	43.08	[g L^{-1}]	KH_2PO_4
	88.86	[g L^{-1}]	$Na_2HPO_4*2H_2O$
B	4.31	[g L^{-1}]	NH_4Cl
	5.39	[g L^{-1}]	$CaCl_2*2H_2O$

	4.31	[g L^{-1}]	$MgSO_4*7H_2O$
	54	[mg L^{-1}]	$FeCl_3*6H_2O$
C	2.00	[g L^{-1}]	$FeCl_3*6H_2O$
	50	[mg L^{-1}]	$NiCl_2*6H_2O$
	500	[mg L^{-1}]	$MnCl_2*4H_2O$
	30	[mg L^{-1}]	$CuCl_2*2H_2O$
	50	[mg L^{-1}]	$ZnCl_2$
	50	[mg L^{-1}]	H_3BO_3
	2.00	[g L^{-1}]	$CoCl_2*6H_2O$
	100	[mg L^{-1}]	$NaSeO_3*5H_2O$
	90	[mg L^{-1}]	$(NH_4)_6Mo_7O_{24}*4H_2O$
	1.00	[g L^{-1}] EDTA	(ethylene-diamine-tetra-acetic acid; $C_{10}H_{16}N_2O_8$)
	1.00	[ml L^{-1}]	HCl (36%)
D	4.0	[g L^{-1}]	ATU (N-Allylthiourea; $C_4H_8N_2S$)

A sample was weighed into a bottle (Schott, 1L). To this 180 ml tap water, 10 ml A, 10 ml B, 0.2 ml C and 2.5 ml D were added. The bottles were sealed by screwing the caps (OxiTop, WTW), fitted with cup 3 (chapter 4) filled with soda lime pellets (Merck), on, and the data collection period was set and started. Then the bottles were placed in a temperature controlled incubator (Innova 4000 or Gallenkamp orbital shaker) at 30°C, and shaken at 120 rpm.

The volume of the bottles averaged 1130 ml. Gas phase volumes for the separate measurements were determined by subtracting added volumes of sample, water, buffer, absorbent and other chemicals from the average bottle volume by using the following conversion factors: liquids 1000 ml kg^{-1}, volatile solids 1400 ml kg^{-1}, and ash 2300 ml kg^{-1}. The pressure drop rate was determined from a linear section of the pressure versus time plot obtained from the data.

Model sensitivity analysis

The MathCAD model used for the calculation of pressure drop graphs requires many input parameters. These parameters can be divided into three groups: 1 sample parameters, 2 biomass parameters and 3 OxiTop parameters. To confirm that the rate of hydrolysis is the major parameter determining the outcome of the model calculations a sensitivity analysis was performed.

To keep the number of model runs reasonable, a standard material and set-up were used, the parameters are listed in table 1. The standard material is fairly stable, with a rate of hydrolysis, R_{hydr}, of 25 $mmol_{COD}$ $kg_{VS}^{-1}h^{-1}$, i.e. somewhere between compost and fresh manure. A medium to high carbon dioxide content, $CO_{2,SM}$, and a low soluble substrate content, S_{SM}, were chosen. The biomass

content, X_{SM}, was chosen to have a maximum rate of substrate uptake that was slightly lower than the rate of hydrolysis (C <1), so that the biomass has to grow before an accurate estimate of the rate of hydrolysis can be obtained. The standard calculation was done using the standard OxiTop set up from chapter 4 modified to improve carbon dioxide absorption (cup 4, highest measured value of K_3), and the measured oxygen transfer rate, K_1. An input sample mass of volatile solids, M_{SM}, of 7.5 g was used, corresponding to a liquid phase rate of hydrolysis, $R_{hydr,l}$, of 1 mmol $h^{-1}L^{-1}$ This was expected to produce a rate of respiration that would deplete the oxygen supply completely in 40h.

Table 1 Value of parameters used in the standard run for OxiTop model evaluation

	Sample Parameters	value	unit
M_{SM}	Mass of hydrolysable volatile solids	$7.5*10^{-3}$	[kg_{VS}]
R_{hydr}	Hydrolysis Rate of the volatile solids	25	[$mmol_{COD}$ kg_{VS}^{-1} h^{-1}]
$CO_{2,SM}$	Carbon dioxide in sample material	22	[g_{CO_2} $kg_{M_{SM}}^{-1}$]
S_{SM}	Free substrate in sample material	5	[g_{COD} $kg_{M_{SM}}^{-1}$]
X_{SM}	Active micro-organisms in sample material	2	[g_{CODX} $kg_{M_{SM}}^{-1}$]
	Biomass Parameters		
m_S	Maintenance requirement	0.023	[COD(S) COD(X)$^{-1}$]
q_{max}	Maximal substrate uptake	0.25	[COD(S) COD(X)$^{-1}$]
$Y_{S,max}$	Maximal yield	0.5	[COD(X) COD(S)$^{-1}$]
K_S	Affinity constant for substrate	0.5	[$mmol_{COD}$ L^{-1}]
K_{O_2}	Affinity constant for oxygen	0.05	[mmol L^{-1}]
	OxiTop Parameters		
V_l	Volume of the liquid phase	0.2	[L]
V_g	Volume of the gas phase	0.9	[L]
K_1	Gas/liquid O_2 mass transfer coefficient	1.9	[h^{-1}]
K_2	Gas/liquid CO_2 mass transfer coefficient	1.9	[h^{-1}]
K_3	Gas/solid CO_2 mass transfer coefficient	2.9	[h^{-1}]
pH	Acidity of the liquid phase	7	

The sample parameters are all expressed on the mass of hydrolysing volatile solids, M_{SM}. When comparisons with real samples are made, M_{SM} is considered the sample size. Biomass and free substrate are also sources of volatile solids, but because the model was written to compare hydrolysis measurements their quantities are not incorporated in M_{SM}. The materials this work focuses on have

large amounts of particulate organic matter that can potentially be hydrolysed, so that biomass and free substrate usually have a negligible contribution to the volatile solids content. In the standard material composition used for model calculations they contribute less than 1% of the volatile solids.

Using this parameter set, the OUR was determined as described in the previous paragraph. A requirement for this is that the pressure drops linearly with time during at least part of the time. The procedure was repeated, varying one parameter by lowering its value by 10%. This was done with every parameter, always keeping the other parameters at their standard value. From the newly derived OUR values the percent change from the standard value was determined.

5.5 Results

Obtaining the hydrolysis limited OUR from pressure drop measurements

From the theoretical model analysis, we may conclude that the OUR during substrate limited degradation can be measured with an OxyTop. This measurement provides a good estimate of the rate of hydrolysis provided:

- sufficient biomass is present
- sufficient oxygen is present.

The results of the evaluation of the model showed that oxygen limitation is less important if the degradation is actually substrate limited. A low gas phase oxygen concentration can provide sufficient oxygen. This theoretical evaluation only shows it is possible to measure the hydrolysis rate, but does not answer the question whether a specific OUR measurement actually fulfils these requirements on oxygen and biomass. The question is: How can one conclude from an OUR measurement that the measurement is adequate to estimate the rate of hydrolysis?

From the theoretical evaluation it is clear that we may need to wait for the degradation in the OxiTop to reach the substrate limited phase. Depending on sample characteristics, this could be reached within a few hours, or it could take more than a day. (If it takes even longer, the assumptions on which the model is based will no longer be valid.) It is also clear from chapter 4 that once the substrate limited phase is reached time is needed to prevent the measurement being affected by CO_2 pressure equalization. Depending on the K_3, and the amount of CO_2, this can be a few minutes to several hours. The question thus becomes: How can one distinguish between the different phases, using only the obtained pressure data?

It can be argued that the presence of a sustained linear pressure drop is a clear indication of substrate limited growth that is neither limited by biomass nor by oxygen. It is general practice to equate a linear drop with the stability of compost.

The initial phase is dominated by unlimited growth or equalization of carbon dioxide. This is followed by a linear phase where growth is substrate limited. After this oxygen becomes the limiting factor. If changes in carbon dioxide pressure are disregarded the expected result is an initial period of accelerating drop in pressure and a final period of decelerating fall in pressure. The transition between these phases will appear linear whether a substrate limited phase occurs or not.

The variation of the OUR with sample size

To be able to measure the substrate limited activity, the sample has to be limited in size because large samples become oxygen limited before they become substrate limited. On the other hand the sample should not be too small, otherwise the experiment takes too long and or the sampling is no longer representative. As an application of the model we will investigate the issue of the sample size.

In figure 4 the results of model calculations for a range of sample sizes, using the standard parameter values from table 1 (except for M_{SM} and K_3) are shown. The numbers next to the lines in the graph are the hydrolysis rate in the system ($R_{hydr}*M_{SM} \equiv R_{hydr,l}*V_l$, equation 8). This entity is proportional to sample size, and is used because it allows for easier comparison between samples with different rates of hydrolysis, R_{hydr}. The initial rise in pressure is due to the fact that the initial gas phase carbon dioxide concentration is set to zero. The rise gives an indication of the partial pressure of the carbon dioxide.

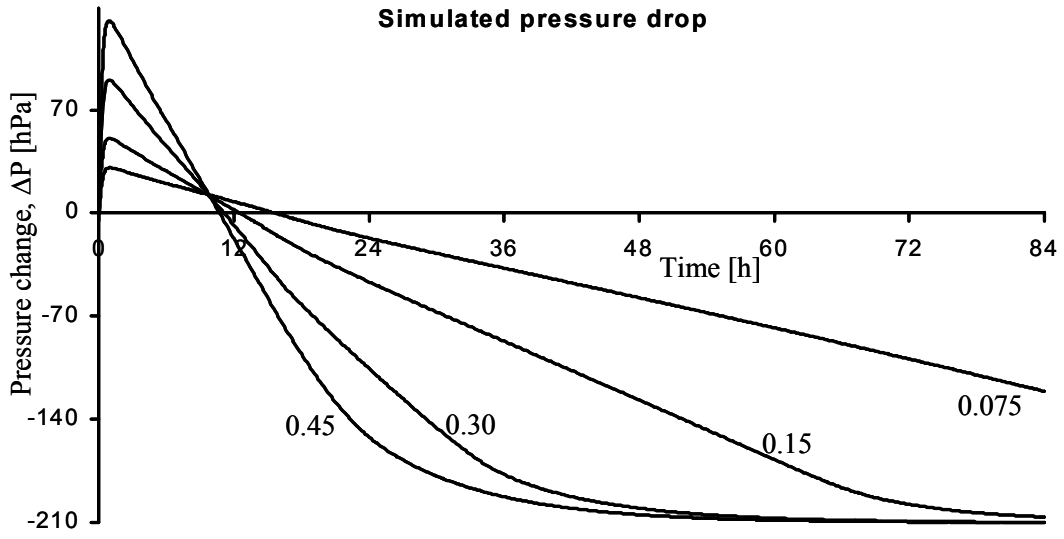

Figure 4 Pressure change graphs calculated by the OxiTop model. Numbers on the graph indicate the rate of hydrolysis of the sample, $R_{hydr}*M_{SM}$.

The graphs in figure 4 seem linear during long time intervals. The smallest sample shown looks completely linear, it certainly would in a real experiment, as the data

from real OxiTop experiments has a much smaller resolution. The largest sample seems biphasic: linear to 20h then decay. The middle samples seem to have two consecutive linear phases, the second beginning after approximately 20 hours followed by decay after 36h and 70h respectively.

In figure 5 the ratio of the rate of hydrolysis used for the simulation to the OUR derived from the pressure data is plotted against the sample size. A limited number of the simulations used to obtain this graph were also used for figure 4. The pressure graph shown as figure 4 was used to determine the linear sections used for the hydrolysis estimate. For the sample sizes with a total hydrolysis rate of 0.3 mmol h^{-1} and smaller, the data from 20 hours, until the pressure reached -140 hPa was used. For the larger samples, the pressure range from -50 to -100 was used.

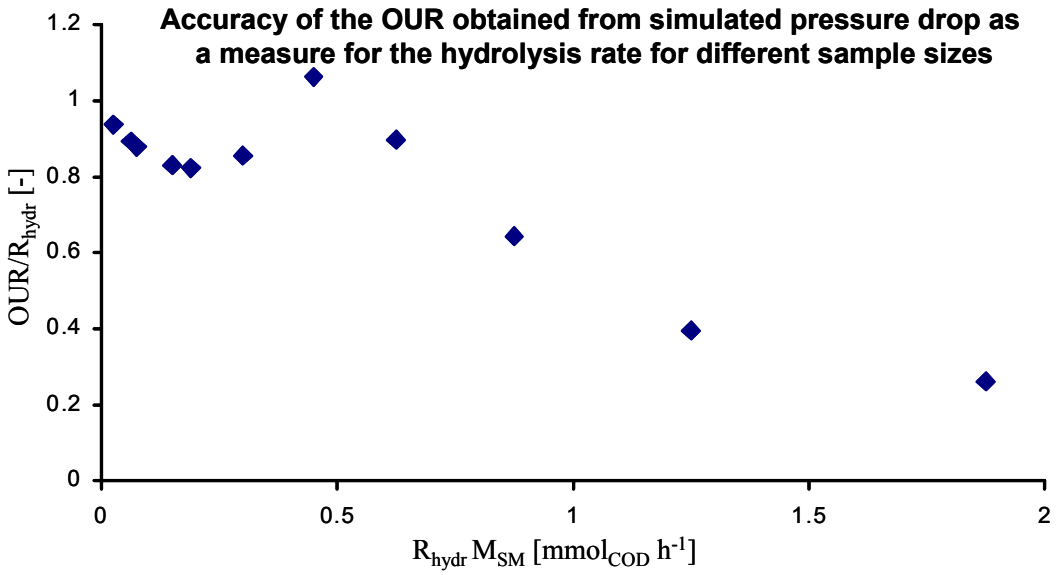

Figure 5 Ratio of the OUR measured from the model's pressure output and the rate of hydrolysis used for the simulation, as a function of the substrate production in the system by hydrolysis.

Figure 5 shows the value of the OUR calculated varies with the sample size. Obviously there is need for a better method to determine the validity of a measurement and the interval of the pressure data that best describes the sample, than linearity of the pressure decrease with time. Each pressure versus time curve was, or at least appeared to be, linear during some time of the measurement, and by using only this criterion every point on the graph of figure 5 could be considered an accurate measurement of the activity. It is clear more criteria are needed, before an accurate measurement of the hydrolysis rate can be done.

The effect of carbon dioxide

To investigate the pressure drop more closely, the pressure graphs of figure 4 were converted to "OUR" graphs, by determining the pressure change rate continuously from two consecutive data points on the pressure time curve. In figure 6 the result is shown for the same data as presented in figure 4. In figure 6 two consecutive constant levels for the pressure drop can be distinguished. The first starts shortly after incubation and lasts for approximately 15 hours, after which the rate of pressure change slows. After 20 hours of incubation the second period with a constant pressure drop starts. It can also be seen that when the oxygen runs out, the pressure change quickly declines to zero. In the largest sample, the oxygen runs out before the second period, so that only one period with a constant pressure drop can be seen.

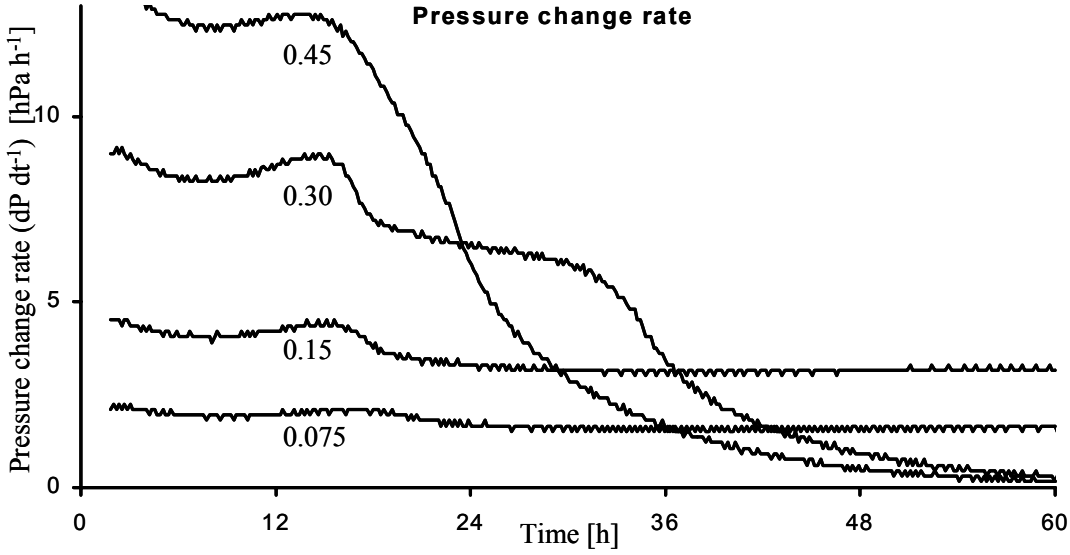

Figure 6 Rates of pressure change predicted by the model. Graphs shown for four values of R_{hydr}*M_{SM} [$mmol_{COD}$ h^{-1}] using standard material.

The pressure calculated by the model is the sum of the change in partial pressure of oxygen and carbon dioxide. From figure 6 it can be inferred that the desired information is obscured by changes in carbon dioxide partial pressure. From the growth model it is expected that an exponential growth phase, where the rate of pressure change increases, is followed by a hydrolysis limited phase where the rate of pressure change is near constant. Carbon dioxide absorption and exponential growth interact so that it seems there is a constant pressure drop during the first 15 hours. Measured OUR values here are, in part, caused by the depleting carbon dioxide concentration. During actual measurements it is quite plausible that the linearity of the pressure change is interpreted to indicate substrate limited growth, leading to mistakes.

The sudden change in the rate of drop in pressure after 20 hours was observed in figure 4 for the middle samples (0.15 and 0.30 mmol h^{-1}), so it would have been possible to discard the values obtained from samples with a rate of hydrolysis of 0.45 mmol h^{-1} and above. However, this interpretation is only possible if data from smaller samples was available! As a single measurement, the observed constant pressure drop from the larger samples would give no reason to doubt the estimated hydrolysis rate.

The effect of sample size

The purpose of the measurement is to measure the change in oxygen partial pressure during the substrate limited respiration phase. With the transition from exponential growth to substrate limited respiration identified at 20 hours, a more accurate measurement of the relation of the OUR with sample size can be obtained. Figure 7 is based on the same data as figure 5, but using different time frames to estimate the OUR. The first time frame uses the data from 26 hours until the pressure reaches –140 hPa, the second uses the time interval from 26 through 29 hours. The time frames are chosen to start at 26 hours, so that the gas phase carbon dioxide concentration can be adjusted to the now constant OUR. In chapter 4 it was calculated that this would take approximately six hours.

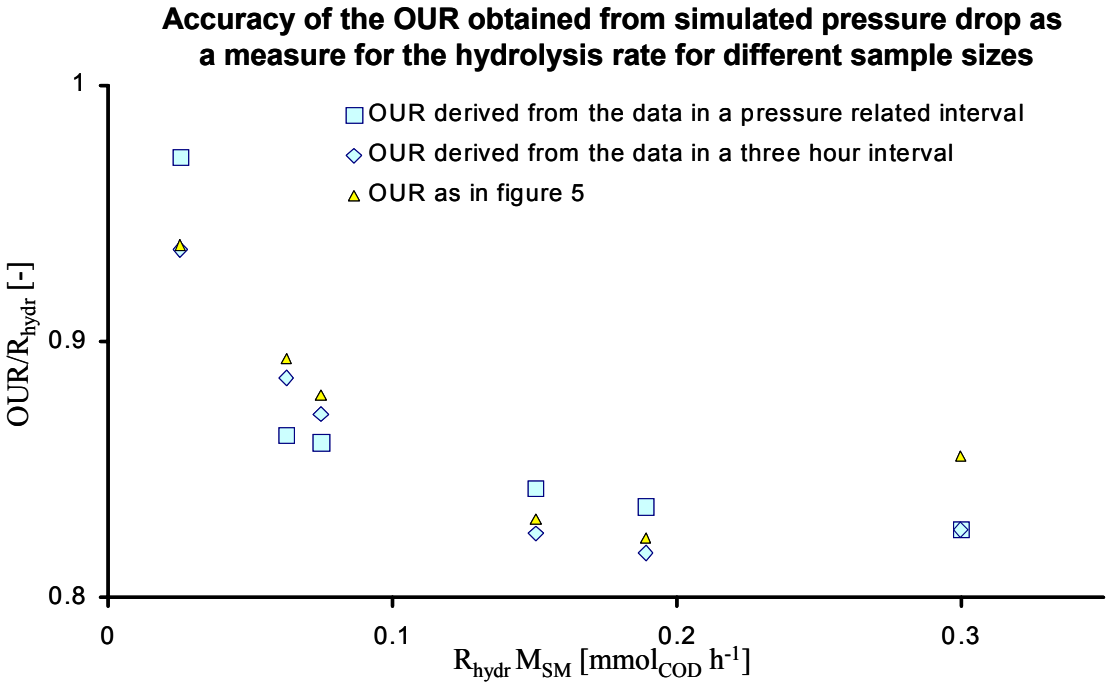

Figure 7 Ratio of the OUR measured from the model's pressure output to the rate of hydrolysis used for the simulation as a function of the substrate formation from hydrolysis in the OxiTop.

In figure 7 it can be seen that the measurement of the hydrolysis rate has improved from figure 5 by omitting the larger samples that were biased by gas phase carbon dioxide concentration changes. Also, taking the measurement at a somewhat later time the pressure related time intervals yield a more constant result than the three hour interval, and the interval used for figure 5. There is still a variation in measured OUR with the sample size. The smaller the sample the higher the measured OUR. The largest OUR found is 19% higher than the smallest OUR found. This is quite a large difference, and as long as the origin of this effect is not identified, there is no certainty that the effect could not be (much) larger under other circumstances.

The observed effect can be explained by inspecting the model more closely. Smaller samples are diluted more by the aqueous medium. For small samples this can lead to initially lower growth rate because of low substrate concentrations. In the suspension the substrate concentration will slowly rise, as the rate of hydrolysis is larger than the rate of uptake of substrate, so the activity increases, leading to an exponential growth phase followed by a substrate limited phase. It takes longer for the rate of uptake of substrate to equal its rate of formation because the bacteria grow more slowly, or start to grow later. Once the combination of the capacity ratio, C, and the substrate concentration becomes large enough, the substrate concentration drops again and any further change in substrate concentration follows the line given by equation 31.

The net result from the model, obtained by analysing numerous simulations, is that the capacity ratio C at any time during simultaneous measurements of the same material is similar for all samples that have reached the substrate limited phase, irrespective of sample size. However, the time passed before the substrate-limited phase begins is longer for smaller samples. If a common timeframe is used to determine the OUR in a range of sample sizes, the smaller samples may still be in the exponential growth phase, and yield a larger OUR. For very small samples it could even be a smaller OUR, if exponential growth is still limited by low substrate concentrations. In figure 7, the smallest sample is still in the exponential phase during the three hour interval. The two next smallest are carbon dioxide influenced, as the transition to substrate limited respiration was less than six hours before the measurement.

The measured substrate limited OUR increases as time passes. This is the effect of substrate limited growth, as was shown in figure 3. In a range of sample sizes, the ones where the timeframe starting latest, or lasting longest, is used will give a higher OUR. These are usually the smaller samples. In figure 7, the OUR is derived from the data obtained after 26 hours, until the pressure reached –140 hPa.

Obviously this takes longer for small samples, as they have a smaller oxygen consumption.

The model predicts that in a range of sample weights, the smaller samples will have a larger respiration rate. This may be due to using different time frames or by measuring during exponential growth. When this is caused by a larger capacity ratio C, due to measuring later, the effect is relatively small, and the higher OUR of the smaller samples is closer to the rate of hydrolysis than the OUR measured for large samples. If however the OUR is measured during exponential growth, the error in estimating hydrolysis can be substantial.

The dilution effect only affects small samples where the initial substrate concentration is low enough to inhibit growth. In figure 7 it can be seen that for somewhat larger samples the OUR found is relatively constant at 83% of the hydrolysis rate. This is therefore considered the most accurate respiration value that can be obtained from the OxiTop measurement, as it gives information over a sample property.

Conclusion

From the growth effects described in the previous paragraphs, it can be concluded that there is a limited band of sample weights that can be used to estimate hydrolysis. On the one hand the measurement should last longer than the exponential growth phase, on the other hand a reasonable pressure drop in not too long a time is wanted. A range of sample weights has to be measured to obtain sufficient reliable measurements, as it is impossible to determine suitable weights beforehand. It will be more difficult to find the right sample quantity for unstable samples, as the time spent in exponential growth narrows the band of suitable weights.

Measuring a range of sample sizes is also necessary to assess which experiments contain reliable information on the rate of hydrolysis. It is very time consuming to convert OxiTop pressure data into a pressure drop rate graph as figure 7. It is easier to evaluate OUR graphs like figure 5, in which a range of sample sizes is compared for OUR's. Normally it suffices to compare "hydrolysis" values determined during an appropriate time interval for the separate samples sizes, as in figure 5. OUR data obtained from a range of sample sizes, and presented in this way, will allow for an accurate estimation of the OUR during the hydrolytic phase. Model calculations suggest OUR values to be 80 $\pm$ 10% of the rate of hydrolysis.

OUR measurements compared to model predictions

To test whether the predictions made by the model could be observed in real measurements, the OURs of a range of materials were measured:

Three week compost	**Composted pig manure, fresh from the compost reactor where it had been composted for three weeks**
Pig Manure	**Freshly separated pig manure solids**
Compost	**Composted pig manure, kept in a dry place for some weeks after composting**
Stable Compost	**Cured compost from pig manure.**
Green waste	**Crushed and cut wood trimmings**
Sewage sludge	**Secondary sludge from a municipal wastewater treatment plant.**
Composted biowaste	**Source separated municipal solid waste, organic fraction, freshly composted for three weeks.**
Washed biowaste	**Source separated municipal solid waste, organic fraction washed on a sieve to remove small particles.**

The OUR measured with OxiTops, measured by using a linear section, are given in figure 8. The relations found between sample size and the measured OUR coincide with model predictions. Analysing the change in measured OUR as given in figure 8, using the raw data as a check, it can be concluded that various processes caused the observed trends in the OUR.

The measurement of stable compost and composted biowaste is without problems. This is because sufficient biomass is present, there is little or no free substrate that has to be consumed first, and carbon dioxide concentrations in the compost are low. The smallest sample of the composted biowaste gives a lower OUR than the other samples. This could be because of difficulties in constructing a representative sample in such small quantities.

Digested sewage sludge and compost both contain high quantities of carbon dioxide. Both show an initial increase in measured OUR with the sample size, followed by a decrease. This is the result of misinterpretation of the pressure graphs by focussing on a linear pressure drop with time.

In the largest samples the oxygen running out causes a sudden drop in the pressure drop rate, similar to the drop observed when the exponential growth changes to substrate limited growth. The high carbon dioxide concentration that is removed fast can seem linear at first glance (see figure 4, 0.45 mmol h^{-1}). This leads to pressure graphs that seem to have the most linear section after oxygen depletion. The pressure decrease measured is therefore pure carbon dioxide absorption by the absorbent. Because the amount of CO_2 produced from using all

the oxygen in the bottle is constant, the relative amount of CO_2 per gram of sample decreases. Therefore the pressure depletion rate per gram of sample decreases.

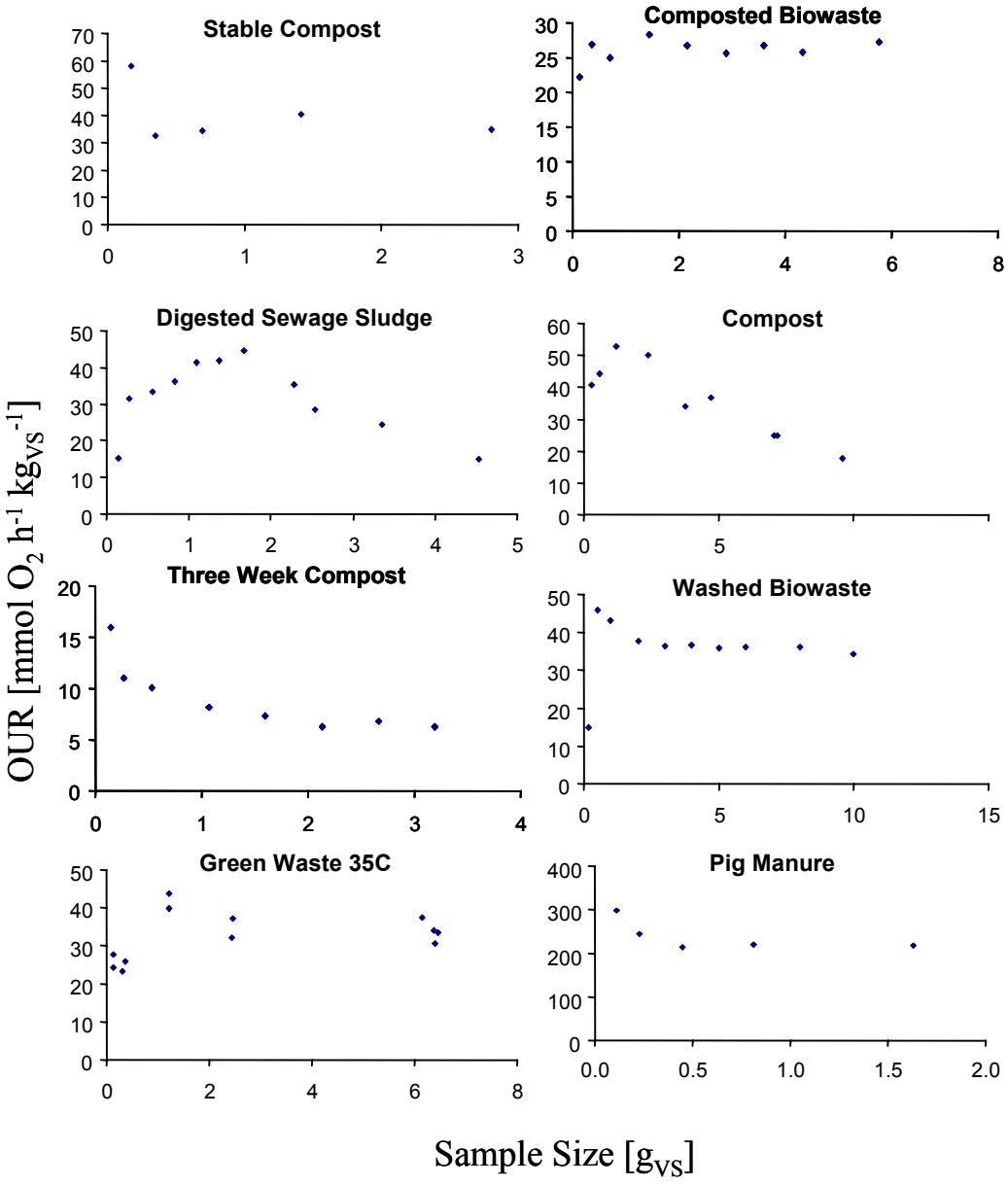

Figure 8 Measured OUR as a function of sample size for various materials.

For the smaller samples, where the OUR-measurement is performed before oxygen is depleted, the relation found depends on whether the same timeframe is used for all samples, and the ratio of the OUR to the carbon dioxide content. In general, the model calculations predict a rise in measured OUR with the sample size, as was observed. This is caused by the exponential growth and carbon dioxide absorption interacting as was described with figure 6. The linear pressure drop found by this phenomenom increases more than linearly with sample size, and an increase of the measured OUR with sample size is found.

Three-week compost and washed biowaste show the dilution effect predicted by the model. Because the result seemed reasonable pressure drops were obtained from one uniform timeframe for the small samples (washed biowaste) or even all samples (three week compost). Both materials are characterised by very low free substrate concentrations. The three-week compost as it is measured directly after removal from the compost vessel, and the washed biowaste because soluble material was removed during washing. As can be seen, this low amount of free substrate has a considerable influence on measured OUR.

Green waste is a heterogeneous material with large particles. This can be seen in the measured OUR, as duplicates show a large spread. Despite this, the trend can be seen. There were twelve samples measured. Green waste contains little biomass, so it took three to four days for the four smallest samples to reach the substrate limited phase. None of the six largest samples had enough oxygen to reach this phase, so that their measured rates are all obtained during the exponential phase. If the OUR of the two remaining samples is measured after the exponential phase is completed, it drops to approximately the value found for the smallest four samples. The correct OUR value is therefore 25 mmol h^{-1} kg_{VS}^{-1}. Because this value is the same for a range of sample sizes, the measurement is expected to have yielded the correct value, despite the low biomass content.

The pig manure shows the same effect as three week compost and washed biowaste. The manure is highly degradable, and contains an active biomass. Despite this, the concentration effect seems to occur. This is expected to be due to the very small sample sizes that have to be used. It is advised to adjust the liquid volume when working with such very small samples.

By way of example the pressure graphs of the pig manure measurements were converted to activity (OUR) graphs, equivalent to figure 6. The result, not normalised to sample size, is given in figure 9. As can be seen, the predicted interaction between carbon dioxide absorption and OUR indeed give a constant pressure depletion during the exponential growth phase. The activity given to the pig manure by the measurement at 20 to 26 hours is however in line with the best estimate from figure 9. Because of the carbon dioxide interference it can not be clearly seen why the smaller samples give a higher OUR. There is not an obvious delay in the start of the substrate limited phase for smaller samples, and the measured value should be considered with caution. Note that after 3 weeks of composting pig manure has turned into 3 week compost. The drop in activity is dramatic, although there is some interference from the 10% green waste used for structure in the compost bed.

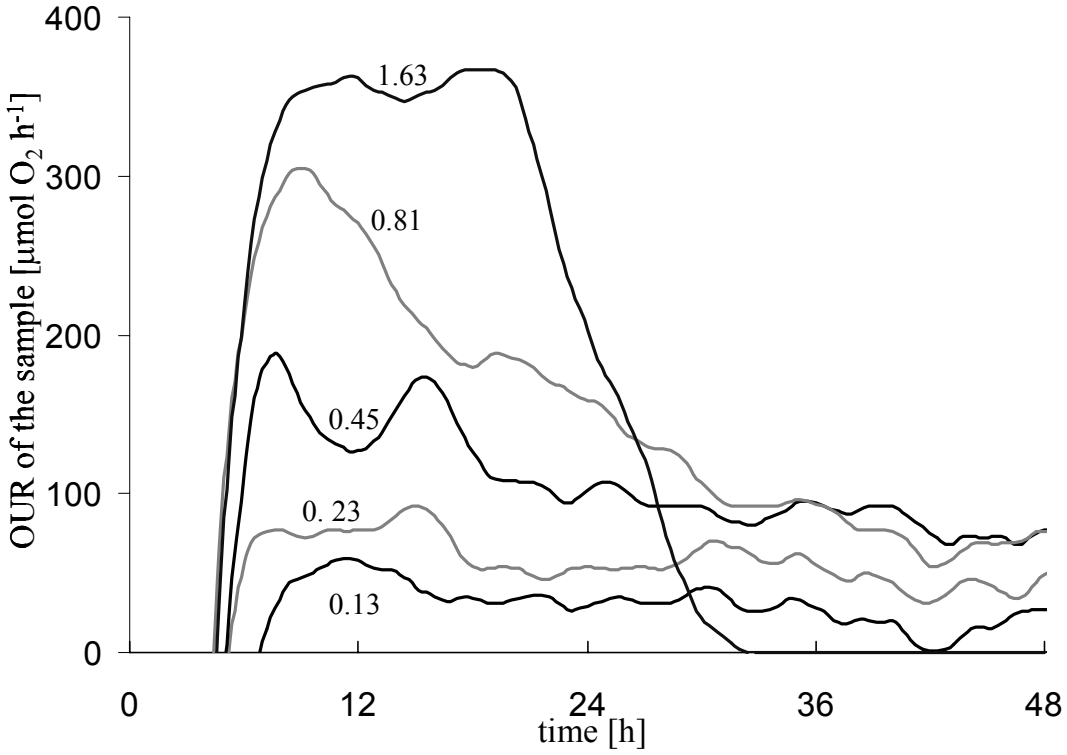

Figure 9 OUR (calculated from the pressure change rate) as a function of time for five different sample sizes of pig manure. Numbers are grams of volatile solids in the sample.

Sensitivity analysis

It was shown that substrate limited respiration is a function of the hydrolysis of the solid organic matter. It is only slightly influenced by other sample parameters such as free substrate and biomass content. Two groups of parameters that are not related to the sample but could influence measurements can be distinguished. On the one hand controllable parameters like liquid volume, shaking intensity, named system parameters, and on the other the biomass properties which are very difficult to control, and mostly unknown. To assess the influence of these three groups of parameters (sample, biomass, system) have on the measured respiration, a sensitivity analysis was performed by comparing model calculations with one parameter changed by 10%.

The results of the sensitivity analysis are given in table 2. The second row gives the OUR calculated from the predicted pressure change for the standard measurement during two separate time intervals (23-24 and 35-36h). The parameters that were varied are listed in the first column. The second column is the value of this parameter in the standard measurement. The third column the value used to assess the sensitivity of that parameter. The last two columns are the percentage change in OUR calculated from the predicted pressure change for the

two time intervals. The changed parameter values used are 0.9 times the standard value, except for the pH where a value of 7.2 was used.

Table 2 Results of the sensitivity check for varied parameters. Calculated value is the substrate limited OUR during the hydrolytic phase. The deviations in outcome from the standard run are given in percentage change from the standard value.

Timeframe used for rate estimation [h]			23-24	35-36
Standard OUR calculated [mmol kg^{-1} h^{-1}]			16.9	17.9
Relevant parameters			Sensitivity	
Varied parameter	Standard value	Changed value	Change in OUR compared to standard value	
Sample parameters				
M_{SM}	7.5	6.75	+0.2%	+0.3%
R_{hydr}	25	22.50	-8.7%	-8.9%
$CO_{2,SM}$	22	19.80	+0.0%	0.0%
S_{SM}	5	4.50	-0.3%	0.0%
X_{SM}	2	1.80	+0.3%	0.0%
Biomass Parameters				
m_S	0.023	0.02	-2.1%	-2.6%
q_{max}	0.25	0.23	+2.8%	+0.7%
$Y_{S,max}$	0.5	0.45	+3.6%	+2.0%
K_S	0.5	0.45	+0.3%	0.0%
K_{O_2}	0.05	0.045	-0.2%	0.0%
System parameters				
V_l	0.2	0.18	+0.3%	0.0%
V_g	0.9	0.81	-0.1%	-0.5%
K_1	1.9	1.71	0.0%	0.0%
K_2	1.9	1.71	0.0%	0.0%
K_3	2.9	2.61	+0.3%	0.0%
pH	7.0	7.20	0.0%	0.0%

The value of the calculated OUR would ideally be 25 mmol kg^{-1} h^{-1} as that was the standard value of R_{hydr} chosen. The model calculations show the resulting OUR is lower than R_{hydr} and increases with time. This is the result of biomass growth, increasing the maintenance requirement of the biomass, so that the yield drops.

This is the expected result from the mathematical evaluation of the growth model. The calculated OUR is 70% of the standard R_{hydr}, so the respiration is at the low end of the expected range.

The model is not very sensitive for most of the sample parameters, as was expected from the previous section. The one sample parameter that was expected to have a big impact is R_{hydr}. As can be seen in table 2 it has the biggest impact of all the parameters on the list. A 10% drop in R_{hydr} does not quite lead to a 10% drop in the calculated value of OUR (as would be expected if OUR = R_{hydr}). The calculated value only drops 8.5 to 9 %, thus improving the estimate of R_{hydr}. This is due to a relative increase in free substrate and biomass, the effect of which was discussed previously.

From table 2 it can be seen that most system parameters have little influence on OUR, as changes are less than 1%. It can be concluded that, according to the model, the measurement is insensitive to the system parameters. The chosen value for the parameters may be wrong (K values) or change from experiment to experiment (liquid and gas volumes, K values if the shaking intensity or measurement temperature is changed), but model calculations indicate that only very different values would substantially influence OUR. If the chosen values are approximately correct, the model can be used to estimate effects caused by changing sample parameters, and the system is suitable to measure substrate limited respiration.

The carbon dioxide mass transfer rate coefficient, K_3, used for the sensitivity analysis is larger than the K_3, of the actual measurements. This was done to see the effect of the other parameters more clearly. The effect of the carbon dioxide absorption was discussed separately (see chapter 4). Also a better cup for the carbon dioxide absorbent has been developed recently. This cup was described in chapter 4 as cup 4.

From table 2 it can also be seen that the model is affected by the chosen biomass parameters, especially the maintenance and yield. However, the equations used to estimate these parameters have been shown to be widely applicable with a satisfactory accuracy. The maximum yield is very constant for aerobic growth, and the maintenance can be estimated with a 40% accuracy (Heijnen 1999). Very large variations can be found in published values for q_{max} and K_S, with a spread over three to four orders of magnitude. This can give large errors due to changes in the substrate concentration. It is however expected that the variation in q_{max} and K_S for the bulk of the substrate formed by the hydrolysis of the polysaccharides (usually the most abundant compounds) will be less.

The results of these calculations indicate OUR is 70% of R_{hydr}, which is close to the value (70-90%) predicted earlier. The sensitivity analysis shows only R_{hydr} has any significant influence on the OUR during the hydrolytic phase. Due to uncertainties in the biomass parameters it will not be possible to predict the ratio of OUR to R_{hydr} more accurately than the estimate given, but the effect of changes in sample parameters on the measured R_{hydr} can be investigated.

5.6 Conclusions

With the modified OxiTop it is possible to measure the hydrolysis limited OUR of active organic solid materials reliably within two days. However, this is not possible when little active biomass or a lot of free substrate is present because this prevents the system reaching substrate-limited respiration within 48 hours.

The determination of the substrate-limited respiration rate is the best characterisation of the degradation rate of organic solid material. The measurement outcome is only slightly influenced by other sample parameters like active biomass and free substrate content. Other methods for determining a respiration rate have the disadvantage that very different combinations of sample parameters can give the same result.

The respiration measurements can be used to estimate the hydrolysis rate of the organic solid material. It was shown that the ratio of the OUR to the hydrolysis rate is between 0.6 to 1.0. Using an average value of 0.8 this measurement of the rate of hydrolysis has an accuracy of 25% for samples with very little or a very high content of active biomass. For typical samples the accuracy will be around 10% or better.

The carbon dioxide absorption system used for the experiments in this chapter (cup 3 in chapter 4) can be used to measure the hydrolysis rate. However, expert insight is needed to interpret the pressure change and OUR versus sample size graphs correctly. Carbon dioxide can cause problems by obscuring the change in respiration rate during transition from exponential to substrate limited growth. This makes the pressure data difficult to interpret. Therefore fast absorption of carbon dioxide is essential for on-farm use of the system, and cup 4 (chapter 4) has to be used. This will also increase the sample size that can be measured, and will therefore make the measurement more accurate.

The growth model constructed for the batch system with hydrolysing organic solid materials yielded a prediction that has been confirmed: Small samples will take longer to reach the substrate-limited phase if the initial substrate concentration limits the exponential growth phase.

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6

Discussion

6.1 Introduction

This research was aimed at optimising the composting of separated pig manure solids within the Hercules system. The objectives of composting were:

- To produce a high quality compost.
- To recover ammonia and heat from the composting process for reuse by cooling the hot process gas.
- To minimize the amount of emitted gas, reducing the cost of possible waste gas treatment.
- To reduce the emission of ammonia and other volatile compounds to the atmosphere by recirculating the cooled process gas. Possibly this could make waste gas treatment unnecessary.

Recirculation of the process gas means that the oxygen content of the gas phase in the compost bed is lowered. Therefore, research was required to investigate the effect of lowering the oxygen concentration on the composting process. From these results and from subsequent composting trials using the different types of pig manure solids available it was concluded that:

- The low oxygen composting process is more sensitive to physical disturbance of the compost bed than conventional composting.
- The pig manure solids produced in the Hercules system are very variable in both structural strength and the degradability of the organic matter.

From these results it was concluded that for the composting to succeed a reliable operator instruction had to be developed on the basis of measurable qualities of the pig manure solids. The measurements had to be easy to perform (preferably on location by non-specialists), and had to provide results within a few days. From literature and from a theoretical evaluation of the composting process two protocols for measurements on solid manure and subsequent data analysis were developed and tested in this research:

1. A simple volume based prediction of maximum activity of a compost bed to evaluate the bed structure.
2. An activity test with an increased potential for predicting organic matter degradation compared to traditional activity tests.

To fully understand the background of these tests it is necessary to understand the conceptual theoretical basis used to explain the phenomena observed during composting. Therefore, this chapter will start in section 1.1 with a brief overview of the theoretical background. It will discuss how the results of this research fit in with the theory, and how they have helped to develop the theory further. Thereafter,

in section1.2, the concept of the low oxygen composting system will be discussed. In sections 1.3 and 1.4 the background, practicality and applicability of the two measurements will be discussed. In section 1.5 a method will be given to construct compost beds on the basis of the measurements developed. Finally, in section 1.6 it will be described how the composting system is currently integrated in the Hercules system.

6.2 Theoretical model of the composting process

In this thesis the particle based composting model (Hamelers 2001) is used to explain and predict the composting process. The conceptual basis of the model is relatively simple. This allows for a conceptual evaluation of the composting process, so that critical factors can be evaluated for their response to a change in operating regime.

The particle based composting model combines three important conceptual ideas:

1. It is assumed that two sources of organic substrate can be identified. Available substrate that can be consumed directly by the micro-organisms, and hydrolysable substrate that has to be hydrolysed by exo-enzymes before it can be consumed by the micro-organisms.
2. It is assumed that the particles and the surrounding water phase form aggregates that are free of gas pores. Therefore, a considerable portion of the aggregates will be anaerobic, as the penetration depth of oxygen in an actively oxygen consuming aggregate is much less than 1 mm.
3. It is assumed that the rate of hydrolysis of the particulate organic matter is independent of the oxygen concentration, and will proceed uniformly throughout the aggregate.

Based on model calculations, Hamelers defined four periods from which the evolution of the oxygen uptake rate of a compost bed can be explained. For a single aggregate the oxygen uptake rate in time will show the following consecutive periods:

Biomass growth limited

During this first period the rate of uptake of oxygen by the aggregate increases. The bacteria on the aggregate surface grow. Inside the aggregate the oxygen concentration decreases rapidly with depth, and the growth of bacteria within the aggregate is very much slower than the growth at its surface. The amount of bacteria on the aggregate surface determines the rate of uptake of oxygen by the aggregate.

Biofilm limited

During this second period uptake of oxygen by the aggregate remains high. The number of bacteria on the aggregate has increased and forms a biofilm completely covering the aggregate. The biofilm consumes all oxygen transferred from the gas phase to the aggregate. This transfer limits the rate of uptake of oxygen by the aggregate.

Transition

During this third period the rate of uptake of oxygen by the aggregate decreases. It is no longer limited by oxygen supply. Instead the supply of substrate from the anaerobic core of the aggregate is now the limiting factor. The rate of uptake of oxygen decreases because the concentration of substrate in the aggregate decreases.

Hydrolysis limited

During this fourth period the rate of uptake of oxygen by the aggregate remains constant at a low level. It is limited by the supply of substrate but the concentration of substrate in the aggregate remains constant because it is produced by hydrolysis at the same rate as it is consumed by the biofilm. The total rate of hydrolysis of the particulate organic matter in the aggregate determines the rate of uptake of oxygen by the aggregate.

In a compost bed not all aggregates have the same surface area to volume ratio. Therefore, the composting process of aggregates that differ in size show differences in the duration of the various composting periods. Hamelers showed that by assuming a gamma distribution in aggregate size the cumulative uptake of oxygen by the aggregates normally observed during composting can be explained. Instead of the 4 periods shown by individual aggregates, the process in the bed shows an initial period with a rapid increase in the rate of uptake of oxygen followed by a period of slow decline in the rate of uptake towards a final constant low uptake of oxygen.

From this model it is concluded that two factors are critical in a composting process. The first is the total aggregate to gas phase interface, which determines the oxygen uptake peak of the composting. The second is the rate of hydrolysis of the particulate organic matter, which is the main determinant of the total uptake of oxygen during composting. Both these factors will be discussed in more detail.

Aggregate to gas phase interface

The area of the gas liquid interface, and the oxygen concentration in the gas phase, limit the maximum activity of a compost bed during the initial high rate phase. It is assumed that per unit area the amount of oxygen that can be transferred is limited,

and it is evident that the mass transfer of oxygen over the interface drops when the oxygen concentration is lowered. Therefore, at low oxygen concentration the maximum activity of a bed will be lower than the maximum activity of that bed at high oxygen concentration.

Before the mass transfer of oxygen becomes limiting, the biomass has to grow so that there are enough bacteria. This growth depends on oxygen, and could therefore be affected by lowered oxygen concentrations. The growth model presented in chapter 5 predicts bacterial growth under growth-limited conditions. This model clearly underlines the importance of distinguishing between growth and activity, and between a limiting concentration and a limiting rate.

The oxygen uptake rate of a microbial cell is equal to the catabolic activity [assuming the respiration ratio, α, = 1 (chapter 5)]. Growth is a result of the anabolic activity of a cell. It is known that the anabolic activity is not linearly related to the catabolic activity. This is why the yield of biomass on substrate or oxygen is not constant. If the activity of a cell is low, it will have catabolic activity, but negligible anabolic activity, and the quantity of biomass remains constant.

A cell activity that is so low that the quantity of biomass remains constant is the result of a limiting concentration (of an essential growth substrate), which determines the activity of every individual cell. Two conditions can cause such a low concentration in a system where potentially enough substrate is present. It can either be the substrate is only available in diluted form, or the supply can be limited by physical barriers. If the supply is limited, an increase in biomass will not influence the total activity of the population. The activity of individual cells will drop. If the limiting concentration is not due to a supply limitation an increase in biomass will increase the total activity of the population, but not influence individual cells. This will be the case provided the increase in activity has only a small effect on the concentration.

The fact that no increase in activity was observed during the initial start up at a 5%(v/v) oxygen concentration (chapter 2) means that growth was very slow. The slow increase in activity at low oxygen concentration observed in chapter 2 can be explained by the low concentration at which oxygen is available. The OUR measured (after start up) at 5% oxygen (see figure 4, middle graph, chapter 2) is high enough to support sufficient activity to raise bed temperatures. Therefore, it was concluded that at liquid phase oxygen concentrations in equilibrium with 5% oxygen in the process gas the growth during start up is not limited by the rate of supply of oxygen.

Hydrolysis rate of the particulate organic matter

The hydrolysis theory explains why the aerobic biodegradation by bacteria after three weeks of composting is similar when either the ambient or a low oxygen level is used for the process (see chapter 2). The total biodegradation depends on the rate of hydrolysis of the solid material, which is strongly influenced by temperature. The amount of substrate degraded during the process has to exceed the amount produced by hydrolysis, otherwise highly active and putrescible product is produced.

The model calculations published by Hamelers (2001) and the growth model used in chapter 5 indicate that the mass of active biomass is small compared to the total mass of volatile solids. This is confirmed by published estimates of the biomass during composting and in the soil (Insam and Parkinson 1989; Haug 1993). It is assumed that after death, the bulk of a bacterial cell is easily degradable, and that cell death does not occur readily in a viable population (Loosdrecht and Henze 1999). Therefore, the accumulation of recalcitrant volatile solids from biomass formed during composting is small. This is corroborated by Adani (1999), who reported that during composting experiments the total amount of humic substances decreased. It is therefore expected that during composting the pool of hydrolysing solid matter is constantly decreasing in a way that can be predicted from the properties of the initial material.

6.3 Composting at low oxygen level

In this research a new composting method in which a greater part of the oxygen in the process air is used was developed. The process was designed to provide an effective, low cost method that also decreases gaseous emissions to the atmosphere. Here, first the theoretical implications will be discussed. Thereafter the planned design, an assessment of the feasibility of the system and the demands on process control will be discussed.

Conceptual model

The key aspect of composting is the creation of an environment where aerobic bacteria thrive. The oxidation of the substrate by bacteria provides the energy needed to evaporate water and to increase the temperature sufficiently to sanitise the manure. Malodorous substances are also biodegraded, reducing the emission of smell. Poorly operated composting facilities are smelly and produce a product that is too wet and phytotoxic due to high concentrations of volatile fatty acids.

The conventional composting process design therefore sought to maximize aerobic activity. This usually leads to a process that is very active for several days, and much less active thereafter. Composting strategies that do not seek to

maximize activity are viewed with scepticism because of the fear of generating malodour. However, this can be avoided. It was shown earlier that the oxygen transfer limited activity of a compost bed can be quite high even at low oxygen concentration. The vital factor is to generate enough bacterial growth during start up. It also important to preserve the biofilm throughout the process.

Hamelers (1993) showed that phenomena observed after turning a normally aerated compost bed can be explained by the particle based composting model. In figure 1 the effect of turning on the OUR is shown. After each turning there is a decline in oxygen uptake rate (OUR), this then increases to a peak. The decline is caused by burying the biofilm, so that the access to oxygen is limited. The height of the subsequent peak depends on the composting phase. It is caused by regrowth of the biofilm on the new aggregates surface. As the hydrolysis, which is independent of the oxygen concentration, continuous, available substrate accumulates during the absence of the biofilm, leading to a peak activity once the biofilm is replaced. At low oxygen concentration the recovery of the activity through bacterial growth is much slower. It is therefore predicted that mixing will seriously impair composting at low oxygen concentration.

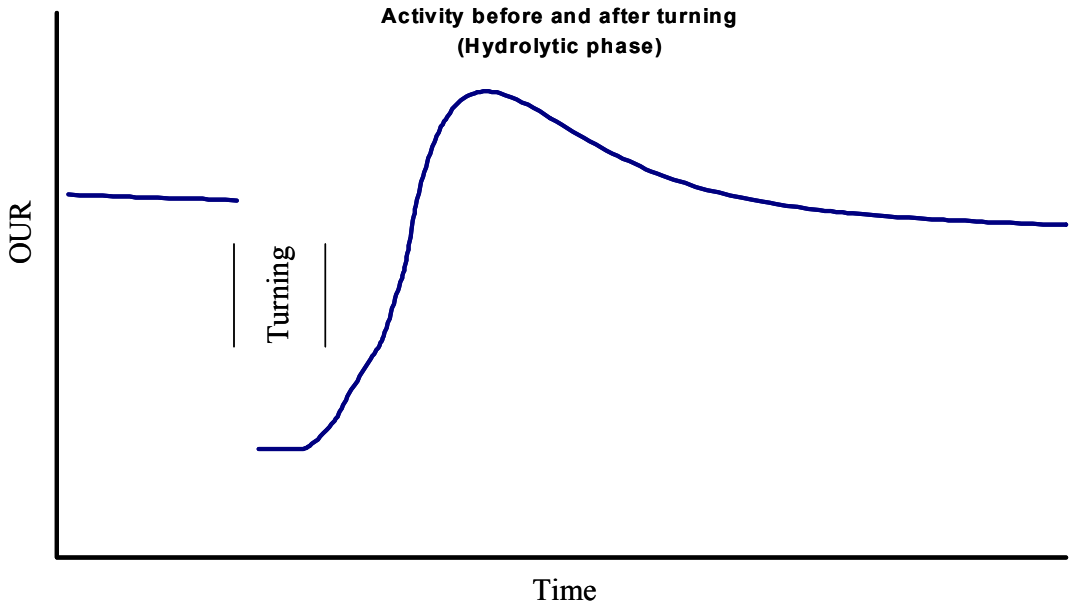

Figure 1 The effect of turning on the oxygen uptake rate of a compost bed during the hydrolytic (constant OUR) phase of composting.

The slower growth rate found at lower oxygen concentration has profound implications for the demands for the compost bed. It was shown that it is vital that sufficient bacteria are present before the oxygen levels are lowered. It was also shown that bacteria have to remain positioned in a biofilm covering the

composting material aggregates. Subsidence of the composting bed, burying the biofilm, and uncovering fresh surface would cause a permanent decrease in respiration. Therefore, especially at low oxygen concentration, the compost bed has to be stable to keep the biofilm intact and in contact with the gas phase.

The conceptual design

In the design, air is recycled through the bed until the oxygen has decreased to the required operating concentration. Hereafter the oxygen concentration in the process gas is maintained by regulating the amount of fresh air supplied to the system while discharging an equal volume of waste gas. This has the advantage that less waste gas is produced, and that the amount of volatile compounds emitted to the atmosphere is reduced. In a conventional composting reactor (without a cooling system), only 10% of the oxygen in the supplied air is used. If 50% of the oxygen available in the supplied air is used in the new process, the amount of waste gas is only a fifth of that in conventional systems, also reducing the cost of waste gas treatment.

In a conventional composting system process air is used for oxygen supply and for temperature control of the process (flow is increased to provide cooling). In the new design the temperature of the compost bed is also controlled by the process air but by cooling the recycled gasses. As the composting is controlled at 55°C, heat can be removed from the system without cooling below ambient temperatures. Therefore, cooling can be done relatively cheaply, and low temperature thermal energy can be extracted and used elsewhere.

Cooling the water saturated gas flow, leads to the formation of a condensate. Water-soluble gasses such as ammonia partly dissolve in the condensate, lowering the gaseous emissions of the process to the atmosphere. The condensate requires further treatment, and can be processed to recover ammonia.

Feasibility of low oxygen composting

The results obtained from the experiments presented in chapter 2 showed that the new composting system is feasible. With the exception of the start up period it was found that the compost bed remained sufficiently active when the oxygen concentration in the process gas was reduced to 1%(v/v). The new process stabilises solid manure, evaporates water and emits ammonia like a conventional composting process, the compost produced is comparable to that produced by conventional means.

The emission of ammonia to the atmosphere is reduced considerably by the ammonia captured in the condensate. The lower the oxygen content of the process gas, the lower the total ammonia emission to the atmosphere. At 10%(v/v) oxygen

in the waste gas, only half of the ammonia emitted from the compost bed is emitted to the atmosphere. At 1% oxygen only 22% of the ammonia is emitted to the atmosphere. These results were achieved with the first prototype of the composting system. It is expected that improving the process will further reduce ammonia emissions.

Lowering the oxygen content of the process air immediately lowers bacterial activity. Most activity takes place during the first days of composting, after which a longer period of low activity follows. By reducing the oxygen concentration, the initial phase, with a relatively high biological activity, is prolonged, because the activity during this period is lower than in conventional composting. This reduces the necessary cooling and aeration capacity, and will lead to a more homogeneous temperature in the compost bed. The cumulative oxygen uptake over a three week period is however comparable to conventional composting systems. The reduced activity does not affect the stability of the compost.

The reduced activity of the bacteria during the initial phase does prevent an initial speedy increase in temperature. Therefore, the start up of the composting process -this is the temperature increase to the desired process temperature- has to be done with a higher oxygen concentration in the process gas. It was found that an oxygen concentration of 10% was sufficient to raise the temperature adequately, so that even during start up the amount of waste gas can be reduced. However, no cooling will be applied during this phase, so that no ammonia can be captured in the condensate.

Process conditions during low oxygen composting

Bacterial growth at low oxygen concentration is slow, making it necessary to compost the material without mixing the bed during the process. Therefore, the bed has to be sufficiently homogeneous, without large unaerated sections, and it should remain stable as the temperature increases and as the bed dries out. Further, the compost produced has to comply with standards regarding dry matter content and stability. Therefore, the feed has to be carefully constructed so that the amount of water present is just enough to facilitate the degradation of the desired amount of organic matter.

In this research two measurements were developed to aid the construction of a suitable compost bed. These measurements follow from the composting theory and the evaluation of the low oxygen composting process as vital parameters to predict the quality of the compost produced.

The area of the gas to aggregate interface determines activity during the initial stages of composting. A speedy start-up is necessary to be able to stabilise the

compost within three weeks, but it is also the factor determining the temperature increase of the compost bed. A prediction of the interface is therefore needed to ensure sanitation requirements can be met.

The hydrolysis rate of the solid organic particles determines the bulk of degradation after a successful three week composting run. An estimate of the degradation is necessary to predict the amount of water that will be evaporated during degradation.

6.4 Bed structure

The first parameter identified as important for composting is the aggregate to air interface area in the compost bed. Therefore, the work presented in chapter 3 was aimed at predicting the free air space required to enable the temperature in the compost bed to increase fast enough to support an effective three week composting run. A rough estimate of the free air space is easily obtained from the mass of material packed into the reactor, and the bed height, making this ideal for use on location. However, it was found that free air space at packing is not the factor determining the low activity observed in practice.

In chapter 3 it was concluded that the increase in bed temperature during start up is linked to the free air space in the compost bed. Published equations give a good estimate of how bed activity changes with the free air space and can be used to calculate the free air space required for a good start up of the composting process. The bed, however, has to remain stable throughout the run, and our results show that the weakening of the bed structure with increasing temperature is a greater problem than the accurate estimation of the volume of free air space required.

During any successful composting operation the amount of compost produced is much less than the initial amount of feed material. A well constructed compost bed does not have a constant height. There are two distinct processes that lead to a lowering of the bed height:

Subsidence	The bed structure collapses, either because structural materials bend or break, or because viscous materials flow down and fill pores. The biofilm loses contact with the gas phase, and microbial activity drops.
Drying	When viscous particle suspensions, like manure, dry, they shrink. This means aggregates become smaller during composting, leading to a decrease in bed height. It may also lead to a partial collapse in bed structure. As long as the biofilm remains intact, the activity of the bed is unaffected.

Compost beds are usually formed by throwing materials onto the bed in small quantities at a time, with the intent that the structure provided by the bulking material will incorporate sufficient air. As soon as the composting process is started, the bed begins to dry. The viscous parts become more viscous, and the loss of water reduces weight and structural strain, so it seems unlikely that subsidence could have a major impact on bed porosity. However, the increase in temperature can weaken the bed structure and cause subsidence.

During experiments no separation of liquid and solids in manure for temperatures up to 60°C were observed when no pressure was applied, but leachate was observed during composting and packed bed experiments. The formation of leachate under conditions where no spontaneous separation of phases was observed, indicates that phase separation is caused by the pressure of the overlaying compost bed. Therefore, not only the bulking material (straw in these experiments) but also the manure caries part of the structure.

Measurements of free air space in relation to applied pressure (Richard et al. 2004) indicated that the more pressure is applied, the less free air space the bed can maintain. With increasing temperatures the free air space diminishes further (Veeken, unpublished data). These data support the finding of chapter 3 that the bed becomes unstable when temperatures increase. Richard et al. (2004) describe a measurement with which this effect can be predicted.

6.5 Manure degradation

The degradation of volatile solids during composting influences compost quality, and therefore a successful compost operation. It was concluded that an estimate of the degradation is needed to successfully construct feed mixes. In this thesis the manure produced by pigs in a Hercules pen had to be composted. This manure will first be described, after which it will be discussed how an estimate of the degradation during composting can best be obtained for this type of material.

Manure variability

The solid manure used in this research came from three different locations. Two were test facilities, where a small number of pigs are kept under experimental conditions. The experimental facility that housed the first group of pigs was the Bantham, located in Maartensdijk. These pigs were fed dry feed, as there were no facilities to provide them with slurry. All pigs had the same age. The solid manure produced here was used for the experiments presented in chapter 2. The solid manure used was collected when the pigs were ready for slaughter.

The experimental facility that housed later groups of pigs was located in Sterksel. These pigs were provided with a feed slurry, and again all pigs in the experiments

had the same age. Multiple batches of solid manure were collected so the age of the pigs varied during the experiments. This solid manure was used for the experiments presented in chapter 3.

The third source of solid manure was a commercial pig farm in Reusel. Here the solid manure obtained came from a mix of all age groups of pigs. This manure was collected in a ditch, and separated into solid and liquid fractions in a centrifuge. No results of experiments conducted with this solid manure are given in this thesis. The analysis of this solid manure is given to underline the finding that solid pig manure is a variable product.

Manure solids separated on a convex conveyor belt

In table 1 the characteristics of the manure from the three sources are given. The solid manure from Bantham and Sterksel are almost identical, except for the dry matter content. From figure 4 in chapter 2 and table 4 in chapter 3 it can be seen that the respiration rate during the start-up phase (the only respiration rate data at high oxygen concentration) is 50 to 150 mmol kg^{-1} h^{-1} for the manure from Bantham, and up to 60 mmol kg^{-1} h^{-1} for the manure from Sterksel. Taking the differences in reactor used for composting, water content and packing density into account, this means that no difference in respiration rate can be demonstrated. Composting degraded up to about 33% of total organic matter in both manures.

Table 1 Characteristics of the manure obtained from three different sources. Values are mean values with the standard deviation in brackets

	DM [g g^{-1}]	OM [g g_{DM}^{-1}]	N_{Kj} [g g_{OM}^{-1}]	NH_3-N [g g_{OM}^{-1}]	Hydrolysis rate [mmol$_{O_2}$ $kg_{OM}^{-1}h^{-1}$]
Bantham	0.34 (0.026)	0.80 (0.038)	50.4 (6.0)	20.0 (1.5)	NA
Sterksel	0.27 (0.023)	0.83 (0.010)	49.4 (3.3)	20.9 (1.3)	± 200
Reusel	0.34 (0.008)	0.63 (0.010)	47.8 (2.1)	33.6 (2.2)	18 (4.2)

The energy needed to obtain dry compost from the wet manure is provided by the biodegradation of organic matter. The difference in dry matter content means more water must be evaporated from the Sterksel solid manure than from the Bantham solid manure to reach the same dry matter content. For the desired compost dry matter content of 70%, approximately 1.5 times as much water has to be evaporated per mass of initial organic matter.

Depending on the available energy (from degradable organic matter) to water ratio either easily biodegradable organic matter or water has to be mixed in with the manure to produce compost with the desired dry matter content. Bantham solid manure had approximately the right energy content to provide the desired level.

The experiments presented in chapters 2 and 3 showed that Sterksel solid manure does not contain enough energy to dry the compost to the desired dry matter content (unpublished results). The experiments with Sterksel solid manure also revealed that the shortage in energy could not be quantified from the dry matter and ash content analysis. The organic matter did not have a constant composition. This was seen from the mass of water that was evaporated for every kilogram of organic matter degraded. This varied from 7 to 13 kg. It is therefore necessary to measure the energy content of the organic matter before the compost bed is constructed. Therefore, the hydrolysis measurement presented in chapters 4 and 5 was developed.

Manure solids separated by centrifugation

The rate of hydrolysis of the solid manure from Reusel is very low compared to that from Sterksel. The rate of hydrolysis is so low that insufficient energy is available to evaporate all excess water. Using the model described by Hamelers (2001 in chapter 8), it was calculated that even if the rate of hydrolysis of the organic matter remains constant at the measured level, after four weeks the dry matter content of the compost would still be only 50%, and the weight loss only 45%. Initially available substrate was ignored in this calculation.

Another problem associated with the low hydrolysis rate of the manure from Reusel is that sanitation might not be possible. The hydrolysis observed (table 1) is much lower than the respiration found during start up in the experiments described in chapter 3 (table 4). In these experiments the start up was often slow, due to a lack of structure in the compost bed. Therefore, when manure from Reusel is composted, start up of the process has to be completed on initially available substrate, rather than on substrate that becomes available through hydrolysis. This is likely to be insufficient to reach the temperature required.

Despite the higher dry matter content of centrifuged manure, it is expected that it would have to be enriched with easily degradable substrate to provide a suitable feed material for composting. This substrate has to be directly available for biodegradation, as the start up of the composting process will depend (in part) on it. It is anticipated this will increase the cost of suitable amendments.

Manure degradability parameters

The more usually used parameter in composting is the degradability of the material. This is the fraction of organic mass degraded after a specified (usually long) degradation period. The remaining organic matter is considered recalcitrant. The degradation is assumed to be a first order process. This enables prediction of the degradation for the length of time used for the degradability measurement. Though this would probably give more accurate predictions than hydrolysis based estimates, it has the drawback that material has to be stored while a portion is composted. Only when the composition of the compost feed is constant can this method be used successfully.

When composting a variable material, like the solid manure produced in the Hercules system, another approach has to be used. From the theory, two types of substrate can be distinguished. The available substrate, and substrate that has to be hydrolysed before it is available for the micro organisms. The available substrate will be degraded quickly during composting. The key factor is to predict how the hydrolysis of the organic particles will change in time.

Hydrolysis rate

In chapter 5 a method for measuring the hydrolysis of the particulate organic matter was presented. The hydrolysis of particulate organic matter has been shown to be linearly related to the surface area of the particles (Sanders et al. 2000; Sanders 2001). Consequently, the rate of formation of substrate by hydrolysis from a batch of particles necessarily decreases during degradation as the particles become smaller and the total surface area decreases. The linear relation with the surface area also means that the degradation rate (expressed in units of $kg_{substrate}$ kg_{VS}^{-1}) of individual particles increases as the surface area to volume (and therefore mass) ratio increases. As the degradation rate of the organic matter diminishes during composting, there must be a mixture of particles from which the most stable automatically remain.

Janssen (1984) related the degradation of solid matter over a period of years to the degradation during the first year. He found that the degradation for many materials proceeded according to the same formula. Therefore, the degradation rate at one point in time can be used to predict degradation over a period of time. It can be shown that the formula found by Janssen is consistent with a lognormal particle size distribution in the hydrolysing particles (appendix). It is therefore expected that also in the soil the hydrolysis of the bulk of the carbon will be the main factor determining degradation. It is further expected that degradation during composting will follow a similar pattern to that predicted by the degradation model by Janssen, even though this relation was derived for soil systems.

The degradation model by Janssen uses a continuous change in degradation rate to predict degradation. Besides the degraded fraction at a point in time, also the initial rate of degradation can be used as input for the model. From the assumption that the model predicts mainly hydrolysis, this should be seen as the initial rate of hydrolysis. The hydrolysis measurement developed in chapter 5 is expected to provide the parameter necessary for a successful application of the model.

Available substrate

In the experiment described as run A in chapter 2, more than 15% of the degraded organic matter consisted of volatile fatty acids. These are readily available substrate, but not the total readily available substrate. Easily hydrolysable substrate that is hydrolysed completely before substrate levels limit bacterial activity is also considered to be readily available. This substrate contributes to the exponential growth phase and is not accounted for in the measured hydrolysis rate, as the particles have been completely degraded by that time. Readily available substrate is therefore not always negligible, and difficult to measure.

In chapter 5 a procedure for measuring the rate of hydrolysis was given. It was shown that after available substrate levels have dropped, and the respiration of the sample becomes substrate limited, the yield of biomass COD on substrate COD can be assumed to be 0.2. The respiration at that time is a good measure for the rate of formation of substrate in COD units. From the same measurement the amount of oxygen used by the sample before it became substrate limited can also be obtained. If the yield during this period were known, the amount of available substrate in the sample could be easily calculated.

The yield of bacterial growth on substrate is known to change according to the Herbert Pirt equation (chapter 5, equation 4). From this equation it can be shown that the bacteria have to be substantially limited in their growth before the change in yield becomes noticeable. Therefore, assuming a maximum yield of 0.5 will normally give a good estimate of the readily available substrate COD.

Therefore, both the readily available substrate and the rate of hydrolysis can be analysed in one experiment. First the hydrolysis is estimated as described in chapter 5. Second, an estimate of the cumulative oxygen consumption of the sample at the transition time from excess-substrate to substrate-limitation is derived from the pressure graphs. The cumulative amount of substrate COD consumed by the biomass is twice the amount of oxygen used. The estimate for initially readily available substrate is found by extrapolating the hydrolysis rate to the start of the experiment, and subtracting the substrate formed by hydrolysis from the cumulative substrate uptake at the transition time.

Degradability of the manure

Calculations and measurements with the model system of the modified OxiTop, presented in chapter 5, confirmed that degradation of solid particles becomes limited by hydrolysis. With the developed respiration method the rate of hydrolysis of the solids and the initially available substrate can be estimated. This information can be used to determine the proportions of substrate or water that need to be mixed with the manure to obtain a feedstock that will produce compost of the desired quality cost effectively. There is however still a lack of data concerning the conformation of the predicted evolution of the rate of hydrolysis during composting.

6.6 Compost quality

To compost manure at low oxygen concentration it is necessary to prepare a balanced mixture, by adding either water or suitable substrate to provide energy for heat. This mixture then has to be mixed with a structural material that is relatively inert and maintains its strength throughout the composting run, to produce a bed that will not subside during composting. This is equivalent to the procedure used by Haug (1986; 1993) for constructing feed mixes.

From the start of the Hercules project it was clear that the composting had to give added value to the manure. This was expressed as better handling quality, better storage possibilities, cheaper to transport, and more value as a fertilizer. Manure is a putrescible substance and contains a lot of water. This means that composting will fulfil all these conditions in one process.

Within the Hercules project three demands for compost quality were formulated

1. The compost has to be sanitised in accordance with EU regulations so it can be exported. This means heating to at least 70°C for at least one hour.
2. The DM content has to be increased to 70% or more to reduce transportation costs, and improve handling properties.
3. The compost has to have a low rate of respiration; it has to be stable. No precise criteria were formulated with regard to this demand. It was interpreted (by us) to mean that contact with water should not lead to renewed bacterial activity.

Constructing the feed mix

From the measured hydrolysis and initially available substrate, an estimate has to be derived for the cumulative oxygen uptake after three weeks of composting. With respect to available substrate this is straightforward. For the hydrolysis equation 13 in the appendix as an approximate fit to the model by Janssen (1984) is

used. These measurements and calculations have to be performed not only for the manure, but also for the amendments available on the farm. For the manure and the amendments a deficit or excess of water is estimated from the measured values using the heat balance also used in chapter 3. Amendments are mixed in with the manure until the mixture has an estimated water deficit of zero. When composted, this mixture will produce compost that is both stable and dry, fulfilling conditions 2 and 3.

Constructing the compost bed

To ensure the compost is heated to 70°C within the first four days of composting, the oxygen uptake of the bed has to exceed 10 $mmol_{O_2}\ h^{-1}\ kg_{wet\ mass}^{-1}$. Using equation 8 in the appendix it is checked whether the available substrate and the hydrolysis combined can yield this amount of substrate. If not, a more readily available energy amendment has to be used.

Bulking materials are added to the mixture until the FAS is large enough according to the model used in chapter 3. The mechanical strength of this mixture is measured using the method described by Richard et al. (2004). More bulking materials are added until the mechanical strength is large enough to maintain the desired FAS, even at high temperature. Biodegradable bulking materials also have to be accounted for in the energy balance.

Appendix Estimation of the evolution of the rate of hydrolysis in time

Janssen published a formula that predicts the degradation of solid organic matter in soils. The formula needs only one, measurable, parameter. This simplicity makes the method very attractive, and it is therefore applied in a soil nitrogen model, Ndicea, often used in the Netherlands. In this appendix it will be shown that the formula is not in contradiction with the surface limited hydrolysis, and that application of the surface hydrolysis model may enable a better parameter estimation.

Hydrolysis of a single particle

The surface limited hydrolysis is built from the assumptions that

- particles degrade at the surface, and that their interior remains unaffected.
- every surface area of a particular composition yields the same amount of substrate per unit of time; i.e. the depth to which the surface is degraded per unit of time is constant.
- particles are homogeneous.

This means the hydrolysis of a single particle can be described by the following formula

$$\frac{dS}{dt} = K_h A \qquad 1$$

S	Substrate formed by hydrolysis	[$mmol_{COD}$]
t	Time variable	[s]
A	Surface area of the hydrolysing particle	[m^2]
K_h	Hydrolysis constant of the material the particle is made of	[$mmol_{COD}\ m^{-2}s^{-1}$]

It is assumed that the substrate formation rate equals the mass loss rate, so bacterial growth is neglected. If this is so for the system, it must also be so for every individual particle. It is further assumed that the hydrolysing particles are spheres:

$$\frac{dM}{dt} = -\frac{K_h}{M_c} 4\pi r^2 \qquad 2$$

M	Mass of the hydrolysing particle	[kg]
M_c	Substrate released per kg mass lost from the hydrolysing particle	[$mmol_{COD}\ kg^{-1}$]
r	Radius of the hydrolysing particle	[m]

If it is assumed all the mass released from the particle surface is turned into substrate the rate of mass loss is also equal to:

$$\frac{dM}{dt} = \rho_p \frac{dV}{dt} = \rho_p \frac{d\frac{4}{3}\pi r^3}{dt} \qquad 3$$

ρ_p Mass density of the hydrolysing particle [kg m^{-3}]

V Volume of the hydrolysing particle [m^3]

Combining equations 2 and 3 gives:

$$\frac{dr}{dt} = -\frac{K_h}{\rho_p M_c} = -K_H \qquad 4$$

K_H Hydrolysis rate of the particle as speed at which the surface is degraded [m s^{-1}]

Integration gives:

$$r(t) = r(0) - K_H t \qquad 5$$

This is the mathematical expression of the second assumption.

By rearranging equation 2 and combining it with equation 5:

$$\frac{dM}{dt} = -\frac{K_h}{M_c}\frac{V}{3(r(0) - K_H t)} = -K_H \frac{M}{3(r(0) - K_H t)} = -\frac{M}{3(L(0) - t)} \qquad 6$$

$L(0) = \frac{r(0)}{K_H}$ Life span of the hydrolysing particle; i.e. the time it takes to completely hydrolyse it. [s]

integration gives:

$$M(t) = \frac{M(0)}{\sqrt[3]{L(0)}} * \sqrt[3]{L(0) - t} \quad \Big| \; t < L(0) \qquad 7$$

Hydrolysis of a particulate substrate

Equation 7 gives the residual mass of a particle, whereby the ratio of r(0) and K_H is the life span of that particular particle. To calculate the residual mass of a waste, the sum of residual masses for all particles has to be calculated. This is equivalent to taking the integral of the residual mass function multiplied by a distribution function. Here a log normal distribution is used:

$$M(t) = M(0) * \frac{\int_{t}^{\infty} \sqrt[3]{L(0) - t} * e^{-\frac{(\ln(L(0)) - \mu)^2}{2\sigma^2}} \frac{1}{\sqrt{2\pi}\ \sigma L(0)} dL(0)}{\int_{0}^{\infty} \sqrt[3]{L(0)} * e^{-\frac{(\ln(L(0)) - \mu)^2}{2\sigma^2}} \frac{1}{\sqrt{2\pi}\ \sigma L(0)} dL(0)} \qquad 8$$

μ	Average value of ln(L(0))	[s]
σ	Standard deviation of the ln(L(0)) distribution	[-]

This formula gives the residual mass of a degrading material assuming all particles are homogeneous and round, accessible to the bacteria, and that bacteria are present. Because particles are defined by their life span, particles do not need to have identical compositions. Life spans can vary because of size, but can just as well differ because of composition. However, particles cannot vary too much in both factors, as otherwise it becomes unlikely that the waste can be described by a single log normal life span distribution.

A one parameter degradation function

The formula Janssen (1984) gives for the residual mass of organic materials in soil is given by:

$$M(t) = M(0) * e^{\left(4.7 * \left((a + f_T * t)^{-0.6} - a^{-0.6}\right)\right)} \qquad 9$$

a	apparent initial age of the material	[s]
f_T	Temperature dependent time-correction factor	[-]

It is quite easy to fit equation 8 to equation 9 by choosing appropriate values for μ and σ. A possible fit (obtained by trial and error) is given in figure 2. As can be seen, the fit is not exact for all values, but is -purposely- very good for predicting residual mass at annual intervals. The fitted function therefore fits the data for greenwaste as used by Janssen quite well. For the more degraded materials (which in Janssen's model have a higher apparent initial age a) a new fit has to be made. In figure 3 a fit is given for the degradation of a material with apparent initial age of 3 year. Again the fit is made so that the degradation at annual intervals coincides with the prediction by Janssen.

In view of the hydrolysis model the relation found by Janssen can be interpreted as a relation between the particle size distribution and the degradability of the particles. For any initial degradation rate a particle life span distribution can be

found that predicts the same residual mass as Janssen. In all cases the best fit is found when σ^2 is approximately 3.

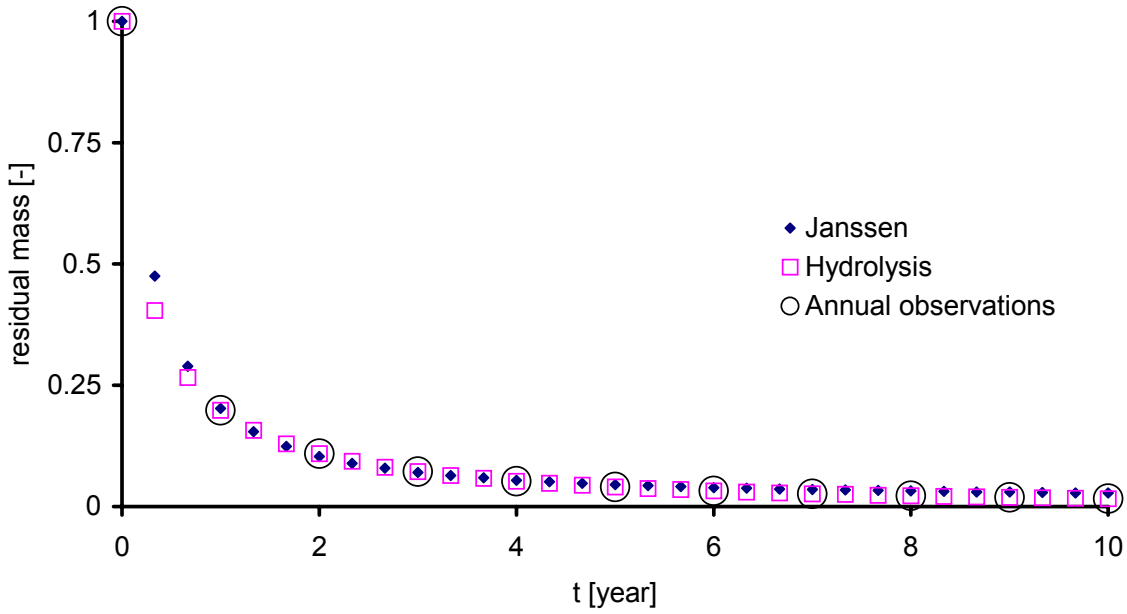

Figure 2 Fit of the hydrolysis model (equation 8) to the model by Janssen (equation9) for a = 1. Three calculated values per year, the whole year values indicated by a circle. Presented values calculated for $\sigma^2 = 3$ and $\mu = -2.14$

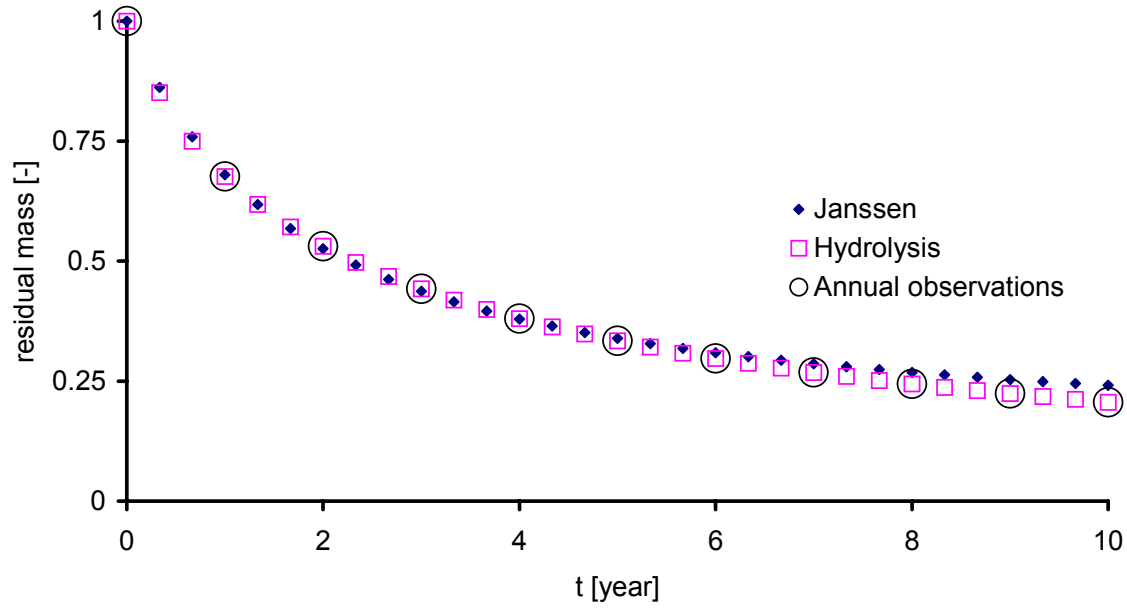

Figure 3 Fit of the hydrolysis model (equation 8) to the model by Janssen (equation9) with a = 3. Three calculated values per year, the whole year values indicated by a circle. Presented values calculated for $\sigma^2 = 2.9$ and $\mu = 0.27$.

As the degradation rate is defined as the first order rate coefficient, the coefficient can be calculated from the formula:

$$\frac{dM(t)}{dt} = -M(t) * k_D(t) \qquad 10$$

$k_D(t)$ Degradation rate of the remaining solids [s^{-1}]

By combining equations 8 or 9 with equation 10 the degradation rate of the remaining solids can be predicted. For equation 9 this yields the equation from which Janssen derived equation 9:

$$k_D(t) = 2.82 * (a + f_T * t)^{-1.6} \qquad 11$$

Substitution of equation 8 in equation 10 yields a formula that cannot be solved analytically. From equation 6 the $k_D(t)$ of a single particle can be obtained, but this cannot be simply combined with the distribution function. In equation 12 the formula for $k_D(t)$ according to the hydrolysis theory is given:

$$k_D(t) = \frac{\int_t^{\infty} \frac{1}{\left(\sqrt[3]{L(0) - t}\right)^2} * e^{-\frac{(\ln(L(0)) - \mu)^2}{2\sigma^2}} \frac{1}{3\sqrt{2\pi}\ \sigma L(0)} dL(0)}{\int_t^{\infty} \sqrt[3]{L(0) - t} * e^{-\frac{(\ln(L(0)) - \mu)^2}{2\sigma^2}} \frac{1}{\sqrt{2\pi}\ \sigma L(0)} dL(0)} \qquad 12$$

Using the hydrolysis rate to predict degradation

Extrapolating the measured degradation to the initial degradation rate, the models predict substantial differences. The hydrolysis model predicts that initially k_D will increase, before decreasing. Janssen's model predicts a continuous decrease in k_D, linear on a log-time scale with the initial age "a" added. In a later paper Yang (Yang and Janssen 2000) presented a model using two parameters, assuming a linear decrease in k_D on the "normal" (not adding or subtracting a correction factor) time scale. On this time scale, the hydrolysis model, after an initial deviation, also yields a near linear relation for k_D, because of the log normal distribution used. Yang and Janssen observed a "lag-phase" in the degradation of materials with a low stability. The hydrolysis model explains why this is: in the initial stages, k_D is not linear because of fast changes in average lifetime. The good fit found by Yang and Janssen, even after relatively short degradation periods of one month or less, indicates that short measurements can yield long term predictions.

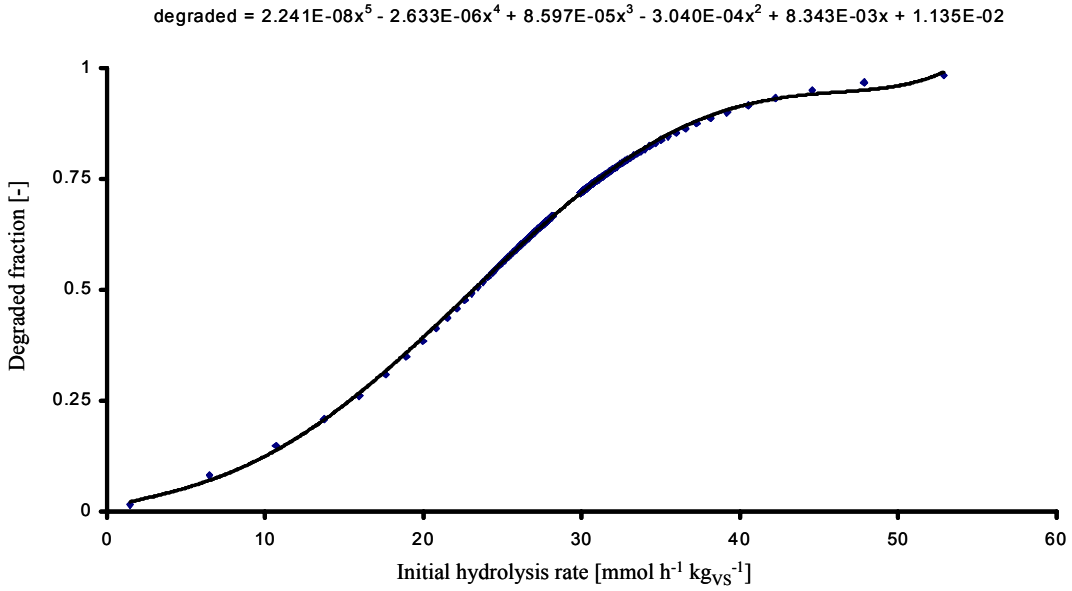

Figure 6 Fitted function of the initial hydrolysis rate and the expected degradation after one year. Both values calculated for soil conditions used by Janssen.

$$D = 2.2\ 10^{-08}\ OUR^5 - 2.6\ 10^{-06}\ OUR^4 + 8.6\ 10^{-05}\ OUR^3 - 3.0\ 1^{-04}\ OUR^2 + 8.3\ 10^{-03}\ OUR + 1.1\ 10^{-02} \quad \textbf{13}$$

In figure 6 the relation between the initial hydrolysis (average degradation during the second day of incubation) and the degradation after one year as calculated with equation 8 is given for $\sigma^2 = 3$. Also the fitted function to the calculated data is given as equation 13. The time scale used for the calculation with equation 8 is valid in the soil, and therefore a correction to the life span (and with that rate of hydrolysis) values has to be used to obtain the values relevant for the OxiTop measurement and the compost bed. In a Dutch publication on this model, Hendriks (1992) states the average temperature of the data used by Janssen can be estimated at 9.5°C.

For the rate of hydrolysis measurement a temperature correction factor of 4 or 5 is predicted (Veeken and Hamelers 1999; Yang and Janssen 2000). Also the ideal conditions in the OxiTop as compared to soil conditions may warrant a correction factor. For the composting, a temperature correction of 20 to 30 is expected. That means that the degradation after three weeks of composting is expected to be comparable to the degradation after one to one and a half years in the soil.

In chapter 6 the hydrolysis of the pig manure from Sterksel was estimated to be 200 $mmol_{O_2}\ h^{-1}\ kg_{VS}^{-1}$. The degradation after three weeks of composting was around 33%. In figure 6 this would be consistent with a correction factor 10 for the hydrolysis, and the degradation during composting equal to the degradation during one year in the soil. This is a very rough estimate, and more data is needed to

corroborate the relation and to accurately obtain the exact value for the correction factors.

Discussion

It is our expectation that by using the hydrolysis model for the initial degradation, a better input can be generated for the Janssen model to predict the long term degradation. It is our hope to be able to predict the degradation over several years from an OxiTop experiment lasting only one week. Whether the same accuracy can be obtained by using initial degradation rates as is achieved by using data obtained during one year is a matter for further research, but seems unlikely.

When mathematical mixtures of the degrading wastes are constructed, the prediction of the residual mass becomes very poor for both models. The initial degradation is determined predominantly by the easily degradable substance, whilst the residual mass after a few years is determined by the more stable substance, and this cannot be corrected for by varying just one parameter in the fit function. This means that a small fraction of easily degradable particles can heavily influence the initial degradation rate, leading to too low estimates for the residual mass.

The fit for the data collected by Janssen is probably so good because most materials are pure in the sense that they have a history as a mixture. This and the fact that the degradation over the first year is used make a prediction for several years possible. Because the manure used in composting has a single origin, it is hoped that predictions from the initial degradation rate will also yield acceptable results. It is however clear that not the feed mixture, but the separate ingredients have to be analysed.

There is a large variation in time scale corrections due to temperature fluctuations. When more data becomes available, these factors can probably be estimated more accurately. But as the degradation proceeds according to a near exponential decrease function, the variation in the predicted degradation is usually much smaller than the variation in the time scale correction. Only for slow degrading substrates is the variation in the predicted degradation as large as the variation in time. Therefore, for substrates that are sufficiently degradable the model can be used without an exact knowledge of the correction factor.

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Summary

The changing attitude of society towards livestock farming necessitates changes in pig farming. The new demands put on the industry are increasingly difficult to achieve by adapting the existing process. Therefore the Hercules project was started. The goal was to devise a new pig-farming concept that would be socially acceptable. This was done by revising the complete chain, from feed supply to produced wastes and by-products. To reduce gaseous emissions from the housing facilities, and to obtain a product more suitable for modern fertilizing techniques, the manure is separated in a solid and a liquid fraction. The research in this thesis deals with upgrading the solid fraction of pig manure to a dry and stabilized fertilizer via composting.

Within the context of the Hercules project, the composting of the manure had to take place on the farm. On-farm composting means there is limited space and knowledge to adjust the process while in progress. Therefore, precise and foolproof criteria have to be formulated according to which the composting must proceed.

Composting can improve the fertilising, storage and handling quality of the manure. However, composting manure emits large amounts of ammonia. This would be unacceptable, and therefore a new low oxygen composting process was designed. In this process the process air is cooled and recirculated, instead of using fresh air. In this way, the amount of waste gas can be reduced.

In composting, the air is not only needed for oxygen supply, but also for cooling the compost bed. To cool the composting process, the recirculated air will have to be cooled. This will produce a condensate in which part of the ammonia emitted from the composting manure will dissolve. The condensate can be added to the liquid manure fraction, and will therefore not create an extra waste stream. As ammonia is removed with the condensate this low oxygen composting process will therefore reduce the gaseous ammonia emissions.

There was little data on how efficient the micro-organisms can take up oxygen from a lower gas concentration. In the low oxygen process discussed in chapter 2, the supply of oxygen is maintained, as the flow of air remains high. The objective of that study was to investigate the change in activity with lowered oxygen levels. Further, it was investigated whether emissions can be lowered by recirculating cooled process air.

It was found that the activity of the micro-organisms drops when oxygen concentrations are lowered. However, in conventional composting systems the activity during a composting run is unevenly distributed. A high initial activity is followed by a much longer phase with a low activity. During low oxygen

composting the initial activity is lower, but the initial high activity phase is maintained longer. It was found that the oxygen consumption of the compost over a three-week composting period was comparable with the conventional process.

The lower initial activity did present a problem in raising bed temperatures. The heat produced by the oxygen impaired process was insufficient, and start-up of the composting process has to proceed at oxygen concentration of 10%(v/v). Once the desired operating temperature was achieved, activity was high enough to maintain this temperature. As the initial high activity phase was longer, the high operating temperature could be maintained longer at lower oxygen concentration. However, the slow increase in initial activity means compost beds cannot be turned during the composting process.

During low oxygen composting, the amount of ammonia emitted from the compost was comparable to the amount emitted during composting at higher oxygen levels. The amount emitted with the waste gas to the atmosphere was strongly reduced because of the cooling of the recirculation. At an oxygen concentration of 10% half of the emitted ammonia was captured in the condensate formed in the cooler. At an oxygen concentration of 1% 77% of the ammonia was captured.

Composting at low oxygen levels has then been proven feasible. The slower degradation rate is an advantage. As the temperature can be kept high during a longer period, the product is better sanitised, and the absence of the high initial activity means less aeration capacity is required. The strong reduction in waste gas flow means treatment of the waste gas becomes cheaper or can be omitted. The produced compost is comparable to compost produced by conventional composting.

After the successful tests of the low oxygen composting process on a lab scale (80L), tests were conducted on a pilot scale (2000L). It was found that the temperature rise of the compost bed appeared to be difficult, even at high oxygen concentration. The composition of the manure was different to the manure used on lab-scale, and a method was sought to predict the phenomenon. On a basis of a system analysis, it was concluded that the gas pore content (free air space, FAS) of the compost bed was the most likely parameter to explain the observed low activity. In chapter 3 data obtained from the pilot scale experiments is used to test two models for their ability to predict activity.

In literature, two models linking activity to FAS were found. The first model is an inductive model based on experimental data. The second model is a mechanistic model that calculates the effect of all three phases: gas, water and solids, on activity. The latter model provides more insight and has the advantage of dealing

with the complete effect of the compost bed on activity. However, no validation of the mechanistic model on data had been performed. The results of the pilot scale experiments, and the correlation between the mechanistic and the inductive model were both used to verify the validity of the mechanistic model.

The activity of the compost beds was estimated from the measured temperature rise, and the FAS was estimated from reactor volume and the mass of the different compost beds. This data was used to test the two models on their ability to predict bed activity. Both models can predict equally well, and results showed that FAS was the parameter determining the activity. The mechanistic model and the inductive model correlated to a high degree. The parameters estimated for the mechanistic model from the experiments predict maximum activity at the same FAS as the inductive model.

The models differed in explanation of the bed with the lowest activity. The inductive model suggested that FAS was too low, the mechanistic model that FAS impaired activity, but that this could not explain the very low activity observed. As the observed activity actually dropped during the initial phases of composting it was concluded that the instability of the bed during a rise in temperature was the reason why start up was so slow.

Composting at low oxygen levels puts high demands on compost beds. As the bed cannot be turned, no adjustments to water content or volatile solids content can be made during the process. Therefore, to achieve high quality compost, the feed mixture has to be carefully constructed. It must be balanced so that the desired stability of the remaining volatile solids coincides with the desired dry matter content of the compost.

To measure the amount of organic matter that has to be degraded for the solid organic matter to reach the desired stability a conceptual model of how degradation takes place is necessary. The hydrolysis model presented by Hamelers was used. This model predicts that there is an independent characteristic of the solid organic matter, namely the hydrolysis rate. This can be measured from the oxygen uptake rate of a sample suspended in water.

As compost feed is highly degradable, the oxygen uptake rate measurement would have to be able to measure high rates. The OxiTop, the method chosen for the measurements is suited for on farm analyses, but was not designed to measure high oxygen uptake rates. Therefore, in chapter 4 the mass transfer constraints on the oxygen supply and the carbon dioxide removal were tested. A model of the OxiTop system was constructed and analysed. On the basis of a thorough analysis system demands in relation to the usefulness and correctness of the measured rate

are presented. These relations can be used for any system measuring oxygen uptake rate or methane formation rate from pressure change.

The mass transfer coefficients of oxygen and carbon dioxide of the OxiTop system were measured. Using model calculations it was concluded that the OxiTop is a good instrument for measuring the oxygen consumption of a sample of organic material. However, the carbon dioxide absorption system provided by the manufacturer does not allow for a reliable measurement of rates. It was shown that with an adapted carbon dioxide absorption system the OxiTop can measure the rate of oxygen consumption. The water phase oxygen concentration was proven to be near equilibrium concentrations for oxygen uptake rates in the measurable region.

In chapter 5 a model for bacterial growth on hydrolysis in a batch system was presented. Analysis of the model showed that bacteria efficiently use the most limiting substance available. In a hydrolytic environment this is the substrate formed by hydrolysis. It was shown that under these circumstances sub-optimal concentrations for other substances do not influence activity if the supply is sufficient. Therefore, activity can be used as a measure for the hydrolysis rate.

The hydrolysis rate is a quality of the degrading material, rather than of the combination of bacteria and degrading material in the sample. It is therefore expected that predictions of degradation during composting based on the hydrolysis rate will prove more reliable than predictions based on other oxygen uptake rate measurements.

It appeared that it is only possible to perform the hydrolysis measurement within a desired period if enough active bacteria are present to reach hydrolytic conditions within that period. Measurements with the modified OxiTop of the rate of oxygen uptake of various samples showed the combined growth and mass transfer model used in chapter 5 can explain the observed variations. The prediction by the model that the hydrolytic conditions are reached later if the sample is diluted over a threshold level was confirmed.

In chapter 6 it is argued that the results of the research presented in this thesis can be used to make a better assessment of the possibilities of integrating a composting unit for the solid manure into the Hercules system or any comparable pig rearing system. There is now a clear and complete insight in the conditions and restrictions to which the system must adhere.

The results have given new insight in the effect of oxygen concentration and free air space on bacterial activity. It is now possible to interpret the effect of sub-optimal conditions better. This insight can be used to optimise the composting

process with regards to other parameters than maximum bacterial activity, not only for composting manure, but for any composting process.

This research has provided a new tool to predict the biodegradation during composting. The developed method for measuring the hydrolysis under aerobic circumstances gives an accurate and reproducible parameter describing the biodegradability of volatile solids. It is argued that this parameter can be used for long term predictions. It was shown that a similar method is in use in soil science, and that the hydrolysis measurement developed in this research can shorten the time needed to measure input data for this degradation model. It is suggested how this model for the degradation of volatile solids in the soil can predict degradation during composting.

Samenvatting

De veranderende houding van de maatschappij ten opzichte van de dierhouderij maakt systeemveranderingen in de varkenshouderij noodzakelijk. Het is voor de bio-industrie steeds moeilijker om aan de nieuwe eisen te voldoen door innovaties in het bestaande systeem. Om deze reden is het Hercules project opgezet. Het doel van dit project was om met een nieuw concept voor de varkenshouderij te komen dat in overeenstemming is met de maatschappelijke eisen. Om dit te bereiken werd de gehele keten, van het gebruikte voer tot de geproduceerde afval- en bijproducten opnieuw ontworpen. In het nieuw ontworpen productiesysteem worden de urine en feces in een vaste en een vloeibare fractie gescheiden. Dit heeft als voordeel dat de uitstoot van ammoniak en stankstoffen verminderd. Bovendien wordt een mestproduct verkregen dat beter aansluit bij de moderne bemestingstechnieken. Door dit mestproduct nog verder op te waarderen richting een hoger droge stof gehalte kan bespaard worden op de opslag- en transportkosten. Dit proefschrift behandelt de wijze waarop de vaste fractie van varkensmest verder kan worden opgewaardeerd via compostering.

In overeenstemming met de doelstellingen van het Hercules project moet de compostering van de mest op de boerderij zelf plaatsvinden. Dit betekent dat er slechts een beperkte ruimte en kennis aanwezig is om het proces tussentijds aan te passen. Een eerste vereiste was dan ook dat er een duidelijk en robuust protocol voor de compostering werd ontwikkeld.

Alhoewel composteren de bemestingswaarde alsmede de opslag en de verwerking van mest kan verbeteren, gaat het composteren van mest wel gepaard met de emissie van grote hoeveelheden ammoniak. Deze emissie zou vanuit maatschappelijk oogpunt onacceptabel zijn, en daarom is een nieuw composteringsproces bij lage zuurstofconcentratie ontworpen. Het voordeel van dit nieuwe proces is dat de geëmitteerde lucht wordt gekoeld en hergebruikt. Door dit hergebruik wordt de hoeveelheid geëmitteerd gas gereduceerd.

In een composteringsproces is lucht niet alleen noodzakelijk voor de aanvoer van zuurstof, maar ook om het compostbed te koelen. Vanwege deze koelfunctie moet de, door de compostering opgewarmde, lucht worden gekoeld voordat deze kan worden gerecirculeerd. Hierdoor ontstaat een condensaat waarin een deel van de uit de mest geëmitteerde ammoniak is opgelost. Het condensaat kan bij de vloeibare mestfractie gevoegd worden, en vormt zo geen extra afvalstroom. Omdat er ook ammoniak oplost in het condensaat zal dit lage zuurstof composteringsproces de gasvormige ammoniak emissie reduceren.

In de literatuur was weinig bekend over de efficiëntie waarmee micro-organismen zuurstof opnemen vanuit een lagere gas concentratie. In het lage zuurstof-proces, beschreven in hoofdstuk 2, wordt de aanvoer van zuurstof op peil gehouden doordat de snelheid van de gasstroom door het compostbed hoog is. Vervolgens is geanalyseerd wat het effect van verlaagde zuurstofconcentraties is op de activiteit van de micro-organismen. Daarnaast is onderzocht of de emissie van ammoniak daadwerkelijk verlaagd wordt door het recirculeren van gekoeld afgas.

Uit de resultaten bleek dat de activiteit van de micro-organismen afneemt als de zuurstofconcentratie verlaagd wordt. In een traditioneel composteringsproces is de activiteit onevenredig in de tijd verdeeld. Na een initiële hoge activiteit volgt een veel langere periode met een lage activiteit. In het lage zuurstof proces was de initiële activiteit dan wel lager, maar doordat de fase met de hoge initiële activiteit langer duurde bleek de uiteindelijke totale zuurstofopname over een periode van drie weken vergelijkbaar te zijn met de opname in een conventionele compostering.

De verlaagde initiële activiteit gaf wel een probleem met het opwarmen van het compost bed. De warmte die geproduceerd werd door het zuurstof gelimiteerde proces was onvoldoende, en de opstart van de compostering moest daarom plaatsvinden bij 10%(v/v) zuurstof. Nadat de gewenste composteringstemperatuur bereikt was, was de activiteit bij lage zuurstof concentratie hoog genoeg om het bed op temperatuur te houden. Daar de fase met de hoge initiële activiteit langer duurde, kon de compostering langer bij deze temperatuur plaatsvinden bij het lage zuurstof proces. De langzame temperatuurtoename betekent echter wel dat de compost bij het lage zuurstof proces niet tussentijds omgezet (gemengd) kan worden.

In het lage zuurstof proces werd een vergelijkbare hoeveelheid ammoniak geëmitteerd door het compostbed als bij hogere zuurstof concentraties. Echter, de hoeveelheid die naar de atmosfeer geëmitteerd werd was veel minder, dankzij de koeler in de recirculatie. Bij een zuurstofconcentratie van 10%(v/v) werd de helft van de geëmitteerde ammoniak in het condensaat gevangen. Bij een zuurstof concentratie van 1% werd 77% gevangen.

Hiermee is aangetoond dat composteren bij een lage zuurstof concentratie mogelijk is. De lagere afbraak snelheid van het materiaal is een voordeel. De temperatuur kan langer hoog gehouden worden, waardoor het product beter gehygiëniseerd is, en de verlaging van de initiële activiteitspiek betekent dat er minder ventilatiecapaciteit nodig is. De sterke reductie in afgasvolume betekent dat behandeling van het afgas goedkoper wordt, of achterwege kan blijven. De geproduceerde compost is vergelijkbaar met conventioneel geproduceerde compost.

Na de succesvolle test van het lage zuursof proces op lab schaal (80 liter) werden tests gedaan op pilot schaal (2000 liter). Hier bleek dat de benodigde toename van de temperatuur in het compostbed moeizaam was, zelfs bij hoge zuurstof concentraties. De samenstelling van de mest was anders dan die van de mest die op lab schaal was gebruikt. Om inzicht te krijgen in de wijze waarop de samenstelling van de mest het composteringsproces beïnvloedt is met behulp van systeemanalyse gezocht naar de belangrijkste parameter die de activiteit kan verklaren. Geconcludeerd werd dat het gas gevulde porievolume van het compostbed (FAS) de meest waarschijnlijke parameter was om de lage activiteit te verklaren. Met behulp van data van de pilot schaal experimenten zijn in hoofdstuk 3 twee modellen getoetst die gevonden werden in de literatuur en die de activiteit voorspellen op basis van de FAS.

Het eerste model is een inductief model gebaseerd op experimentele data. Het tweede model is een mechanistisch model dat het effect van de drie fasen, vast vloeibaar en gas, op de activiteit berekent. Het tweede model geeft meer inzicht en heeft als voordeel dat het het gehele effect van de bedstructuur op de activiteit beschrijft. Het mechanistische model was echter nog niet gevalideerd. De resultaten van de pilot schaal experimenten, en de correlatie tussen het mechanistische en het inductieve model zijn gebruikt om het mechanistische model te valideren.

De activiteit van de compostbedden werd geschat met behulp van de gemeten temperatuurstoename, en de FAS werd geschat uit het reactorvolume en de massa van de verschillende compostbedden. Deze data werd gebruikt om de voorspelling van de activiteit door de twee modellen te testen. Beide modellen bleken de activiteit even goed te voorspellen. Daarnaast kwam uit de resultaten naar voren dat de FAS inderdaad de parameter is die de activiteit bepaald. Er was een grote mate van correlatie tussen de modellen. De uit de data geschatte parameters voor het mechanistische model voorspellen de maximale activiteit bij dezelfde FAS als het inductieve model.

Echter, de modellen verschilden in hun verklaring van het bed met de laagste activiteit. Het inductieve model gaf aan dat de FAS te laag was. Het mechanistische model gaf aan dat de lage FAS de activiteit wel verlaagde, maar dat dit onvoldoende was om de extreme verlaging van activiteit te verklaren. Doordat de activiteit in dit bed afnam gedurende de compostering werd geconcludeerd dat de lage activiteit het best verklaard werd door de instabiliteit van het compostbed bij toenemende temperatuur.

Composteren bij lage zuurstof concentraties stelt hoge eisen aan het compostbed. Doordat het bed niet tussentijds kan worden omgezet, kan het watergehalte of de

hoeveelheid afbreekbaar materiaal niet aangepast worden tijdens het proces. Om een hoogwaardige compost te verkrijgen moet het uitgangsmateriaal daarom nauwkeurig samengesteld worden. Dit uitgangsmateriaal moet zo gemengd worden dat de gewenste stabiliteit van de overgebleven organische stof op precies dat moment bereikt wordt dat de compost het gewenste watergehalte heeft.

Om te meten hoeveel organische stof afgebroken moet worden om de gewenste stabiliteit te bereiken is een conceptueel model van de afbraak noodzakelijk. Hiervoor is het hydrolyse model van Hamelers gebruikt. Dit model voorspelt dat er een onafhankelijke eigenschap van het organische materiaal is, namelijk de hydrolyse snelheid. Deze kan gemeten worden door de zuurstof consumptie snelheid van een monster organisch materiaal gesuspendeerd in water te meten.

Omdat het uitgangsmateriaal bij composteren makkelijk afbreekbaar is en dus veel zuurstof verbruikt, moet de zuurstof consumptie snelheidsmeting hoge opnamesnelheden kunnen meten. Alhoewel de OxiTop, de gekozen methode, geschikt is voor metingen op de boerderij, is deze niet ontworpen om hoge zuurstof consumptiesnelheden te meten. Daarom zijn in hoofdstuk 4 de massatransport limitaties van de zuurstof aanvoer en de kooldioxide afvoer getest. Hiertoe werd een model van de OxiTop geconstrueerd. Vervolgens konden op basis van een uitvoerige analyse de systeem voorwaarden in relatie tot de bruikbaarheid en de juistheid van de gemeten snelheden worden gevonden. De gevonden relaties gelden voor alle systemen waarin de zuurstof consumptie snelheid of de methaan productie snelheid gemeten wordt op basis van drukverandering in het systeem.

De massatransportcoëfficiënten van zuurstof en kooldioxide in de OxiTop zijn gemeten. Met behulp van modelberekeningen werd geconcludeerd dat de OxiTop een goede methode is om de zuurstofconsumptie van een organische stof monster te meten. De kooldioxide absorptiesnelheid in het geleverde systeem is echter onvoldoende om de snelheid van consumptie te meten. Er is aangetoond dat met een aangepast kooldioxide absorptiesysteem ook de consumptiesnelheid met de OxiTop gemeten kan worden. Er is bewezen dat de zuurstofconcentratie in de waterfase bij metingen binnen het bereik van de meting nagenoeg de evenwichtsconcentratie met de gasfase is.

In hoofdstuk 5 is een model voor bacteriële groei op een hydrolyserend substraat in een batch systeem gepresenteerd. Analyse van dit model liet zien dat de bacteriën het meest limiterende substraat efficiënt opnemen. Onder hydrolyserende omstandigheden is dit het substraat dat door hydrolyse vrijkomt. Er is aangetoond dat onder deze omstandigheden suboptimale concentraties van andere stoffen de activiteit niet beïnvloeden als de aanvoer ervan voldoende is. Daardoor kan de activiteit als maat voor de hydrolyse gebruikt worden.

De hydrolyse snelheid is een kwaliteit van het hydrolyserende materiaal, en niet van een combinatie van het materiaal en de aanwezige biomassa. De verwachting is daarom dat voorspellingen van afbraak tijdens het composteren gebaseerd op de hydrolysesnelheid meer betrouwbaar zullen blijken dan voorspellingen gebaseerd op andere zuurstofconsumptie metingen.

Het bleek dat het alleen mogelijk is de hydrolyse meting binnen een gewenste periode te doen als er voldoende biomassa aanwezig is om binnen die periode hydrolyserende omstandigheden te krijgen. Metingen van de zuurstofconsumptie-snelheid van verschillende monsters met de aangepaste OxiTop lieten zien dat het gecombineerde groei en massatransportmodel uit hoofdstuk 5 de waargenomen variatie kan verklaren. De voorspelling van het model dat hydrolyserende omstandigheden later bereikt worden als het monster over een drempelwaarde verdund wordt, werd bevestigd.

In hoofdstuk 6 wordt beargumenteerd dat de resultaten van dit onderzoek gebruikt kunnen worden voor een betere evaluatie van de mogelijkheden om een composteringsunit voor de vaste mestfractie in het Hercules systeem, of een vergelijkbaar varkenshouderijsysteem, te integreren. Er is nu een duidelijk en compleet inzicht in de condities en randvoorwaarden waaraan het systeem moet voldoen.

De resultaten hebben een beter inzicht opgeleverd in het effect van de zuurstofconcentratie en de FAS op de bacteriële activiteit. Het is nu mogelijk om het effect van sub-optimale condities beter te interpreteren. Dit inzicht kan gebruikt worden om het composteringsproces te optimaliseren in relatie tot andere parameters dan een maximale activiteit. Dit geldt niet alleen voor het composteren van mest, maar ook voor alle andere composteringsprocessen.

Dit onderzoek heeft een nieuw gereedschap opgeleverd om de biodegradatie tijdens het composteren te voorspellen. De ontwikkelde methode om de hydrolyse onder aërobe omstandigheden te meten geeft een accurate en reproduceerbare parameter die de biodegradeerbaarheid van de organische stof beschrijft. Er wordt aannemelijk gemaakt dat deze parameter gebruikt kan worden voor lange termijn voorspellingen. Er wordt aangetoond dat een vergelijkbare methode in de bodemwetenschappen gebruikt wordt, en dat de ontwikkelde hydrolyse meting de benodigde tijd om de input parameter te meten, kan verkorten. Tevens wordt aangegeven hoe het biodegradatie model voor de bodem ook de biodegradatie tijdens composteren zou kunnen voorspellen.

Curriculum Vitae

Dale Philip Rudrum werd op 19 juni 1969 geboren te Vlaardingen, waar hij in 1987 hij zijn VWO diploma behaalde aan de openbare scholen gemeenschap Professor Casimir. In datzelfde jaar begon hij met de studie moleculaire wetenschappen aan de Landbouw Universiteit Wageningen. In 1992 staakte hij deze studie. In 1995 begon hij aan dezelfde instelling aan de studie milieuhygiëne, die hij in 1998 afrondde. Na een korte carrière als enquêteur bij Vragenderwijs begon hij in 1999 als AIO bij de sectie Milieutechnologie van de Landbouw Universiteit Wageningen. Naast het onderzoek dat beschreven is in dit proefschrift heeft hij daar een inventarisatie gemaakt van de gebruikte labinfrastructuur van Milieutechnologie en de te verwachtten onderzoeksvertraging door verplaatsing van de daar gebruikte reactoren bij een verhuizing van de sectie. Ook heeft hij als adviseur meegewerkt aan een kort project voor de gemeente Gemert Bakel. In dit project werden voorstellen ontwikkeld voor de reconstructie van het platteland. Momenteel is hij werkzaam voor het LEI, alwaar hij meewerkt aan een milieu-, economisch-optimalisatiemodel van de melkveehouderij.

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Hoewel alleen mijn naam op de kaft staat, is dit proefschrift het resultaat van een gezamenlijke inspanning. Zowel op het werk als thuis heb ik veel ondersteuning gekregen, en zonder die hulp zou dit werk niet in deze vorm bestaan hebben. Zonder contract, en dus zonder kinderopvang, was het schrijven een moeizame klus van uren sprokkelen, vaak 's nachts. Johan die ook vaak nachtwerk verricht(te) maakte het verblijf op het Biotechnion een stuk gezelliger. Ook bedank ik mijn ouders en Tanja die de zorg van Corijn en Janna regelmatig overnamen zodat ik weer een paar uur of dagen overdag kon werken. Speciaal wil ik mijn vader noemen die aan dit proefschrift meer dan alleen het engels verbeterd heeft.

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De vakgroep is te groot om iedereen bij naam te noemen, ik kom bijvoorbeeld al op 16 kamergenoten. Ik heb er prettig gewerkt, zeer veel geleerd en ook lol gehad. De vakgroepuitjes, de borrels en de vrijdagmiddagen voordat ik kinderen had, waren mooie momenten. Het geven van practicum en de ver en in-huizing- en nieuwbouw-perikelen waren leuke nevenactiviteiten. Wel heb ik gemerkt dat als je even op een andere locatie bent het contact snel verwaterd. Ik vind het dan ook een blijde gebeurtenis dat B'kom nu bij de rest is gevoegd. Ik hoop alleen wel dat er goed nagedacht is over de invloed hiervan op het werk van individuele onderzoekers.

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