DRY ANAEROBIC DIGESTION OF THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

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Dry Anaerobic Digestionof the Organic Fraction of Municipal Solid Waste

PROEFSCHRIFT
ter verkrijging van de graad van
doctor in de landbouw- en milieuwetenschappen,
op gezag van de rector magnificus,
dr. H.C. van der Plas,
in het openbaar te verdedigen
op woensdag 21 april 1993
des namiddags te vier uur in de Aula
van de Landbouwuniversiteit te Wageningen.

STELLINGEN

NN08201, 1613

1. Het door De Baere en Verstraete gerapporteerde maximale droge stofgehalte van 40 %, waarbij anaërobe vergisting van vast organisch afval mogelijk is, wordt niet gestaafd door hun experimenten. Het werkelijk maximale droge stofgehalte, waarbij anaerobe vergisting van vast organisch afval mogelijk is ligt hoger en bedraagt 50 %.

Dit proefschrift.

De Baere, L. and Verstraete, W., (1984), Anaerobic digestion of solid and semi-solid substrates, In: G.L. Ferrero, M.P. Ferranti, and H. Naveau [Eds.] Anaerobic digestion and carbohydrate hydrolysis of waste, Elsevier Applied Science Publishers, London, p.195-208.

2. Bij anaërobe vergisting van vast organisch afval, waarbij de deelprocessen met evenhoge snelheid verlopen, leidt een verlaging van de proces-temperatuur bij de opstart van 35 °C naar 30 °C of lager tot ontkoppeling van de zuur-vorming en waterstof-vorming enerzijds en de methaanvorming anderzijds door een verschil in temperatuur-respons van deze deel-processen.

Dit proefschrift.

3. Bij de bestudering van een mogelijk toxische effect van niet-gedissocieerde vluchtige vetzuren op de acetolastische methanogenese bij verschillende pH-waarden wordt een mogelijk remmend effect van de aanwezige kat-ionen door Attal et al. ten onrechte verwaarloosd.
Attal A., F. Ehlinger, J.M Audic and G.M. Faup, (1988). In: E.R: Hall and P.N. Hobson (Eds.) Anaerobic Digestion 1988, p.71-78.

4. Door het onvermeld laten van de optimale recirculatie-verhouding van onbehandeld afval en vergist afval in het DRANCO-proces doen De Baere et al. afbreuk aan het wetenschappelijk gehalte van hun publikaties, waardoor terecht ernstige twijfel ontstaat omtrent hun werkelijke kennis van het proces.

De Baere, L. and Verstraete, W., (1984), Anaerobic digestion of solid and semi-solid substrates, In: G.L. Ferrero, M.P. Ferranti, and H. Naveau [Eds.] Anaerobic digestion and carbo hydrate hydrolysis of waste, Elsevier Applied Science Publishers, London, p.195-208.
De Baere L., Verdonck, O., and Verstraete, W. (1986). High rate anaerobic composting process for the organic fraction of solid wastes, Biotechnol. Bioeng. Symp. No.15:321-330.

5. De door Gijzen et al. gerapporteerde hoge omzettingssnelheid van cellulose-houdend materiaal in het RUDAD systeem moet niet zozeer worden toegeschreven aan een bijzonder hoge activiteit van de ciliaten, maar kan veeleer worden verklaard uit de geringe deeltjesgrootte van het organisch materiaal, dat in het RUDAD systeem aan vergisting wordt onderworpen.

Gijzen H.J., Lebbering, H.J., Verhagen, F.J. Zwart, K.B., Vogels, G.D., (1987). Application of rumen organisms for an enhanced anaerobic degradation of solid organic waste materials, Biol. Wastes 22:81-95.

6. In het algemeen kunnen de micro-organismen die aktief zijn bij aërobe omzetting van organisch afval worden gekenmerkt door 'grijp wat je grijpen kunt', terwijl anaërobe microbiële populaties hierbij kunnen worden gekenmerkt door 'overleven in goede samenwerking'.

R.A. Prins, NVA-TCA workshop, Veldhoven, 1992.

7. De dreiging van het ontstaan van een 'GFT-compostberg' is het gevolg van het onevenwichtige overheidsbeleid inzake de inzameling en verwerking van Groente-, Fruit- en Tuinafval, waarbij voornamelijk wordt gekeken naar de 'grondstof', (dat wil zeggen naar het beperken van de milieuvervuiling door afval), en de 'produkt'-zijde wordt verwaarloosd.

8. Het hoge honorarium, dat aan een topvoetballer wordt betaald, bewijst, dat het werkelijk belang van iemands werkzaamheden omgekeerd evenredig is met de hoogte van de toegekende honoraria.

9. Voor het elimineren van milieuvreemde stoffen uit grond geldt, dat deze verbindingen hierbij soms in meerdere opzichten een onopgelost probleem vormen.

10. Bij het ontbreken van humor in het merendeel van de wetenschappelijke publikaties geldt als kanttekening, dat sommige publikaties desondanks lachwekkend kunnen zijn.

11. Voor het terugbrengen van het cadmium-gehalte in GFT-compost verdient het aanbeveling, het gebruik van cadmiumhoudende kunstmest bij het kweken van groenten te verbieden.

12. De huidige besteding van het overheidsbudget voor bodemsanering, waarbij voor het daadwerkelijk reinigen van grond slechts een beperkt deel van het beschikbare budget wordt aangewend, gebeurt inefficiënt en leidt daardoor tot onnodig hoge kosten.

13. Bij het gegeven, dat in Nederland jaarlijks talloze fietsen worden ontvreemd, zonder dat de overheid hiertegen veel actie onderneemt, kan de overheid als excuus aanvoeren, dat het milieuvriendelijke aspect hierbij, namelijk het ontvreemden van een milieuvriendelijk vervoermiddel, belangrijker is dan het criminele aspect.

Stellingen bij het proefschrift "Dry anaerobic digestion of the organic fraction of Municipal Solid Waste" van E. ten Brummeler, Wageningen, 21 april 1993.

"Along with death and taxes, garbage is one of life's great certainties"

VOORWOORD

Een proefschrift heeft veel weg van de spreekwoordelijke ijsberg, het merendeel wat eraan ten grondslag ligt blijft onzichtbaar. Op deze plaats wil ik toch een aantal mensen bedanken die een aanzienlijke bijdrage hebben geleverd.
Het onderzoek is uitgevoerd onder de dagelijkse leiding van Iman Koster, wiens stimulerende invloed en ideeën onmisbaar zijn geweest bij het uit de grond stampen van een vrij nieuw onderzoeksgebied. Hij zorgde tevens voor het vasthouden van de hoofdlijnen en voor motivatie voor het schrijven van publikaties, die hebben geleid tot dit proefschrift.
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De begeleidingscommissie van het BIOCEL-project, onder voorzitterschap van ir. H.J.M. Kruijdenberg van NOVEM, zorgden voor een kritische kijk vanuit de praktijk.
Jan Zeevalkink en Harry Beukema, tijdens het onderzoek nog werkzaam bij initiatiefnemer Heidemij, wil ik bedanken voor de prettige samenwerking bij de pogingen om het BIOCEL-concept tot een succes te maken.
Mijn huidige werkgever, Heidemij Realisatie BV, heeft een soepele afronding van het proefschrift mogelijk gemaakt door in te stemmen met een tijdelijk part-time dienstverband, daarna door de goede en stimulerende werksfeer.

En, 'last but not least', Gatze Lettinga wil ik bedanken voor zijn bereidheid als promotor op te treden, ondanks zijn zeer drukke werkzaamheden. Zijn kritische beoordeling van het manuscript, en zijn vele ideeën voor verbetering, hebben het eindresultaat sterk bepaald.

Het onderzoek is gefinancierd in het kader van het NOH-programma, beheerd door NOVEM en RIVM.

Omslag-ontwerp:Simon Sprietsma

ABSTRACT

Ten Brummeler, E., (1993) Dry Anaerobic Digestion of the Organic Fraction of Municipal Solid Waste, Doctoral Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Anaerobic digestion is an attractive technology for solid waste management. This thesis describes the technological potentials of dry anaerobic digestion of the organic fraction of Municipal Solid Waste (MSW) using batch systems. In 1985 a research programme was started to develop the so- called BIOCEL system based on batchwise anaerobic digestion yielding biogas and compost. The research programme was financially supported by the Dutch National Programme for reuse of Waste (NOH), which is coordinated by NOVEM, the Dutch Organization for Energy and the Environment and RIVM, the Dutch Institute for Public Health and the Environment. The research was carried out on laboratory scale as well as on pilot-plant scale. This study presents the results of the experimental work.

For start-up of the dry digestion of the organic fraction of MSW, the addition of a methanogenic inoculum appears to be essential. The best results are obtained with the digested residue as the methanogenic inoculum at start-up. Start-up of dry anaerobic digestion of Vegetable Fruit and Yard (VFY) waste, the source-separated organic fraction of Municipal Solid Waste, is also investigated. The total solids retention time (SRT) at an inoculum factor of 0.50 is 28 days.

The influence of temperature and the total solids (TS) concentration on the rate of the anaerobic digestion process was investigated. Depending on the start-up procedure, anaerobic digestion proceeds in the range of 10 to 50 % TS at similar rate. The optimum temperature of the process is 40 °C. The acid formation rate shows less response to a temperature increase then does the methanogenesis.

The effect of suboptimal transport of free liquid phase in the solid waste bed of solid waste digesters was studied. It has been found that dry anaerobic batch digestion of solid organic wastes can proceed at pH values as low as 5.2 and organic acid concentrations of 40-50 g COD/l in the digester environment. Methanogenesis takes place in zones that are formed in the solid waste bed due to heterogenous mixing characteristics of the reactor contents. The phenomenon of methanogenesis in dry anaerobic digestion of solid wastes under extreme conditions, such as pH values below 6, and volatile fatty acid concentrations up to 40 g/l was studied. Methanogenesis is possible at an initial acetate concentration as high as 583 mM (38 g/l) and at pH = 7.0. Microscopic observations of enriched cultures show that the predominant organisms resemble the genus *Methanosarcina sp.*

Pilot-scale experiments (5 m^3, 450 m^3) illustrated the technological potentials of the BIOCEL process. Based on the results of the experiments on several scales it can be concluded that the process is ready for full-scale application. Future research should deal with the microbial and kinetic aspects of the hydrolysis of particulate organic matter present in the organic fraction of Municipal Solid Waste.

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

Background of this thesis

Environmental pollution as a result of waste production has been found since human communities exist. As early as the Middle Ages, provisions were made for pollution in the cities; the result of several types of wastes, mainly of agricultural origin (Van Zon, 1986). During the course of the 19th century the formulation of regulations for waste disposal by Dutch local authorities was stimulated by increased medical knowledge. However, a central law for the efficient regulation of waste disposal and waste treatment was not established. The institutions involved with these regulations had only an advisory function, and were unable to enforce measures. The need for a central law concerning waste production and waste treatment increased even further after World War II when waste production, industrial as well as non-industrial, raised explosively.

In The Netherlands in October 1977, an act concerning the management and disposal of waste material (Afvalstoffenwet) became effective (IMP, 1984). The aim of this law was to regulate waste material production, to stimulate the reuse of wastes, and the elimination of wastes within a juridic scope. Since 1977 the 'Afvalstoffenwet' progressed in phases. Januari 1st 1993 the 'Afvalstoffenwet' is replaced by the 'Wet Milieubeheer', an integrated law for several environmental legal regulations.

In 1988 a list of thirty waste materials with priority was assessed. Four groups of waste materials are distinghuished (Staatsblad, 1977):

1 all solid household waste and wastes from industry with similar composition which could be treated at the same time;

2 other industrial wastes that could not be treated with household waste, and waste from the construction and destruction of buildings;

3 car wrecks;

4 all other groups of wastes (sewage sludge, wastes from hospitals, agricultural wastes).

The policy for waste management in The Netherlands will be based on three major concepts:

1 prevention and limitation of the production of waste

2 separation of waste components

3 reuse and recycling of waste materials.

For household waste (Municipal Solid Waste), which is produced at a rate of $6x10^6$ tons per year (400 kg/inhabitant/yr), referred to as MSW, this policy has already had some success for some components, such as paper and glass (Doekemeijer and Van Ierland, 1987; IMP, 1984).

Presently however, the most applied methods for MSW treatment are landfilling (46 %) and incineration (34 %), while only 20 % is recycled (IMP, 1984). Landfilling and incineration are not definitive solutions, as they do not eliminate completely the waste materials. Landfilling is partially a waste reduction, but rather more a concentration of waste, requiring large land areas and leading to emissions of several pollutants (Hoeks, 1983). Incineration leads to the emission of air pollutants and fly ashes, while a large amount of ash and residues from off gas treatment require further treatment. The incineration process needs advanced technology to minimize the effects on the environment. However, from an economic point of view both methods are still attractive.

Until recently, (aerobic) composting, one of the oldest methods for MSW treatment, was of minor importance. Only 3.7 % of the MSW that is produced yearly in The Netherlands was disposed of with this method (Bretthouwer, 1989). Until the beginning of the 20th century compost was used as a soil fertilizer (Van Zon, 1986). With the introduction of industrially produced fertilizer and due to decreasing quality of the compost, the large-scale application of this method of treatment was terminated.

Compost can be produced from the organic fraction of MSW, the so-called Vegetable, Fruit and Yard (VFY) waste, which is by far the largest fraction of MSW produced in The Netherlands (Fig. 1). Composting the total amount of VFY can result in a 50 % increase in the amount of recycled MSW, given that the compost produced can be applied as soil conditioner. The applicability of the compost is determined by the grade of contamination with potential toxic compounds such as heavy metals. Since the year 1991, compost must meet certain standards for these compounds (Ministerie VROM, 1986; BOOM, 1991).
The heavy metal content of compost is determined by the way the MSW is composted (Van Roosmalen et al., 1986). The contact time of the contaminating compounds plays a role in this respect. Three ways of compost production can be distinguished:

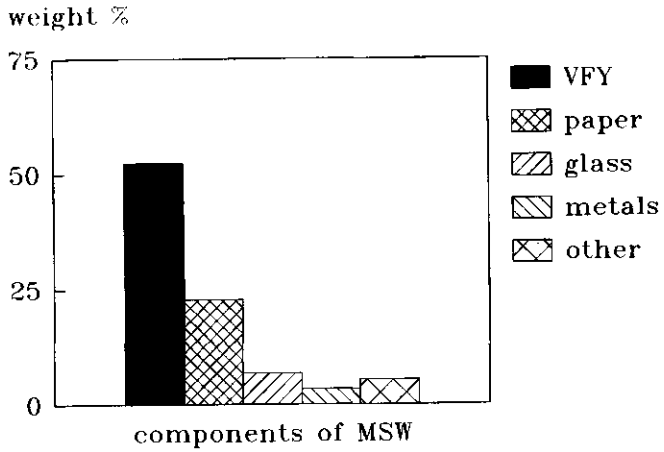

Fig. 1 Composition of Municipal Solid Waste in The Netherlands today.

- composting of MSW followed by separation of the inorganic components from the compost,
- mechanical separation in several fractions followed by composting of the separated organic fraction,
- source separation of the VFY, i.e. the organic fraction is separated by the households themselves, followed by composting.

In The Netherlands, separate collection of VFY has proven to be successful (Lustenhouwer and Reyenga, 1987). Compost which is produced from the source separated VFY will meet the 1995-1999 standards, while the compost from the mechanically separated organic fraction just meets the standards of 1987-1991 (Martens and Lustenhouwer, 1986). By the year 1995 the VFY waste must be collected separately by the responsible authorities according to the most recent governmental policy (NMP+, 1990).

An attractive alternative for the aerobic composting of the organic fraction of MSW as a biotechnological stabilization process for this fraction could be anaerobic digestion. This method offers an advantage over aerobic composting the production of biogas. In this way an energy carrier can be recovered from the waste, while during aerobic composting the potential available energy is released as heat. The use of biogas as a fuel will also contribute

to a lower release of carbon dioxide produced from fossile fuels. The fast increasing carbon dioxide concentration in the atmosphere due to the incineration of fossile fuels is believed to be responsible for the so called 'Green House Effect'. Due to this effect the mean temperature on earth is increasing and the climate may change worldwide.

Under optimal conditions the heat production in aerobic composting may lead to the removal of moisture from the waste by evaporation. The digested residue is similar to the compost from an aerobic process, but it generally has a higher moisture content.

However, successful application of anaerobic treatment so far has been mainly limited to wastewaters and slurries (De Baere and Verstraete, 1984; Ghosh, 1984). The potentials of anaerobic digestion for the treatment of organic solid wastes have not yet been shown by a number of large scale applications.

In the next paragraph the anaerobic digestion of solid waste will be discussed in more detail. After this an overview will be given of several potential attractive systems for anaerobic digestion of the organic fraction of MSW.

Anaerobic digestion of the organic fraction of Municipal Solid Waste

The substrate

As discussed above, 50 % of the total weight of MSW produced in The Netherlands (and of most western countries) consists of Vegetable, Fruit and Yard waste (De Baere and Verstraete, 1984; Vokes, 1983; Handboek Composteren, 1991). This fraction forms the biodegradable part of the MSW, although paper, which is mainly composed of fairly biodegradable carbohydrates, cellulose and haemi-cellulose, (Chandler et al., 1978; Pirt, 1978), also belongs to the biodegradable fraction. The paper content of organic fractions of MSW depends on the separation process applied. The organic fraction from a mechanical separation process, during which MSW is shredded or hammer-milled, generally contains a substantial amount of paper, while this is not the case for source-separated VFY-waste. In relation to the composition of the organic waste, the C:N:P ratio of the substrate is an important parameter which has to be considered. A high fraction of paper will result in a sub-optimal C:N:P ratio for microbial growth. An indication of the optimum nutrient ratio can be derived from the ratio of the nutrients present in the biomass of bacteria, which is 25 : 4 : 1 (C:N:P, w/w). Literature data show that the ratio normally found in organic fractions from MSW in Europe is in the optimum range (Cecchi et al., 1988). However, an optimum ratio in the waste does not necessarily mean that the nutrients are available to the microorganisms. Analysis of leachate from landfills where anaerobic digestion of MSW was found, indicated that sufficient amounts of S, N and P compounds should be available for the microorganisms (Rees, 1980a). These data suggest that growth rate limitation by nutrients is unlikely in the anaerobic digestion of organic fractions of MSW.

The composition of the particulate organic matter depends greatly on the source of the organic fraction. Roughly, it reflects the composition of ligno-cellulosic biomass, but also contains lipid, starch and sugar compounds (**TABLE 1**).

Table 1 Composition of the volatile solids of two organic fractions of MSW compared to biomass (compound as % of volatile solids)

substrate	cellulose + hemicellulose	lignin	proteins	starch	lipids	cell solubles
biomass	26-75	3-28	0-30		0-2	3-40
organic fraction 1[1]	55	16	12	1	10	6
organic fraction 2[2]	54	21	15	5	3	7

[1]fraction from a mechanical separation
[2]fraction from source separation (VFY-waste)

A certain part of the organics is not present in particulate form but is dissolved in the water phase. The amount of the dissolved organic compounds depends on the age of the organic fraction. The amount of the solute can amount to 10-13 % of the volatile solids (Traverso and Cecchi, 1985). As is known from ensilage fermentation, water solubles, such as sugars and amino acids, are rapidly released from plant cells during storage of biomass and are fermented at high rate by specific groups of bacteria (McDonald, 1982).

The microbial degradation of the cellulosic part is often thought to be the most difficult step since this compound is bound to the lignin in many types of biomass, the so-called ligno-cellulose complex. This compound has a high crystallinity and a high lignin content. Both factors limit the rate and the degree of the degradation process (Chandler et al., 1978; Tsao, 1984).

Numerous experimental data exist in the literature about the anaerobic degradability of the categories of compounds present in the organic fraction of MSW in well-defined systems, such as lipids, proteins and carbohydrates. However, the organic fraction consists of a highly concentrated mixture of these compounds, which might lead to deviating degradability and degradation kinetics as compared to the pure compounds. The potential biogas yield of the biodegradable organic fraction of MSW can be estimated on base of the following formula:

$$C_nH_aO_bN_d + (n-a/4-b/2+3/4d)H_2O \longrightarrow$$

$$(n/2-a/8+b/4+3/8d)CO_2 + (n/2+a/8-b/4-3/8d)CH_4 + dNH_3 \quad (1)$$

In the specific case of glucose as a substrate equation (1) evaluates to:

$$C_6H_{12}O_6 + H_2O \longrightarrow 3CO_2 + 3CH_4 \quad (2)$$

Table 2 Estimation of the biogas and compost yield of the organic (VFY) fraction of municipal solid waste after anaerobic digestion

VFY-waste[1]:	
- total solids (TS, w/w %)	40
- volatile solids (VS, % of TS)	60
- maximum m^3 STP biogas/kg VS	0.83
- maximum m^3 STP biogas/kg VFY	0.23-0.30
- actual biogas yield[2] (STP m^3/kg)	0.09
- maximum VFY waste production (tons/yr)	3.0×10^6
- potential biogas yield in The Netherlands from VFY-waste (STP m^3/year)	270×10^6
- natural gas equivalent (STP m^3/yr)	181×10^6
- total compost yield (tons/year,70 % TS)	1.2×10^6

[1] data from Mooijman et al. (1986) and Handboek Compostering van GFT-afval (1991)

[2] mean value adapted from Cecchi et al. (1988)

Due to the heterogenous composition of the organic fraction of MSW reliable data are not available in the literature for the composition of this material. Assuming that carbohydrates are the main biodegradable compounds, an indication can be given for the biogas yield of 1 kg biodegradable dry organic matter from the organic fraction of MSW (TABLE 2). The data from TABLE 2 are calculated for organic fractions that were free of paper. When an organic fraction contains significant amounts of paper, i.e. more dry biodegradable organic matter, the total solids content will be higher and consequently, the biogas yield per kg 'wet' organic

fraction will also be higher. A biogas yield of 180-200 m^3/ton was reported for an organic fraction of 56 % TS, which still contained the paper fraction (De Baere and Verstraete, 1984).

Assuming 50 % degradation of the volatile solids (= organic matter) the total amount of biogas (CO_2 : CH_4 $\approx$ 1:1 by volume) that can potentially be produced yearly from the organic fraction of MSW in The Netherlands by anaerobic digestion (TABLE 2) can be estimated at 181 x 10^6 Nm^3 natural gas. Apart from biogas, compost is produced. From a volatile solids reduction of 50 %, the residue yield amounts to 0.88 kg/kg VFY-waste; the digested VFY will have a total solids concentration of 30 %. Increasing the total solids concentration of this residue to 70 %, the more or less standard value for compost, the potential yield of compost would be 1.35x 10^6 tons/year.

Microbial aspects

Anaerobic digestion of the organic fraction of MSW is the result of the activity of several groups of anaerobic bacteria which degrade the (mostly particulate) complex organic matter to the simple end products, carbon dioxide and methane, in the absence of other electron acceptors such as sulfate and nitrate (Fig. 2) (Gujer and Zehnder, 1983; Koster, 1988). Many bacterial species with unique types of syntrophic relations are found during this process (Zeikus, 1982; McCarthy, 1982). Four groups of bacteria which differ in their metabolic reactions can be distinguished during anaerobic digestion of complex organic matter (Zeikus, 1982).

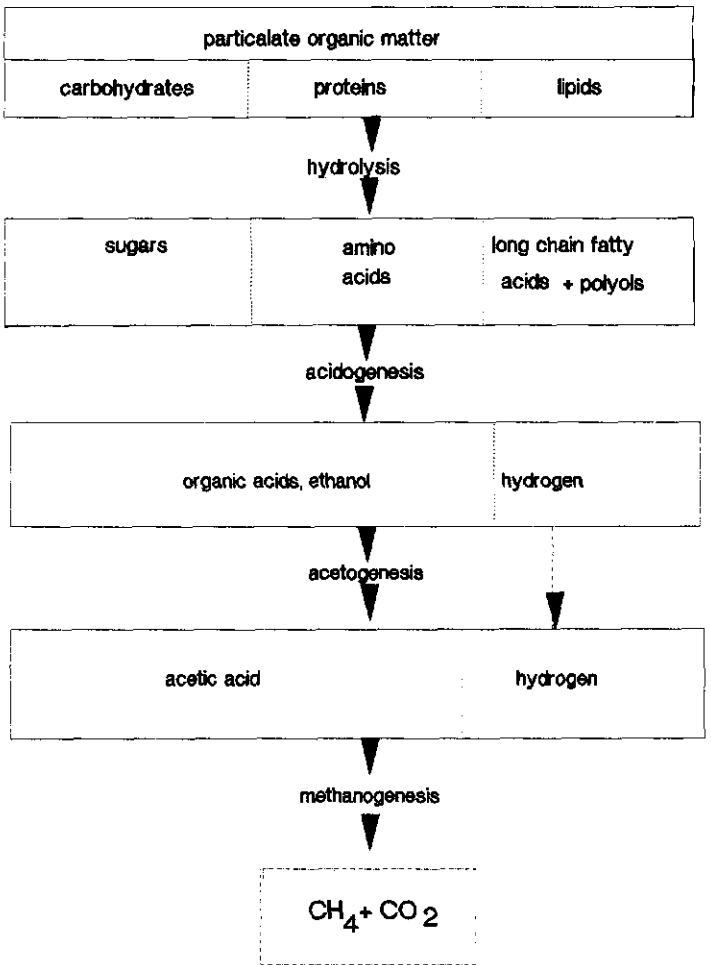

Fig. 2 The four stages during anaerobic digestion of particulate organic matter

The four steps which can be distinguished in the anaerobic degradation of particulate organic matter are:

1 Hydrolysis: liquefaction of the polymers present in particulate (insoluble) form. The products of the hydrolysis are the soluble monomers, unlike in the case of lipids, where the higher fatty acids are insoluble;

2 Acidogenesis: fermentation of soluble compounds (sugars, amino acids, alcohols, higher fatty acids) to the main products volatile fatty acids, hydrogen and carbon dioxide, by acidogenic bacteria; under some conditions lactic acid and/or ethanol also are being formed;

3 Acetogenesis: oxidation of the products of the acidogenesis to acetate, hydrogen and carbon dioxide by acetogenic bacteria. These bacteria can only function in a syntrophic relation with hydrogen oxidizing bacteria (Boone and Bryant, 1980);

4 Methanogenesis: formation of methane from the products of the acetogenesis by decarboxilating acetate by acetotrophic methanogens and by hydrogenization of carbon dioxide by hydrogenotrophic methanogens. Tracer studies as well as thermodynamic calculations show that 70 % of the methane is produced by acetate decarboxilation and 30 % by hydrogenation of carbon dioxide (Jeris and McCarthy, 1965, Kaspar and Wuhrmann, 1978).

Significance of process balance

A simplification of the four-step model for bacterial activity during anaerobic digestion can be made by assuming that in fact, two principally different groups of organisms are abundant during anaerobic digestion of particulate organic matter, viz. the acid formers and the methane formers. The methanogenic bacteria are a more sensitive group than the acid formers with respect to environmental conditions such as pH, temperature, and toxic compounds. The difference in physiology and sensitivity for stress conditions is further illustrated by the fact that the methanogens belong to the archae-bacteria, while the other three groups belong to the eu-bacteria (Zehnder, 1978).

It is known that fermentative bacteria have a far higher tolerance for low pH values (lower than 6) than methanogens (Pohland and Ghosh, 1971; Koster, 1988). The former bacteria have a pH optimum in the range 6.7-7.4 (Zehnder et al., 1982). From silage fermentation it is known, that among fermentative bacteria there are also differences in tolerance for low pH values (McDonald, 1983). During silage fermentation, e.g. fermentation of grass, lactic

acid is being formed from soluble sugars by lactic acid bacteria at pH values, where other microbial activity is not observed. At a certain pH level, usually lower than pH = 5, the metabolic activity of the lactic acid formers ceases because of the exhaustion of the soluble sugars and not because of the low pH. At that point the silage is stable, i.e. the biomass is prevented from being fermented further due to low pH and high lactic acid concentration. It is known that certain organic acids formed anaerobically from glucose can inhibit the growth of certain groups of acidogenic bacteria, and that the inhibiting compound is the undissociated acid (Van den Heuvel, 1986). This phenomenon can be indicated as product inhibition. The generally accepted mechanism for the inhibition is the dissociation of the free undissociated acids which can easily pass the cell membrane inside the cell plasma, thereby abolishing the trans-membrane pH gradient (Van den Heuvel, 1986). To maintain a constant internal pH the excess of protons is exchanged with Na^+ and K^+ ions at the expense of ATP (Padan, 1981). The pH gradient is essential to ATP formation and therefor to bacterial growth (Henderson, 1971). For lactic acid bacteria, which are abundant in silage fermentation, the lethal concentration of the undissociated acid was found to be higher than 7 g/l (Wieringa and De Haan, 1961). For anaerobic digestion, i.e. a system with acid production and acid consumption, also a situation might prevail where the pH is too low for any metabolic activity. In this respect a very important aspect in the engineering of an anaerobic waste treatment process is to balance properly the acid formation and methane formation. As already found in earlier studies on the digestion of sewage sludge (Buswell and Hatfield, 1930), process failure mostly could be due to an imbalance between these processes. As acid formation is the less sensitive step, the imbalance results in low pH values by acid formation when the intrinsic buffering capacity is insufficient to maintain the pH in the neutral range. The low pH and the high concentration of undissociated volatile fatty acids that characterize an unbalanced digestion may inhibit the methanogenic bacteria as was described earlier in this chapter for other groups of bacteria. The methane formation is related to the pH in a digester (Buswell, 1938; Anderson et al., 1982; Kroeker et al., 1979). Although methane formation generally is strongly inhibited at pH values below neutral, a low pH is not bactericidal, which was demonstrated by Keefer and Urtes (1963), who were able to restore a digester that was maintained at a pH lower than 5 during two months within 1 week. For a system with acetic acid (and other mono-carboxylic acids) the fraction of the free, undissociated acids ([HAc]) can be calculated from the pH and the total acetate concentration of the system with the following equation:

$$f[HAc] = \frac{10^{(pK'a-pH)}}{1+10^{(pK'a-pH)}} \qquad (3)$$

where f [HAc] is the fraction undissociated acid, [HAc], $[H^+]$, and $[Ac^-]$ are molar concentrations, K'Ac is the dissociation constant of the acid in an aqueous solution, pK'Ac

and pH are defined as -log[H$^+$] and -logK'Ac respectively.

The maximum concentration of acetate and other volatile fatty acids that can be allowed in an anaerobic methane producing digester has been reason for some controversy because it was believed that high concentrations of acetic acid, and other volatile fatty acids, such as propionic acid and butyric acid, which coincidence mostly with low pH values, are a result of the inhibition of the methane formation and not the cause (McCarthy and Mckinney, 1961; Kugelman and Chin, 1971). By correcting the pH with buffer chemicals such as NaOH to neutral values salt toxicity can inhibit methane formation even more than the undissociated acetic acid. This was illustrated by McCarthy and McKinney (1961) by comparing the anaerobic batch digestion of equal amounts of sodium acetate and calcium acetate (22 g/l acetate) at pH 7.0. The latter experiment showed an almost identical removal rate as the control experiment (8 g acetate/l), while the former compound showed a much lower removal rate as the control experiment. The concentration of 22 acetate/l at pH 7.0 corresponds to an undissociated acid concentration of 125 mg/l. Anderson et al. (1982) reported a threshold level of 30 mg/l undissociated acetic acid. From results presented by Attal et al. (1988) a threshold level of 17 mg/l can be deduced. The large difference in the observed inhibition level between these studies might be caused by a different methanogenic biomass predominant in the digester sludges. The pH range for optimum methanogenic activity, and hence the threshold level for inhibition by the undissociated volatile fatty acids may depend on the microbial composition of the methanogenic biomass. Methanogenic biomass which is predominated by *Methanothrix sp* might show a lower tolerancy level than biomass predominated by *Methanosarcina sp*, since the first type of methanogenic bacterium has a more narrow pH growth interval (Zehnder et al., 1982). From these findings it could be concluded that, apart from the existence of a significant difference in cation toxicity between Na^+ and Ca^{2+}, in fact the pH itself and not the concentration of the free acid determines the conversion rate of acetate to methane. High acetic concentrations at neutral pH might be allowed, depending on the type of buffer used for maintaining the pH at neutral values and the type of methanogenic biomass. The acetoclastic methanogens are found to be more sensitive to low pH values than the hydrogenotrophic methanogens (Attal et al., 1988). Methane formation from hydrogen by methanogens which are present in peat is found at pH 3.1 although at a pH less than 5.3 growth is unlikely (Williams and Crawford, 1985). However, the experiments described were carried out in the absence of acetic acid, so the sensitivity of the hydrogenophilic methanogens to undissociated volatile fatty acids is still unclear. Results from Lettinga et al. (1979) showed that methane production from methanol, which is unionisable, can proceed at pH values lower than 4.5. The methane formation from hydrogen or methanol at low pH values suggests, that a different ATP-generating system exists for these types of methanogens in comparison to acetoclastic methanogens. The hydrogenophilic methanogenic organisms can function at low pH values presumably by a

proton extrusion system, which is part of the energy producing system (Attal et al., 1988). However, several authors report methane formation at pH lower than 5 in presence of volatile fatty acids (Zehnder et al, 1982; Attal et al., 1986). The existence of micro-environments, where higher pH values are abundant, could be responsible for this phenomenon.

It can be concluded from the literature, that the acidogenic organisms which are active during anaerobic digestion of organic wastes can tolerate pH values as low as 4.2, and product (= acids-) concentrations of 25 g/l. Also it can be concluded that methane production at low pH values can proceed, but to obtain a stable process the pH should be maintained well above 6, preferably higher than 6.5. The sensitivity of acetoclastic methanogens towards low pH values might be the result of a detoriation of the energy generating process of the organisms. Hydrogen utilizing methanogens show a greater tolerance towards low pH values. Since energy generation is essential to cell metabolism, the activity and growth of the methanogens will diminish at low pH values. The existence of an inhibiting action by the unionized acids, which also can influence the energy generating process, is not yet fully clear, but may depend on the type of acetoclastic methanogen present in the biomass.

Kinetic aspects of anaerobic digestion of organic wastes

The rate of the anaerobic process as described above depends on several environmental and kinetic factors. To predict the overall rate of the anaerobic digestion of the complex organic matter of the organic fraction of MSW, the kinetics should be sufficiently understood. In kinetic studies of microbiological conversions, such as specific anaerobic conversions, the Monod equation is frequently used. The Monod equation gives the relation between the growth limiting substrate concentration and the actual growth rate of the micro-orgnisms (Monod, 1949):

$$\mu = \mu max.S/(Ks+S) \qquad (4)$$

where μ is the maximum specific growth rate of the microorganisms (d^{-1}), μ is the actual specific growth rate (d^{-1}), S is the substrate concentration (mol/l) and K_s (saturation constant, mol/l) the value of S when μ is half times μmax.

Although the Monod equation is widely used in anaerobic digestion studies (McCarty, 1964; Ghosh and Pohland, 1974; Ripley and Boyle, 1983) with satisfactory results, it is only valid for systems with soluble substrates such as glucose or volatile fatty acids. From an earlier study by Faire and Moore (1932) and from more recent work by Eastman and Ferguson (1981) concerning sewage sludge digestion, it already appeared that when the substrate is

mostly in particulate form, first-order kinetics are more likely. The equation for substrate removal following first-order kinetics is:

$$r = dS/dt = -k.S \quad (5)$$

where k is the first order rate constant. Although equation (4) is widely used in digestion studies of complex wastes, such as sewage sludge, organic fractions of MSW, and wheat straw (Eastman and Ferguson, 1981; Pfeffer, 1974; Jewell, 1982) it is doubtful whether the substrate concentration S was really known during these studies. As was mentioned earlier, these substrates contain a soluble fraction and several polymers in particulate form, such as proteins, lipids and cellulose. These compounds all show a different degradation rate during anaerobic conditions and are mostly found to be rate limiting (Noike et al. 1985; Gujer and Zehnder, 1982). Consistent and fundamental studies concerning the kinetics of hydrolysis in anaerobic digestion of complex wastes are absent in the literature. The rate of hydrolysis will depend on the type of substrate, the pH and temperature, and presumably, by the presence of inhibiting compounds (Gujer and Zehnder, 1983).

As was reported by Pfeffer (1974), for anaerobic digestion of shredded MSW the rate limiting step is the hydrolysis of the particulate cellulosic fraction of the substrate resulting in first-order kinetics. The assumption can be made that the bacteria which are active during the hydrolysis of particulate organic matter are in excess in the free liquid of a completely mixed digester, as was reported by Hobson (1987). A short period (several hours) after start up of the digestion, even when a sub-optimal amount of bacteria is present, the particles will be covered with fermentative bacteria that produce the hydrolytic enzymes. The period needed for sufficient enzyme production is believed to be very short compared to the total digestion time of complex wastes (Hobson, 1987). The rate of the process is therefore more related to the specific surface area of the particulate substrate that can be attacked by the hydrolytic enzymes than to the biomass concentration and the substrate concentration. Dependent on the particle size, the surface will decrease with time, as will the substrate removal rate. In the case of cellulose as the main compound of the particles, it is apparent that, apart from the surface area of the particles the structural order of the cellulose also sets the overall rate of hydrolysis. Since cellulose is a complex substrate, a simple description of this relationship is hard to give. About the particulate proteins and lipids in organic fractions of MSW and sewage sludge the same conclusion can be drawn.

For a heterogeneous particulate substrate such as the organic fraction of MSW, with a hardly known composition, first-order digestion kinetics seems the most simple but also the most realistic approach to describe the overall process. However, as mentioned earlier, a certain fraction (10 -13 % of the volatile solids) of the organic compounds of this substrate is digested at higher rate than the other fraction, but which also follow first order reaction

kinetics. Very likely this fraction consists of sugars and amino acids, because for these compounds the removal rates are significantly higher than cellulose (Noike et al., 1985). According to Cecchi and Alvarez (1991) a third fraction is present, which is formed by the volatile fatty acids already formed during storage of the waste. However, since this fraction is not always present, its effect on the kinetics is ignored. As was done for predicting gas production rates in landfills (Emcon Associates, 1979; Hoeks, 1983), it can be presumed that the organic fraction of MSW consists of several fractions. The equation describing the substrate removal rate in the anaerobic digestion of an organic fraction of MSW consisting of two compounds in that particular case would become:

$$r = dS/dt = dS_1/dt + dS_2/dt = -(k_1.S_1 + k_2.S_2) \quad (6)$$

The substrate concentrations S_1 and S_2 refer to the concentration of Volatile Solids, consequently equation (6) can also be written as:

$$r = -(k_1.VS_1 + k_2.VS_2) \quad (7)$$

where k_1 and k_2 are the first order rate constants for compound 1 and compound 2, VS_1 and VS_2 are the volatile solids concentration (kg/m^3) of compound 1 and compound 2 respectively. Because the VS1 and VS_2 concentrations are difficult to assess during a digestion process, equation (7) is of less importance for practical situations. However, as the rate constants k_1 and k_2 can be determined separately under controlled experimental conditions with pure compounds, e.g. glucose and cellulose, equation (7) can give an indication about the removal rate of the volatile solids in the digestion process. In practice the remaining volatile solids concentration (VS) ($= VS_1 + VS_2$) can be determined indirectly by measuring the methane production. For a balanced digestion process, the removal rate of the biodegradable volatile solids is almost equal to the methane production rate (Gujer and Zehnder, 1983) because the biomass production can be neglected:

$$r = -r_{CH4} \quad (8)$$

where r_{CH_4} is the methane production rate. The amount of volatile solids can be expressed as the Chemical Oxygen Demand (COD, Standard Methods, 1976). As the amount of methane also can be expressed in terms of COD, the amount of volatile solids degraded during the digestion can be estimated as follows:

$$r = dVS/dt = -(k.VS) \quad (9)$$

where k is the overall rate constant (day^{-1}), which gives after integration:

$$VS_t/VS_0 = \exp(-k*t) \quad (10)$$

A COD balance over the VS:

1 kg biodegradable VS	= a kg COD
1 kg CH_4	= 4 kg COD
1 kg VS	= a/4 kg CH_4

where a is a characteristic constant for each type of compound that can be assessed for each substrate.
Equation (8) can then be written as:

$$LN(1-CH_4t/CH_4max) = \exp(-k*t) \quad (11)$$

CH_4t is the total amount of methane that is produced after a certain time t (e.g. in days) while CH_4max is the maximum amount of methane that can be produced from the organic substrate. By measuring the methane production the VS degradation rate can be easily followed.

Fig. 3 shows the course of the substrate concentration during a batch digestion of two model organic fractions of MSW calculated according to equation (6). Fraction 1 is mainly composed of cellulose, fraction 2 consists of 85 % cellulose and 15 % glucose. The kinetic data are adapted from De Baere et al. (1986) and Noike et al. (1985). According to the first-order model, the digestion time for 99.9 % reduction of the volatile solids amounts to 21 days (temperature = 35 °C). The two-compound organic fraction shows an higher initial degradation rate than the one-compound organic fraction. As a consequence, the acid formation will start with an higher initial rate than will be found with the one-compound fraction. The methane formation should therefore also proceed at higher initial rates to prevent an imbalance in the digestion process. The existence of two different types of compounds in the organic fractions of MSW can be deduced from the high organic acid concentrations and consequently low pH values, in leachate from 'young' landfills, i.e. landfills where MSW is still being dumped. The hydrolysis plus acidogenesis of the easily

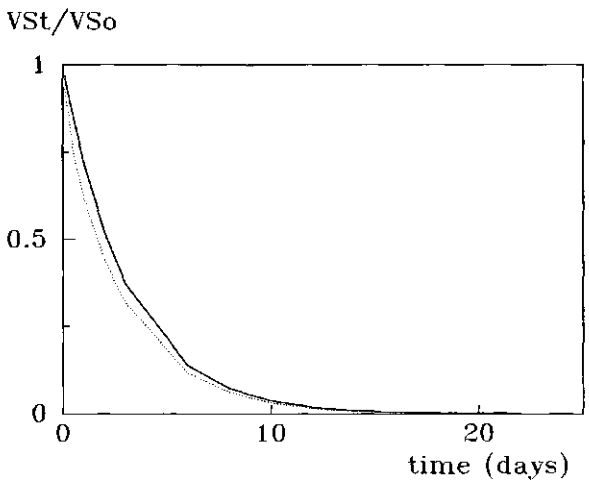

Fig. 3 Pattern of the volatile solids (VS) degradation of the organic fraction of Municipal Solid Waste during anaerobic batch digestion of a one-component (————)— and a two-component organic fraction (.....).

degradable part in the organic fraction of MSW is never rate-limiting (Hoeks, 1983).
The methanogenic biomass which is initially present in a very low amount will develop after completion of the degradation of the easily degradables. During the degradation of these compounds the main products are organic acids, carbon dioxide and hydrogen, while the pH drops to values in the range 5-5.5. At the time the hydrolysis of the particulate matter becomes rate-limiting, the methanogenic biomass will develop gradually after removal of the organic acids with the landfill leachate. The landfill environment has entered the methanogenic stage at this point.

Summarizing it can be concluded from available literature data that the anaerobic hydrolysis in the anaerobic digestion of the organic fraction of MSW proceeds according to a first-order reaction degradation pattern. Two types of compounds seem to dictate the degradation rate of the biodegradable organic matter: the easily degradable compounds, consisting of sugars and amino acids are being converted at high rate to hydrogen and volatile fatty acids, while the particulate matter, mainly consisting of cellulosic compounds are degraded at relatively lower rate.

Effect of the temperature

Besides the type of substrate, also the temperature determines the rate of the digestion process. During anaerobic digestion, specific biochemical reactions take place which show higher rates with increasing temperatures. The choice for the proper process temperature will be discussed further on in this study during the evaluation of several digestion systems.

Anaerobic systems for the digestion of the organic fraction of MSW

Conventional, slurry digestion.

In the early days of the application of anaerobic treatment of wastes, the use of the process was limited to concentrations occurring in sewage and in sewage sludge (McCarthy, 1982). One of the first attempts to dispose of 'garbage' (= Municipal Solid Waste) with a controlled digestion process was described by Fox (1924). This work concerned the combined aerobic treatment of sewage with ground MSW. More successful attempts of the combined anaerobic digestion of MSW and sewage sludge in sludge digesters are reported by Keefer and Kratz (1934), Babbitt et al. (1936), and Bloodgood (1936). However, for several reasons combined digestion with sewage sludge was never applied at large-scale a serious lack of fundamental microbial knowledge and also because of economic and technical problems. In the early fifties another attempt was reported by Ross (1954). The combined digestion of MSW and sewage sludge in a completely mixed sludge digester resulted in an satisfactorily proceeding process. However, this method of MSW disposal was never adopted on large scale for several reasons. The main reasons for this are the low profits of the biogas produced and the changing composition of the MSW. Due to an increased percentage of packing materials in MSW, problems arose regarding the separation of the MSW for obtaining a suitable feed for the reactors (Pfeffer, 1978). In the early seventies the interest in applying anaerobic digestion for energy production from wastes made a comeback. The so-called 'energy crisis' stimulated the development of energy extensive treatment systems for wastes and the reuse of wastes. During that time the work concerning the assessment of the potential of anaerobic digestion for Municipal Solid Waste management and disposal was mainly focused on an optimization of the biogas yield in slurry reactors, i.e. reactors with shredded MSW at total solids concentrations lower than 5 % (Johnson et al., 1972; Pfeffer, 1974; Cooney and Wise, 1975; Stenstrom et al., 1983). Most of these studies report that the addition of primary sewage sludge increased the rate of the process. The stimulatory effect of the addition of sewage sludge could be attributed to the more optimal C/N ratio for biodegradation of the sludge/MSW mixture in comparison to the separate MSW.

In 1978, a large-scale project concerning combined digestion of an organic fraction of

shredded MSW (100 tons/day) and sewage sludge was started in Pompano Beach (Florida, USA) (Pfeffer, 1978). The digesters here could only be operated at 3.5 % TS at a hydraulic retention time of 20 days instead of at 6-8 % TS as planned, due to mixing problems and formation of scum layers. After completion of the digestion the slurry could be dewatered up to 30 % TS, while the filtrate was recycled to dilute the MSW (Walter, 1982). Experiments conducted in Europe concerning the combined conventional digestion of several types of organic fractions of MSW and sewage sludge have been summarized by Cecchi et al. (1988). The largest reactor (2000 m^3, demonstration-scale) was built with the financial support of the EEC in Broni, Italy. Good results are reported, with minimum solids retention time of 15 days, and a biogas yield of 0.65 m^3/kg VS degraded (Cecchi et al., 1988). In The Netherlands, laboratory scale experiments were carried out with an organic fraction of MSW obtained by mechanical separation (Van der Vlugt and Rulkens, 1984). These experiments were carried out on labscale only and also showed promising results. However, experiments at a larger scale could not be carried out, mainly due to the economic feasibility of the process. The conditions applied in various conventional slurry digestion systems used for MSW (and sewage sludge) is given in TABLE 3, together with the measured biogas yield.

The reason for the limited success of conventional slurry digestion of the organic fraction of MSW sofar (with or without co-digestion of sewage sludge) at low solids concentrations (generally lower than 12 %) is mainly economical. The price of biogas produced from waste still cannot successfully compete with that of mineral fuels. The costs for large reactors and the equipment for residue dewatering and wastewater treatment mainly are responsible for low economic feasibility of slurry digestion of OFMSW. The lack of data from operating demonstration-scale digesters and full-scale digesters also limits the value of preliminary economic studies.

Anaerobic digestion in landfills

Anaerobic digestion of OFMSW and thus biogas production, also occurs in landfills. The anaerobic processes proceeding in landfills were firstly described by Farquhar and Rovers (1973). They discussed the potential hazards of biogas (which forms a highly explosive mixture with air), the effects of biogas on the vegetation adjoining a landfill, and groundwater pollution by the landfill leachate. Dependent on the age of the landfill, the leachate contains higher or lower concentrations of organic acids resulting from anaerobic decomposition of the organic matter, and it frequently has a low pH (Hoeks, 1983). The leachate can contaminate the groundwater and the surface water seriously depending on the local geohydrological conditions.

Large-scale recovery of biogas produced in a landfill was firstly applied in Palos Verdes, California, USA (Wilkey and Zimmerman, 1982). Since then, several projects with biogas recovery from landfills have been started around the world. In The Netherlands, landfill gas

is recovered at least 14 locations (e.g. Heidemij, 1982; Jans and Luning, 1986; Van Wezel et al., 1989; Bretthouwer, 1989). Anaerobic digestion in landfills proceeds uncontrolled and at very low rates in comparison to that of anaerobic digestion in controlled digesters. Many studies were carried out to optimize the rate of the digestion process in a landfill by simulating the process in laboratory-scale digesters. (Dewalle et al., 1978; Rees, 1980b; Stegmann and Ehrig, 1980; Buivid et al., 1981; Hartz and Ham, 1983). By reducing the amount of inorganic and inhibitory or toxic wastes dumped together with MSW, and by optimizing the temperature and the moisture content of the waste, anaerobic digestion in a landfill may be completed within 2-6 years (Mata-Alvarez and Martinez, 1986; EMCON Associates, 1979). An important aim for start-up of a landfill is to get the digestion process balanced. A landfill which is in balanced methanogenic stage gives less concentrated leachates (Ehrig, 1986; Hoeks, 1983). A major drawback of landfills is that only a part of the potential amount of the generated biogas can be recovered, which still can be a considerable part, namely 30-70 % (Jans, 1985). When the optimizing of the anaerobic processes in landfilling with respect to biogas recovery and leachate treatment, the effects on the environment can be reduced considerably. However, since no substantial reduction of waste is obtained by landfilling, the need for large areas of land remains. The need for optimization methods for the anaerobic digestion, leachate treatment, and large land area will increase the cost for landfilling. In the Netherlands, where land is becoming scarce for landfilling, even when applied in combination with biogas recovery, very likely will become economically and ecologically unattractive in the near future in comparison to other treatment systems for MSW.

In TABLE 3 landfills are compared with various other anaerobic digestion systems.

TABLE 3 Comparison of anaerobic digestion systems for municipal solid waste

system	type of MSW	digester-TS (%)	T (°C)	SRT (days)	ORGANIC LOADING RATE (kg COD/(m^3.day))	BIOGAS YIELD[1] (m^3/kg VS)[6]	ref.
landfill	untreated	20	30-40	∞	0.009-0.049	0.24	Emcon associates, (1979)
landfill	untreated	45-70	20-30	∞	0.0002-0.0004	0.07	Tabasaran, (1981)
slurry	shredded MSW	35	30	30	1.8	0.40	Pfaffer, (1978)
slurry	org. fraction +sewage sludge = 20:80(TS/TS)	3-8	37	15-30	1.5	0.40	Stenstrom et al., (1983)
slurry	org. fraction + sewage sludge 85:15 (TS/TS)	8	38	20-30	2.6	0.43[c]	Szikriszt et al., (1988)
slurry	org. fraction	2.4	35	15	6.7	0.65	Cecchi and Traverso (1988)
slurry	org. fraction	12	30	20	5.5	0.43[c]	Rulkens, (1986)
two-phase[2]	org. fraction	30-35	35	49	2-6	0.5[3c]	Voetberg, (1983)
two-phase[2]	cellulosic fraction	26	22	76	0.7	0.61[3]	Ghosh, (1984)
two-phase[2]	org. fraction	6	39	2.5	42	0.44[4]	Gijzen et al., (1987)
two-phase	org. fraction (source sep.)	10	35	2	20-25	0.40	Kubler, (1992)
two/three-phase	org. fraction	nr	39	nr	nr		Brinkman and Hack, (1992)

BLE 3 -CONTINUED

stem	type of MSW	digester -TS (%)	T (°C)	SRT (days)	ORGANIC LOADING RATE (kg COD/(m^3.day))	BIOGAS YIELD[1] (m^3/kg VS)[6]	Reference
y digestion atch)	org. fraction	28	nr[5]	180	0.5	0.32	Augenstein et al., (1976)
y digestion atch)	org. fraction (source sep.)	35	35	37		0.34[c]	Spendlin & Stegmann, (1988)
y digestion ontinuous)	org. fraction	35	35	15	19.1	0.35	Cecchi et al.(1988)
y digestion ontinuous)	org. fraction	30	55	9	23.1	0.40[c]	Baguelin et al.(1988)
y digestion ontinuous)	org. fraction	40	35	30	3.3	0.50[c]	Klein and Rump, (1979)
y digestion ontinuous)	org. fraction	25	55	10	22.5	0.42	Marique et al., (1989)
y digestion ontinuous)	org. fraction	35	35	21	18.1	0.49[c]	De Baere &Verstraete, (1985)
y digestion ontinuous)	org. fraction (source sep.)[7]	35	55	11	10	0.49[c]	Six et al. (1988)
y digestion atch)	org. fraction (source sep.)	35	35	30	8-10	0.40[c]	Chapter 6
y digestion atch)	org. fraction	35	30	36	3-5	0.5[c]	Chapter 2

ean composition: CH_4 = 55 vol. %, CO_2 = 45 vol % [2] characteristics of first reactor [3] biogas yield of both phases [4] biogas eld calculated from first phase [5] not reported [6] per kg VS degraded [7] :source-separated organic fraction of MSW (Vegetable, Fruit d Yard waste) [c] :includes compost production

Two-stage digestion.

The application of phase separation in anaerobic digestion of organic wastes in which hydrolysis and acidogenesis are spatially separated from methanogenesis by using two serial reactors, was originally first proposed by Pohland (1971). As the acid forming bacteria and methanogenic groups of bacteria differ with respect to their nutritional requirements, physiology, pH optima, growth kinetics and sensitivity to environmental stress, optimal process conditions in principle could be adjusted for both groups of organisms (Ghosh and Klass, 1978; Zoetemeijer et al., 1982; Ghosh, 1987). According to the inventors phase separation would lead to a greater process stability, and consequently, to higher turnover rates. These higher applicable loading rate would compensate for the higher cost for operating two reactors instead of one. On the other hand a major drawback of a two-phase system is its more complicated process engineering. It should be understood that a higher stability only can be accomplished when the methanogenesis is the rate-limiting step, e.g. in the case of glucose as feeding substrate for the first stage. As the specific growth rate of acid forming organisms is higher than the specific growth rate methanogens, the methanogens are outcompeted at certain hydraulic loading rates (Cohen et al., 1979).

It should be understood that in the case of glucose a one-stage balanced digestion is well feasible, provided of course serious process disturbance doesn't occur, e.g. toxic compounds are unlikely. As in the case the substrate consists of cellulose, the hydrolysis of this compound will in general be the rate-limiting step and hence phase separation will not result in a greater process stability (Cohen, 1983; Noike et al., 1985) because the formation of VFA and hydrogen cellulose will proceed at a significantly lower rate than their degradation by the grown methanogenic biomass. In the anaerobic digestion of the organic fraction of MSW, which contains soluble sugars and cellulose, methanogenesis will be the rate-limiting step in the very initial stages, depending on the amount of methanogenic biomass, but in due time by hydrolysis of cellulose will become rate limiting. The potential advantage of application of phase separation, if any, therefore will depend on whether the turnover rate is limited by the degradation of the easily degradable compounds or by hydrolysis of cellulose.

The first laboratory scale experience on phase separation with the organic fraction of MSW using two sequential conventional slurry reactors was reported by Keenan (1976). Phases could be separated by maintaining the pH of the first reactor at 6.0 max. and the second reactor at 7.0. In the first digester no methane production was observed during the experimental period of c. 100 days. However, despite phase separation higher maximum loading rates were not reported for the two-stage digestion in comparison to the one-stage set-up.

A more advanced two-stage system for the anaerobic digestion of solid wastes was introduced by the Institute for Storage and Processing of Agricultural Produce (IBVL) in The Netherlands (Rijkens, 1980; Rijkens, 1981; Hofenk et al., 1983). In this process, leachate from the liquefaction/acidification reactor, which is operated in a batch mode, is fed to a high-rate methane reactor of the UASB-type. The effluent of the methane reactor is recirculated to the liquefaction reactor. Once acid formation in this reactor becomes rate limiting, the methane reactor is uncoupled from the batch reactor because at this stage sufficient methanogenic seeding has been accomplished by the effluent recirculation is sufficient for establishing a stable methanogenic biomass in the batch reactor. A possible advantage of this system could be the fact that slurrying of the solid waste to 5-10 % total solids concentration is avoided. The residue left in the liquefaction reactor is a more or less stable compost-like end product which can be dried by applying aerobic composting for

several months (Rijkens, 1981). Most laboratory scale and pilot-scale experience obtained with the system sofar are with agricultural solid wastes, such as tomato stalks, and onion waste. Preliminary experiments conducted with an organic fraction of MSW also were considered as rather promising (TABLE 3). However, the big limitation of the system concerns the serious clogging problems occurring in the solid waste bed in the batch reactor, moreover also problems occurred in the methane reactor (Voetberg, 1983). A similar system is presently being tried out in Germany at pilot-plant scale for Vegetable, Fruit and Yard Waste (Spendlin and Stegmann, 1988); so far experimental results have not been reported. A similar approach for anaerobic digestion of an organic fraction of MSW was chosen by Pauss et al. (1984) in Belgium, although they used a Fluid Bed (FB) in the second stage. They reported a ten times higher applicable loading rate in the leach bed reactor than in a one-stage CSTR reactor. However, no figures were provided for the overall loading rate. Also Ghosh (1984) and Ghosh and Lull (1988) reported about a similar system was described for treatment of a cellulose-containing organic fraction of MSW; the methane reactor consisted here of an anaerobic filter. An overall minimum retention time of 76 days could be applied at 20 °C in this system; this is longer than for slurry reactors (TABLE 3).

A new approach for a two-phase process was chosen recently in The Netherlands, the so called RUmen Derived Anaerobic Digestion (RUDAD) process. This process is based on the use of rumen organisms. The idea is that protozoa are the main type of organisms degrading the cellulose at remarkably high rate (Gijzen et al., 1987). The improved conversion rate of cellulose in comparison to other systems was believed to be the result of the high cellulase activity of the rumen microbial population. The role of the reduced particle seize of the waste, which might also enhance the rate of cellulose degradation, was not included in the investigations. In the RUDAD process the first phase consists of a slurry reactor ($\approx$ 6 % TS). The effluent of the first phase reactor is the feed for the second phase reactor, a UASB-type methane reactor. The effluent of methane reactor is recirculated to the slurry reactor. For the first phase reactor the hydraulic retention time applied is four times the solids retention time (15 hours and 60 hours respectively) (Gijzen et al., 1987; Zwart et al., 1988). High loading rates (up to 34 g COD/l.day) with degradation efficiencies ranging from 60-70 % could be applied for the first phase digester with an organic fraction of MSW as substrate (Gijzen et al.,1987). In the first stage a degradation of lignin of up to 48 % was observed.

However, long-term experiments with reactors of 20 liters showed variable results, which could partially be explained by technical problems (Zwart et al., 1988). The mixing of the first-stage reactor, and the separation of the non-biodegradable solids from the effluent of the first-stage reactor represent the major problems, similar as the technical problems encountered in the conventional slurry digestion of the organic fraction of MSW. It is quite questionable whether or not the economics of the RUDAD process are favourable despite the high loading rates that are supposed to be applicable in this process.

It can be concluded that two-phase digestion processes seem only economically feasible for organic fractions of MSW when the first-phase reactor can be operated at high solids. The need for a second-phase reactor complicates the system which negatively effects the economics of the process quit detrimentally. Recently a combination of the two stage process with a third reactor, based on the RUDAD process, is presented (Brinkman and Hack, 1992). In this three-stage system the waste is pulped, and slurried. The slurry is acidified in a acidification reactor. The remaining solids are separately digested in a RUDAD reactor, while the effluent from the first stage is digested in a UASB-reactor. High efficiencies are claimd for this system, although results from pilot scale were not available for publication.

Dry anaerobic digestion

As mentioned earlier, application of anaerobic digestion were originally limited to digestion operated at total solids concentrations lower then 12 % TS (De Baere and Verstraete, 1984). However, it is known for quite some time that various microbial fermentations, e.g. aerobic composting, can proceed quite well in the absence of free water (Cannel and Moo-Young, 1980a,b). A satisfactory application of one-stage anaerobic digestion of dry organic wastes at total solids concentrations that resemble the total solids concentration of solid wastes, would be a major advance. In comparison to conventional slurry digestion systems, anaerobic digestion at high solids concentrations limits the need for the supply of additional water, of intensive mixing, of residue dewatering and of the heating capacity. Apart from stabilization and biogas production, anaerobic digestion at high solids concentrations of dry wastes means the production of compost-like residues, which do not need an intensive dewatering process. In this respect, anaerobic digestion at high solids concentrations can prove to be a more economical way of waste disposal than other anaerobic digestion systems, such as slurry digestion (Jewell, 1982).

Early experience with digestion of highly concentrated fibrous wastes at solids concentrations exceeding 12 % was described by Buswell (1936), however large-scale applications were not reported of. Keefer (1947) investigated anaerobic digestion of partially dewatered raw sewage sludge (15-35 % TS) in comparison to conventional sludge digestion at 5 % TS, to reduce the digester volume needed. At 25 % TS or higher, a retarded digestion was found. Schulze (1958) found that sludge digestion at 30-40 % TS is feasible. Although positive results were obtained, sludge digestion at high solids concentrations so far was never applied on full-scale, which presumably can be attributed to the need of applying of a dewatering step before digestion.

In France, a batch process for anaerobic digestion of dry agricultural wastes was developed which was widely used during World War II (Claquin and Claire, 1986). The first dry anaerobic batch digester treating organic agricultural wastes at high total solids concentrations (> 20 % TS), showed similar biogas production rates to those found for slurry reactors (Wong-Cong, 1975). Slurry digestion of these types of wastes, which generally have total solids concentrations exceeding 10 %, showed many technical problems. At that time the anaerobic digestion at total solids concentrations exceeding 20 % TS was defined as dry anaerobic fermentation (Wong-Chong, 1975). In this study this criterium is also adopted as dry anaerobic digestion. The concept of dry anaerobic digestion at high solids concentrations in batch reactors was further developed by Jewell and co-workers for agricultural wastes, such as wheat straw, dried manure, and cornstalk (Jewell et al., 1981; Wujcik and Jewell, 1980). Several other authors reported on similar systems also for the digestion of agricultural wastes (Ammann et al., 1986; Molnar and Bartha, 1989). The potentials of controlled dry anaerobic digestion of MSW, in fact a dry waste, was not studied until the middle of the seventies, when it was recognized that anaerobic digestion occurs in landfills at high total solids concentrations, namely 20-60 % TS (Rees, 1980b). It is questionable whether or not the anaerobic processes in landfills can be considered as a true dry anaerobic digestion because a landfill is a very heterogeneous system where large variations in moisture can occur with solids concentrations which are even lower than 10 % (Stegmann, 1982). Controlled dry anaerobic digestion (20 % TS) of a selected fraction of MSW, mainly consisting of organic materials, in a packed bed batch reactor was studied by Augenstein et al. (1976). They attempted to control the process by leachate recycling, the addition of a methanogenic seed sludge and buffer. The required digestion time amounted to 9 months, which obviously is rather long in comparison to that applied in conventional slurry digestion

systems (TABLE 3). As the experimental conditions were not well described in these experiments, the reasons for the retarded digestion are not clear. A process based on continuous dry anaerobic digestion of the organic fraction of MSW was developed in France (Membrez and Nicolet, 1985; Begouën et al., 1987). A detailed description of the reactor system, the start-up procedure and the way it is fed is not yet available, presumably because of commercial reasons. As this system is shows many similarities with the DRANCO process, which will be discussed here later on, it is very likely that the reactor is a plug flow type and that a high amount of digested waste is recirculated and mixed with fresh waste. As in this process similar or even shorter solids retention times can be applied compared to conventional digesters. Consequently also the loading rates are much higher, and consequently because of the higher TS-concentration in the feed (30-35 % TS), higher biogas production rates (in m^3 biogas per m^3 reactor per day; both at 35 °C and at 55 °C as well) (TABLE 3). The residue could easily be dewatered to 55 % TS by pressing. The process is known as the VALORGA process, and was tested at full scale with a reactor with a 500 m^3. Results from experiments carried out at 55 °C showed that even higher loading rates are applicable (Begouën et al., 1988). Similar processes have been developed in Germany and Belgium; in Germany the KWU/Fresenius process, the TUHH (Technische Universität Hamburg-Harburg) process, and in Belgium the Dry Anaerobic Composting process (DRANCO) and the Liège process (Belgium) (Spendlin and Stegmann, 1988; Klein and Rumpf, 1987; Six and De Baere, 1988; Marique et al., 1989). The characteristics of these processes are shown in TABLE 3. For the continuous dry anaerobic digestion processes high loading rates and high biogas yields are reported. However, a high-grade technology is required for these systems. As a consequence, the total costs per ton of treated waste can increase in comparison to simpler systems.

A simpler batch process for dry anaerobic digestion of organic solid wastes which is the objective of study in this thesis and which is called BIOCEL, has been studied intensively at the Wageningen Agricultural University. This process can be considered as an appropriate low technology system although the conversion rate that occurs in the BIOCEL process is similar to that in advanced continuous dry digestion systems. Dry anaerobic digestion according to the BIOCEL concept is carried out in batch operation at mesophilic temperature conditions and at 30-40 % total solids. At the start the solid waste is mixed with a methanogenic inoculum, leachate solution from a former digestion run and brought into the reactor as a static pile. At full-scale the reactor volume obviously consists of several units, which have to be loaded separately. Depending on the amount of free water in the solid waste bed, leachate is recycled during the process and biogas is extracted from the reactor during the digestion process. The residue needs to be dewatered to produce a stabilized, compost-like end product. A schematic diagram of the process is shown in Fig. 4. Results of experiments conducted at laboratory scale and at pilot-plant scale show that both the batch loading rates applied and the biogas yield are similar to those found in continuous mesophilic dry anaerobic digestion. (Chapter 6, Chapter 7). Apart from the technical, economical aspects have to be considered when evaluating the feasibility of an anaerobic digestion system. In a preliminary study concerning the economics of several anaerobic digestion systems for the organic fraction of MSW it was concluded that one-phase batch digestion is the most attractive system from an economical point of view. This conclusion will be discussed later on in chapter 8 in relation to the results of the investigations.

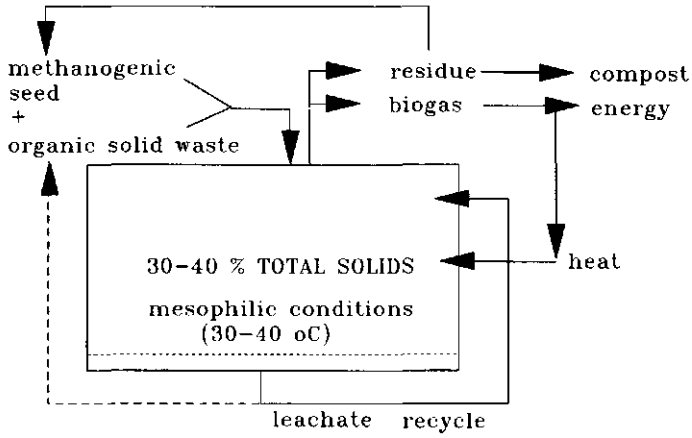

Fig. 4 Flow sheet of a BIOCEL digester for dry anaerobic batch digestion of organic solid wastes.

Start-up methods for dry anaerobic batch digestion of solid organic waste

Balanced anaerobic digestion, i.e. a balance between acid production and acid consumption is essential for a stable process proceeding at the highest possible rate. Several researchers reported that in anaerobic batch digestion of solid wastes the process passes through typical characteristics of imbalance between acid formation/hydrogen formation and methane formation (Jewell et al,1981; Ghosh and Lall, 1988). The exact calculation of the existing process imbalance from the literature data is impossible due to the incomplete description of the experiments. Wujcik and Jewell (1979) reported maximum concentrations of 0.33 M volatile fatty acids and simultaneous methane production in dry mesophilic anaerobic batch digestion of cellulosic wastes. Prevailing pH values during their experiments are not provided. Although methane production occurred, the time needed to complete the digestion, i.e. the conversion of the biodegradable part amounted to 60 days at the minimum. Stegmann (1982) reported maximum total organic acid concentrations of 0.42-0.5 M (25-30 g acids/l) and pH values around pH = 6, in experiments concerning controlled batchwise digestion of Municipal Solid Waste. The digestion time at 35 °C amounted 3 months. Other researchers reported significantly shorter digestion times of less than 21 days for this type of wastes in continuously fed digesters (Pffeffer, 1974; De Baere et al., 1984). In these types of digesters low volatile fatty acids concentrations and neutral pH values prevail, indicating that the process proceeds well-balanced. The lower rate of the digestion process observed during the batchwise digestion may be due to the low pH and the high acids concentration. Both are the result of the imbalance of acid production and acid consumption.

From the data mentioned above it can be concluded that batchwise anaerobic digestion as described in literature, proceeds at suboptimal rates in comparison to continuously fed digesters. At the start of our investigations start-up methods for dry anaerobic batch digestion could not be abstracted from the relevant available literature. Therefore start up methods to optimize the rate of the digestion process had to be adapted and tested during digestion experiments. In this respect a start-up method must aim at a well-balanced digestion, i.e. an equal rate of acid plus hydrogen production and consumption of these compounds at any time of the process. The start-up methods which are relevant for this study are:

- **addition of a sufficient amount of methanogenic seed material,**
  as acid and hydrogen formation from the organic fraction of MSW normally proceeds without seeding, because of the presence of native acidogenic bacterial population, the addition of a sufficient amount of methanogenic bacteria prevents unbalanced conditions. Generally, every material that contains a high amount of methanogenic organisms can be used as a seed, viz. digested sewage sludge, sludge from UASB reactors digested manure and the digested residue, because this can partially can be recycled after a batch digestion.

- **addition of buffers,**
  the addition of buffers is useful or even sometimes a prerequisite to maintain the pH around 7, when the acid formation exceeds the acid consumption, and the buffering capacity of the system itself is not sufficient.

- **dilution of the waste,**
  the rate of the acid formation may be lowered by diluting the substrate with stabilized solids. Stegmann (1982) reported that after addition of compost to MSW less unbalanced conditions were observed in anaerobic digestion. Apart from compost addition, addition of a methanogenic seed was not essential

- **aerobic pretreatment,**
  a certain part of the easy degradable volatile solids may be responsible to a great extend for the imbalance of the dry anaerobic digestion of solid waste. Jewell et al. (1981) discussed the possibility of an aerobic pretreatment of the waste to obtain lower acid formation rates during the subsequent dry digestion process. It was believed that during the aerobic pretreatment the easy degradables were partially aerobically degraded, while the fraction with a slower degradation rate would remain.

- **spatial separation of acid formation and methane formation combined with leachate recycling,**
  in landfill simulation studies recycling of free liquid was found to improve the rate of the anaerobic digestion process (Ghosh, 1984). The lowering of the volatile acids concentration in the landfill was believed to be the main positive effect of this method. Leachate recycle in active methanogenic landfills is believed to stimulate the biogas production by enhanced distribution of moisture over the methanogenic zones in the landfill (Leckie and Pacey, 1979; Klink and Ham, 1982). The imbalance of the digestion may be prevented by separating the acid formation and the methane formation during the first phase of the process. This can be done by filling a digester

with separate layers of substrate and methanogenic seed. The volatile acids, produced in the substrate layers are transported to the methanogenic /seed layers by recirculating the free liquid (leachate) of the digester. The balance between acid formation and methane formation can establish after a certain increase of the methanogenic biomass, and exhaustion of the easy degradable part of the substrate.

Aim of this study

In 1985, a research project was initiated by the Dutch Agency for Energy and the Environment (NOVEM, formerly PEO) with the financial support of the National Research Program for Reuse of Wastes (NOH). The project concerned the anaerobic digestion of the organic fraction of MSW at high total solids concentrations yielding biogas and compost with a low technology process (Heidemij, 1985). The scientific part of the project was carried out by the Wageningen Agricultural University, Department of Environmental Technology. The overall project management was carried out by Heidemij.

The first part of the project was formed by an evaluation of the potentials of anaerobic digestion for the organic fraction of MSW and the several systems already available for anaerobic digestion of the organic fraction of MSW. This evaluation is presented in former sections of this chapter.

The second part of the project consisted of a research program for the development of start-up procedures of a reactor for dry anaerobic batchwise digestion of the organic fraction of MSW. The research had to be carried out on laboratory scale as well as on pilot-plant scale. In Chapters 2 to 8 of this thesis the experimental work that was carried out in the research project is presented.

The aim of this study is to establish the difficulties and main features of a suitable first start-up and the proper conditions of regular start-up of the batch-wise dry anaerobic digestion of organic fractions of Municipal Solid Waste. For this purpose microbiological and physical factors that determine the rate of the anaerobic digestion at high total solids concentrations (> 20 % TS) have to be investigated so that the insight in the digestion process prevailing under this condition will become sufficiently understood. Chapter 2 describes several (first and regular) start-up methods for dry anaerobic batch digestion. The application of pH controlling chemicals, a pretreatment step of the substrate before commencing the start-up and the addition of several types seed material has been investigated. Chapter 3 reports the studies concerning the influence of temperature and total solids concentration on the rate of the digestion. Chapter 4 the results of investigations on the role of methanogenic zones during anaerobic digestion at high total solids concentrations are presented. Chapter 5 describes the type of methanogenic organisms that are predominating in dry anaerobic batch digestion. Chapter 6 describes the proper start-up procedures for dry anaerobic batch digestion of a source- separated organic fraction of MSW. The results of dry anaerobic digestion experiments at pilot-plant scale (5m^3, 450 m^3) are reported in chapter 7. Chapter 8 gives a final discussion and the most relevant conclusions.

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CHAPTER 2

START-UP METHODS FOR DRY ANAEROBIC BATCH DIGESTION OF THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

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START-UP METHODS FOR DRY ANAEROBIC BATCH DIGESTION OF THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

SUMMARY

Several start up methods of dry anaerobic digestion of the organic fraction of Municipal Solid Waste (MSW) were investigated. For start-up of the dry digestion of the organic fraction of MSW the addition of a methanogenic inoculum is essential. The first start-up of such a batch reactor is unbalanced at a seed/substrate solids ratio of 0.04 - 0.08. This imbalance results in pH values below 6, organic acid concentrations up to 40-60 g COD.l^{-1} and ethanol concentrations up to 15 g.l^{-1}. Under these conditions production of methane was negligible. To enhance the start-up, the addition of several pH control chemicals has been investigated. The best results were obtained with $NaHCO_3$ at a buffer/substrate solids ratio to 0.06 (kg.kg^{-1}). The potential specific methane yield of 80 l STP of methane per kg of organic fraction is then obtained within a period of 6 months. $Ca(OH)_2$ has a minor effect on the pH of the system. $CaCO_3$ did not control the pH and inhibited the biogas production. The pH control chemicals which were found to provide optimum pH control also cause toxic cation levels for the methane production due to the high concentrations that have to be applied. The period required for adaptation of the methane producing bacteria to these inhibitory cation concentrations limits the benefits of buffer additions during dry anaerobic digestion.

For a fully balanced start-up of the process the addition of methanogenic inoculum (digested sewage sludge) up to a total solids concentration of 35 % is not sufficient. The unbalanced conditions result from the rapid degradation of easy degradable compounds which are present in the organic fraction of MSW. It was attempted to enhance the first start-up of the dry batch digestion by applying an aerobic precomposting step. Such an aerobic treatment could be useful in removing the easily degradable compounds, leaving the conversion of the ligno-cellulose part of the organic fraction to anaerobic digestion. At least 19.5 % of the Volatile Solids should be converted in the aerobic composting period to bring the acid formation in balance with the methane formation. This amount of aerobically degraded VS results in a 40 % loss of a potential methane production, which obviously represents a major drawback of using the partial composting as a method to enhance the start-up of the digestion under 'dry' conditions. Therefore a shorter composting period combined with another start-up procedure is more attractive to improve the net output of the dry digestion process. The dry anaerobic digestion of the pure, undiluted organic fraction of MSW is not accelerated by applying

partial spatial separation of the substrate and the methanogenic inoculum (granular sludge) or by leachate recycle, or both. When employing these three methods, high organic acid concentrations and low pH values were observed in the reactor after 30 days, indicating a sour system, which is unable to establish significant methane production. However, when digesting the organic fraction in presence of compost at a ratio of 40/100 w/w, based on the initial amount of solids and with applying leachate recycling, the degradation rate of the volatile solids increased significantly. Leachate recycling in combination with partial spatial separation of the substrate/compost mixture and the inoculum gave the shortest lag phase in the methane production and consequently also the shortest digestion time. When using the digested residue of a completed digestion as the methanogenic inoculum at a ratio of 40/100 w/w based on the initial total solids the required digestion time becomes even shorter. The results allow to conclude that dilution with compost affects the start-up of the dry anaerobic digestion positively and also compensates for a suboptimal amount of initial methanogenic biomass. The rapid recovery of the methane formation from an initial overloading during the start-up of dry anaerobic batch digestion of MSW is found to be the result of:

1) a population shift in the methanogenic biomass and,
2) the existence of zones in the reactor with far more optimal conditions for methanogenesis, i.e. higher pH and lower organic acid concentrations.

The required digestion time under these conditions is 36 days. Start-up with compost and methanogenic seed sludge, or start-up with digested organic fraction are the procedures, which deserve more intensive investigations for further optimizing of dry anaerobic digestion.

INTRODUCTION

At the time we began our investigations of dry anaerobic digestion of the organic fraction of Municipal Solid Waste (OFMSW), proper start-up methods that are applicable for this particular substrate were not available. Dry digestion was limited to dry agricultural wastes (Jewell et al., 1982) and non-separated Municipal Solid Waste (Stegmann and Ehrig, 1980; Buivid et al., 1981). Papers concerning the already existing systems for dry anaerobic digestion of MSW, viz. the VALORGA process, and the DRANCO process, did not provide sufficient reliable information on the suitable start-up conditions for the dry anaerobic digestion, presumably because of commercial reasons (De Baere and Verstraete, 1984; Membrez and Nicolet, 1985).

The main point at the beginning of our research was to achieve a working batch digester. After this aim was accomplished, the factors that determine the rate of the process had to be assessed. In fact this part of the investigations constitutes the main body of this thesis. In Chapter 1 of this thesis several potential start-up methods for dry digestion of solid waste were selected. These are summarized in TABLE 1. This chapter experiments are described to investigate the selected start-up methods for their applicability for dry anaerobic batch digestion of OFMSW. The most proper start-up method will be applied to the critical situations assessed in the investigations concerning the limiting factors of dry anaerobic batch digestion, which are described in Chapters 3-6 of this thesis.

TABLE 1 Potential start-up methods for dry anaerobic digestion of the Organic Fraction of Municipal Solid Waste

METHOD	FEATURE	REF.[1]
addition of methanogenic seed sludge	compensates for the low amount of methanogens in the substrate	1,2
addition of seed sludge plus buffer *potential buffers*: $Ca(OH)_2$ $CaCO_3$ $NaHCO_3$	maintain pH at neutral values	1,3,4
addition of seed sludge plus compost	dilution of the substrate	2,4,7
partial composting of the substrate	degradation of the easily degradable compounds	2
spatial separation of acid formation and methane formation combined with leachate recycling	prevention of overloading distribution of moisture and bacteria in digesting	5
addition of digested substrate for seeding	includes the advantages of an adaptated microbial population	6

[1]: 1:Buivid et al., 1981; 2:Stegmann, Stegmann and Ehrig, 1980; 3: Jewell et al., 1981; 4: Stegmann, 1982; 5: Ghosh, 1984; 6: Van Meenen et al., 1988; 7:Ten Brummeler et al., 1988.

MATERIALS AND METHODS

TABLE 2 Composition of the organic fractions of Municipal Solid Waste used in the present study

parameter	OFMSW1[1]	OFMSW2[2]	
total solids concentration	50.8	36.0	% of total weight
volatile solids	29.4	25.0	,,
Carbon	8.9		,,
Nitrogen	0.5		,,
Phosphorous	0.5		,,
COD	0.4		kgO/kg TS
Methane Yield[3]	80	59	l STP/kg
volatile solids:			
cellulose + haemicellulose	57.9		% of VS[4]
lignin	27.3		,,
proteins	5.6		,,
lipids	5.9		,,
starch	0.1		,,
soluble sugars	3.1		,,
PARTICLE DIAMETER (d) DISTRIBUTION OF[5]:			
d > 20 mm	0	78	
13.6 mm < d < 20 mm	39	9	
6.8 mm < d < 13.6 mm	40	6	
d < 6.8 mm	21	7	

[1]: organic fraction from mechanical separation process

[2]: organic fraction from source separation (VFY waste)

[3]: determined in a batch assay at 3 % TS and 35 °C

[4]: percentage of weight

[5]: percentage of total weight

Characteristics of the substrates used. The substrates used in the experiments described in this chapter are organic fractions of MSW obtained from the Recycling Zoetermeer Separation Plant for MSW and from source separation in Wageningen, the so-called Vegetable Fruit and Yard Waste. The weight distribution of the fractions obtained after the mechanical separation process is shown in Fig. 1. In TABLE 2, the composition of the organic fraction used in the experiments is shown. The organic fraction was passed through a 12 mm sieve mesh in the separation plant to separate the organic particles from the plastic particles.

Apparatus. For practical reasons the experiments were carried out in reactors that differ in volume (Fig. 2, Fig.3). The reactors used in the experiments with buffer addition and aerobic pretreatment and in which biogas production and biogas composition were monitored had a volume of 6 litres. The pH, the organic acid concentrations, and alcohols concentrations were measured in bottles of 0.5 litres each. Each sample for pH and acids determination corresponds to such a reactor of 0.5 litres.

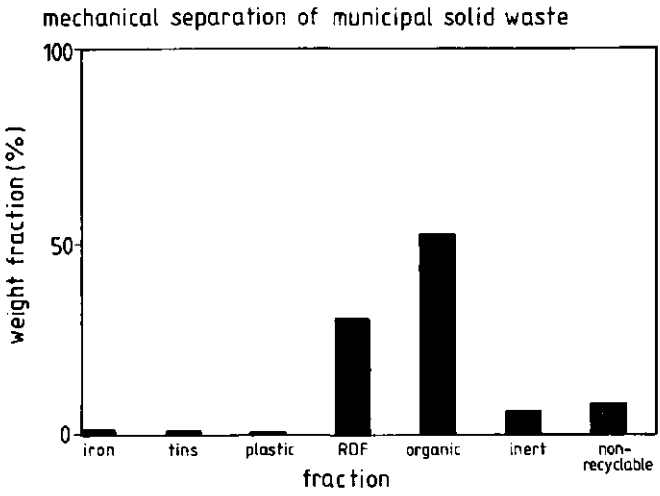
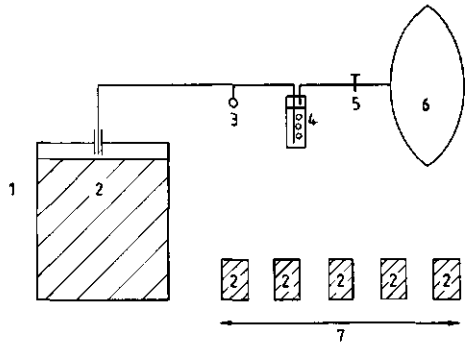


Fig. 1 Several fractions obtained by mechanical separation of Municipal Solid Waste.

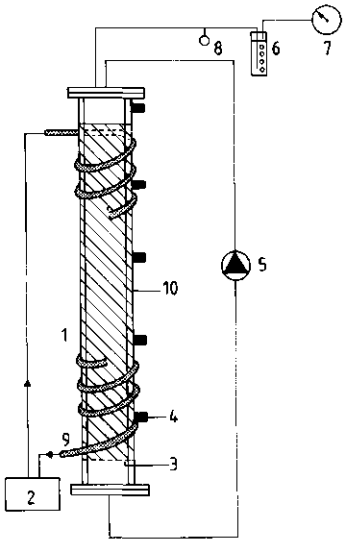


1,7 batch reactor (6/ 0.5 l)
2 seed/substrate / buffer/ tap water mixture
3 septum
4 waterlock
5 tap
6 gastight bag

Fig. 2 Small scale reactors for the dry digestion experiments of the present study.

In each separate experiment five small reactors were used, which were filled under the same conditions as the main reactors of 6 litres. The main batch reactors were connected to a water lock and a gas tight bag of 10 l. A biogas sampling device with a septum was placed between the reactor and the water lock .

The experiments in which leachate recycling was applied, and also partial spatial separation of substrate and seed material, were carried out in PVC reactors with an internal diameter of 0.19 m and a total height of 3.00 m. (Fig. 3). The working volume of these reactors was 78 litres. The reactors were connected to a water lock and a wet test gas meter. Between the reactor and the water lock a biogas sampling device with a septum was placed. Leachate recycle was applied by collecting the leachate at the bottom part of the reactors and pumping it with a continuous flow to the top with a peristaltic pump. The initial flow was 0.5 $l.h^{-1}$, but after 30 days the recirculation flow was lowered to 0.15 $l.h^{-1}$ to prevent leaking of leachate through the biogas outlet.



1 PVC-reactor (78l) 6 waterlock
2 thermostated bath 7 wet test gasmeter
3 perforated plate 8 septum
4 sample port 9 heating tube
5 peristaltic pump 10 insulation layer

Fig. 3 78-litres bench-scale BIOCEL-reactors used in the start-up experiments of the present study.

Buffers and compost. The chemicals used as buffer were (NaHCO3, $Ca(OH)_2$, and CaCO3), all of analytical grade, and were supplied by MERCK, Darmstadt, Germany.
The compost was obtained from a static pile, where the organic fraction was composted during six months. The TS concentration amounted to 57 %, the VS concentration was 30 % (% of the TS).

Partial composting. The organic fraction from the mechanical separation process was used for partial composting experiments. The composting process was carried out in a 1.28 m high plexiglass column which was 0.44 m in diameter. The column was insulated with a polyamide jacket. The column was filled with 60 kg of organic fraction, without compression of the contents. The aeration of the column was carried out with a gas pump which was set at a flow rate of 750 $l.h^{-1}$. The temperature of the inlet air was 20 °C. During the experimental period the temperature of the composting mass was in the range 40-68 °C. At intervals samples of ca. 5 kg were taken for the subsequent dry digestion experiments. The total content of the column was mixed before the sampling was carried out. The total solids content of the composting mass was maintained at 50-55% TS by additions of tap water to the column, every time a sample was taken.

Procedures. The reactors were filled with a mixture of organic fraction, methanogenic seed, tap water and when necessary buffer or compost. The mixing of substrate, seed and buffer or compost was done with a dough mixer (small scale reactors) or manually (digesters of 78 litres). The initial seed/substrate total solids ratio was 0.04 $kg.kg^{-1}$, unless indicated otherwise. In order to avoid pH values higher than 9 the buffers were mixed with the organic fraction before the seed sludge was added. The initial compaction amounted to appr. 0.3 kg TS/l obtained by manual compression. The total solids concentration applied in the experiments was 35 %, unless indicated otherwise. The reactors were flushed for two minutes with nitrogen gas before closing.
The small scale experiments were carried out in a temperature controlled room at 30 °C. The reactors 78 litre reactors were maintained at 35 °C (± 1 °C) using temperature controlled water baths connected to a heating tube coiled around the reactors. These reactors were insulated with a polyurethane jacket.

Analyses. Biogas. Biogas composition (CO_2,CH_4,H_2,N_2,O_2) was determined using a gas chromatograph (Packard 407) equipped with a TCD detector and two parallel columns: a column of 1.5 m x 1/8", teflon packed chromosorb 108, 60-80 mesh and a 1.2 m x 1/8" mol. sieve 5A, 60-80 mesh. The column split ratio was 1:1. Samples of 100 µl were taken with a glass syringe. For the small scale reactors (0.5 and 6 litres) the measurement of the biogas volume was carried out by pumping the biogas, collected in gastight bags of 10 l, at intervals through a wet test gas meter. The measurement of the biogas volume produced by the reactors of 78 litres was carried out by daily reading of the wet test gas meter connected to the reactors. The gas volumes produced were recalculated to standard temperature and pressure (STP:0 °C, 1 atmosphere).
Organic acids, alcohols and pH. Liquid samples for VFA, lactic acid and alcohol analysis were obtained from the contents of a 0.5 l reactor and the (solid) samples taken from the 78-l by extracting the solids with 1500 ml tap water. After shaking for 30 minutes on a shaking table the liquid was filtered. The filtrate was used for the Volatile Fatty Acids determination. Volatile Fatty Acids (VFA), methanol and ethanol were determined by gas chromatography, using a glass column 2 m x 4 mm, packed with Supelcoport (100-120 mesh) coated with 10 % Fluorad FC 431, temperatures (°C): column 180, injection port 220, flame ionization detector 240, carrier gas (50 ml min^{-1}): nitrogen saturated with formic acid. For methanol and ethanol analysis a column temperature of 90 °C was applied. Lactic acid was determined on a HPLC, equipped with an UV detector (Kratos Spectraflow 773) and an organic acid column (Chrompack, 300x6.5 mm). The injection volume was 10 µl, the eluent 0.01 N H_2SO_4 with a flow of 0.8 ml/min. The wave length during the detection was set at 210 nm, the absorption range 0.050. Through out this chapter the concentration of organic acids is given as the concentration in COD equivalents in the aquous solution of water present in the

original sample. The conversion factors from grams acids to grams COD are 1.067, 1.514 1.818 and 1.067 for acetic, propionic butyric and lactic acid respectively.

The pH of the samples was determined with a Knick mV-meter and a combined glass electrode directly in the solid waste samples.

Methanogenic inocula (seed sludges). The methanogenic seed sludges which were investigated were obtained from the sewage sludge digester in Veenendaal and from an Upflow Anaerobic Sludge Blanket (UASB) reactor treating potato waste water. The TSS and VSS of the sludges were determined according to Standard Methods (1975), the specific methanogenic activity was determined according to De Zeeuw (1984). In one experiment the seed material was obtained from a former digestion run. The TS of the digested sewage sludge amounted to 4.2 %, with a VS-content of was 55 % of the TS, and the maximum methanogenic activity amounted to 0.065 kg CH_4-COD/kg TS.day at 30 °C (0.116 kg CH_4-COD.kg^{-1} VS.day^{-1}). The TS concentration of the UASB sludge amounted to 10 %, the maximum methanogenic activity was 0.15 CH_4-COD.kg^{-1}TS.day^{-1} and 0.23 kg CH_4COD.kg^{-1} TS.day^{-1} (0.3 & 0.4 kg COD.kg^{-1} VS.day^{-1}) at 30 °C and 35 °C respectively. The TS of the digested OF was 26.3 %, the VS amounted 30.0 % of the TS, the methanogenic activity was 0.011 kg CH_4-COD kg^{-1}TS.day^{-1} (0.038 kg COD kg^{-1} VS.day^{-1}) at 35 °C.

RESULTS AND DISCUSSION

Preliminary experiments

The effect of the addition of methanogenic seed sludge without addition of any other material was studied in a number of dry digestion runs conducted at 35 % TS. The amount of seed sludge that could be added viz. 0.4 kg per kg substrate was limited by this TS concentration. A higher amount of seed sludge would lead to a lower TS concentration. The results of the experiment with digested sewage sludge are shown in Fig. 4 and Fig. 5. From Fig. 5 the rapid formation and build up of organic acids becomes apparent and the strong drop of the pH down to 5.0 as well. As can be abstracted from Fig. 5 the conditions were quite detrimental to the methanogenic biomass; any methane was not produced during this period. On the other hand hydrogen was produced in substantial amounts showing its maximum value 25 days after the start and then it gradually dropped to zero during the next 45 days. The main products that accumulated during this phase were acetic acid, lactic acid and butyric acid. Other products were ethanol, propionic acid, capric acid and valeric acid, but these compounds were not found to appear at concentrations exceeding 0.1 g COD.l^{-1}. The total amount of COD-dissolved was similar to the sum of the VFA plus lactic acid. The

formation and subsequent degradation of lactic acid could be responsible for a characteristic pattern of the pH during the unbalanced dry digestion of the substrate. It is known from silage fermentation that lactic acid and acetic acid are formed from soluble sugars, present in the silage biomass (McDonald, 1982). At pH values exceeding 5, and total salt concentrations below 2.5 %, the lactic acid is metabolized by other than lactic acid bacteria to butyric acid. The slight raise of the pH might be the result of the formation of one mole of butyric acid out of 2 moles of lactic acid, and a higher pKa' of butyric acid (4.8 at 30 °C) in comparison to the pKa' of lactic acid (3.9 at 30 °C). If the solution just contains 15 g/l (0.25 mol) lactic acid the pH is 2.3. After complete conversion to butyric acid the pH will be 2.9. That the pH after degradation of lactic acid to butyric acid is 5.8 is suprising, but indicates that other buffering compounds in the system are interfering, which results in a higher pH of the solution than is calculated.

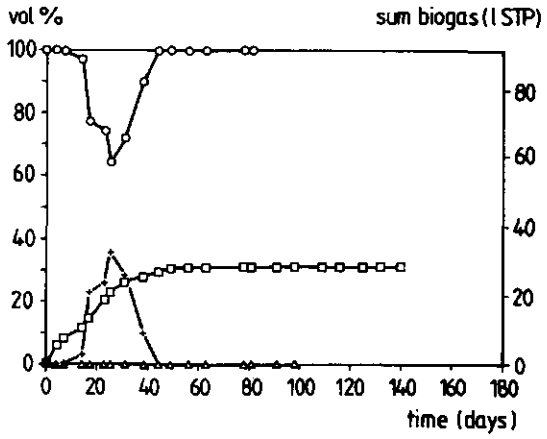


Fig. 4 Biogas production and biogas composition during dry anaerobic digestion of the fraction of MSW with addition of digested sewage sludge as methanogenic seed; (□) cumulative biogas production; (△) vol. % CH_4; (○) vol.% CO_2; (+) vol.% H_2.

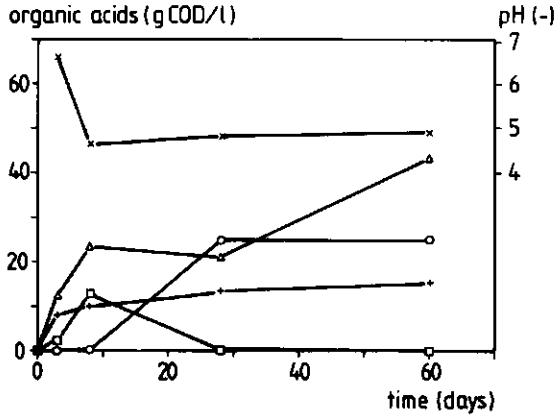


Fig. 5 The course of the pH and of organic acid formation during the dry digestion of the organic fraction of MSW with addition of digested sewage sludge; (□) lactic acid; (+) acetic acid; ( ) butyric acid; (△) total organic acids; (×) pH; (ethanol + methanol < 0.1 g/l).

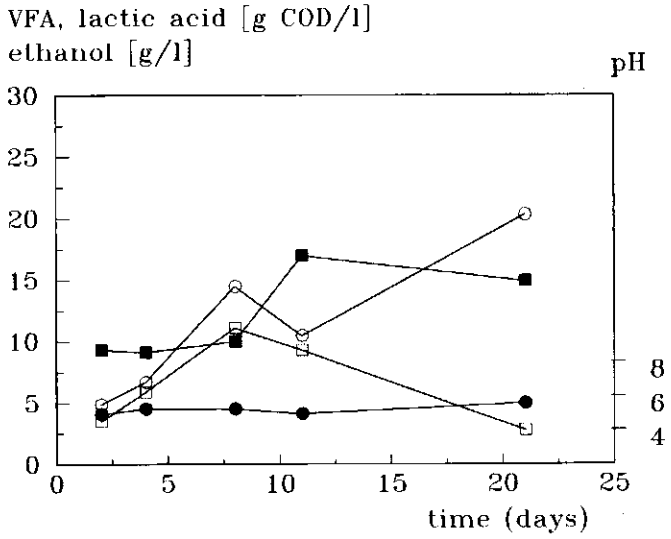


Fig. 6 Dry anaerobic digestion of the source separated organic fraction of MSW with digested sewage sludge as methanogenic seed. (●) pH; (□) lactic acid;(○) VFA's; (■) ethanol. *(Propionic acid and methanol: < 0.5 g.l^{-1}).*

From the following equation:

$$2CH_3CHOHCOOH \longrightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2$$

it is clear that the biogas will consist of carbon dioxide and hydrogen which indeed is in accordance with the results in Figs. 4 and 5 (day 25-55). Other hydrogen producing acidogenic and acetogenic reactions can be ignored since the acetic acid concentration remains almost stable during the period lactic acid is converted into butyric acid.

Another compound that might have influenced the pH pattern shown in Fig. 5 concerns NH_4^+, because the formation of this will increase the pH buffer capacity of the system. The concentration of this compound increased from 300 mg NH_4^+-N.l^{-1} at day 1 to 1500 mgNH_4^+-N.l^{-1} at day 20, and then remains stable. From the dissociation konstant K of this compound (pK = 4.75 at 30 °C) can be calculated that the pH of the solution theoretically is 5.2 and 5.5 respectively.

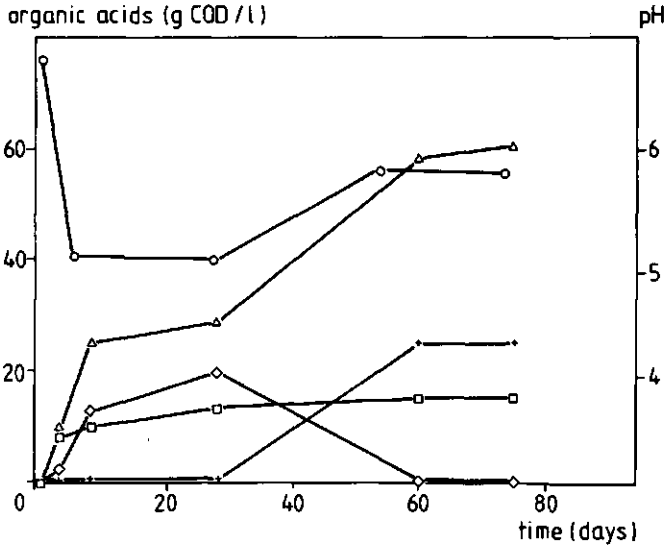


Fig. 7 The course of the pH and of organic acid formation during the dry digestion of the organic fraction of MSW with addition of granular sludge; (◇) lactic acid; (□) acetic acid; (+) butyric acid; (△) total organic acids; (○) pH. *(ethanol + methanol < 0.1 g/l).*

Since the increase starts after day beyond day 25, the increase of the pH can not directly be attributed to the NH_4^+ formation observed during day 25-55.

The buffer capacity, as calculated according to Wellinger (1985), increased between day 0-20 (pH = 5.2): from 0.35 meq/pH to 4.1 meq/pH due to the formation of NH_4^+, but is still rather small. The pH increase during day 25-55 only can be the result of the conversion of lactic acid to butyric acid.

The formation of ethanol was rather small in the experiment discussed, (less than 0.1 g COD/l), despite the fact that ethanol can be formed by hetero-fermentative lactic acid bacteria (McDonald, 1982). However, a dry digestion experiment with source separated OFMSW and digested sewage sludge as seed, a substantial amount of ethanol built up, viz. up to 15 $g.l^{-1}$, (Fig. 6), while also methanol was formed up to 0.5 $g.l^{-1}$ (pH = 5.0). In this experiment any methane formation was not found and organic acids and hydrogen were produced at high rate till day 25.

From the results discussed so far, it can be concluded that the digestion process proceeds highly unbalanced under the experimental conditions discussed. From Figs. 4 & 5 the initial hydrogen plus acid formation rate has been calculated, expressed as g COD formed per reactor volume per day, and amounted to 6 g $COD.l^{-1}.day^{-1}$. Comparing this value to the available methanogenic capacity of the seed sludge added, which amounted to 0.6 g $COD.l^{-1}.day^{-1}$, it is clear that the formation rate of acids and hydrogen is a factor 10 times higher. Addition of a higher amount of methanogenic biomass in order to prevent an unbalanced digestion process, was tested by seeding the system with UASB sludge which resulted in an initial methanogenic capacity of 3.2 g $COD.l^{-1}.day^{-1}$ at 30 °C and a ratio of seed solids and substrate solids of 0.08 $kg.kg^{-1}$. Also in this experiment methane formation was not found and organic acids were formed at high rate (Fig. 7). From the results it therefore can be concluded that a rapid first start-up of dry anaerobic digestion of OFMSW can not be accomplished by adding only a methanogenic seed sludge. The methanogenic capacity of the sludges tested are to low to compensate for the high rate acid plus hydrogen formation. Consequently, high concentrations of organic acids (up to 60 g $COD.l^{-1}$, and ethanol (up to 15 $g.l^{-1}$) and low pH values are observed. These conditions are detrimental to methane formation, as already was explained in chapter 1 of this thesis.

Addition of buffer

The need of using buffers in the first start-up of dry anaerobic batch digestion of OFMSW was investigated on basis of the results of the preliminary experiments discussed above. The formation of organic acids and other intermediates reached a maximum concentration of 60 g COD/l in the liquid phase. This value represents the maximum concentration that can be

obtained when the organic fraction of MSW is hydrolysed anaerobically without further conversion of the intermediates to methane and carbon dioxide. Hydrolysis plus acidogenesis of the volatile solids in the experiment described terminated when 13 % of the VS was converted into to organic acids and hydrogen. This maximum concentration of liquified COD and the observed pH (= 5) corresponds well with the results of other researchers (De Baere et al., 1985). The cumulative amount of the acids formed corresponded to the formation of 0.8 a formation of 0.8 mols acids per kg of Total Solids. Therefore the maximum amount of buffer which has to be added for neutralization of the acids is 0.8 equivalents per kg Total Solids. As was discussed in the former paragraph, also NH_4^+ is formed and buffers the solution. However, since the buffer capacity at pH 6-7 is rather low (c. 4 meq/pH) this is not accounted for. The assumption is made that the hydrolysis is rate-limiting when 13 % of the VS (≡ 0.8 mol acids/kg TS) has been converted.

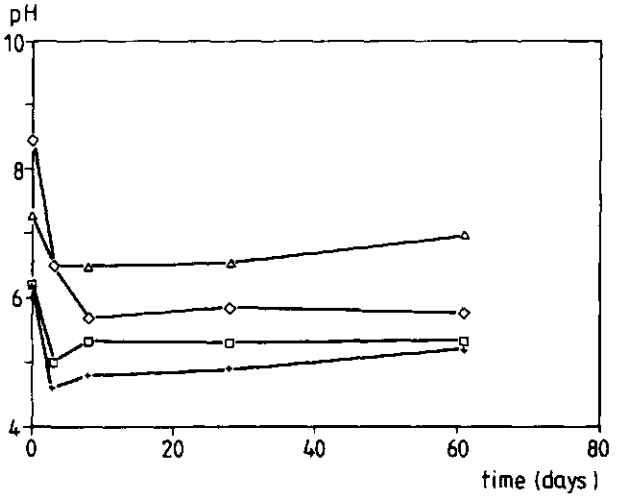


Fig. 8 The influence of pH controlling chemicals on the pH during dry batch digestion of the organic fraction of MSW. (◇) 90 g $CaOH_2$/kg TS (2.41 eq/kg TS); (+) 75 g $CaCO_3$/kg TS (1.50 eq/kg TS); (△) 60 g $NaHCO_3$/kg TS (0.71 eq/kg TS); (□) no buffer.

The above estimated value for the required amount of buffer is only valid when the buffer is present completely in the water phase and when little if any buffer is present from origine and/or will be formed. In testing the estimated amounts of $CaCO_3$ (40g.kg^{-1} TS), $CaOH_2$ (31 g/kg TS) and $NaHCO_3$ (67 g/kg TS), it appeared that higher amounts had to be tested of $CaCO_3$ and $Ca(OH)_2$ had to be employed during the period of imbalance. Apparently the dissolution rate of these buffers might be rather slow during the dry digestion process. The effect of the three pH control chemicals applied were tested in several dry digestion experiments with a varying buffer/substrate solids ratio corresponding to a maximum ratio of 4.25 equivalents buffer per kg TS.

The pH was maintained above 6.5 by $NaHCO_3$ at a buffer/substrate solids ratio of 0.06 kg.kg^{-1} (= 0.71 eq/kg TS) (Fig. 8). In the case of $Ca(OH)_2$ the pH drops to 5.8 at a buffer/substrate solids ratio of 2.31 eq/kg TS (Fig. 8). $CaCO_3$ additions up to 5.68 eq/kg TS did not show any buffering effect on the pH around neutral values. VFA 's were not analyzed during these experiments. When no buffer was added, 20 litres STP of biogas (CO2 + H2) is produced per kg substrate within a period of 90 days, while with $CaCO_3$ additions 2.5 litres STP biogas (CO_2 + H_2) per kg substrate is produced. The insufficient buffering action of $CaCO_3$ confirms the findings of Jewell et al. (1981). On the other hand, Buivid and co workers reported that $CaCO_3$ stimulated the methane production from shredded MSW at 25 % TS (Buivid et al., 1981). The amount of acids produced in this experiment did not exceed 0.20 equivalents/l (≡ 12 g acetic acid/l) while we found 0.62 equivalents/l in our experiments. Since no data about a blank experiment were provided by Buivid et al., in fact the definite conclusion about the effect of $CaCO_3$ additions cannot be drawn from this experiment.

The low solubility of $CaCO_3$ at pH values exceeding 6-7.5 (Capri and Marais, 1975) limits the buffering action of this compound presumably due to low reaction rate between the VFA formed and solid buffer particles.

$Ca(OH)_2$ is only partially effective as a pH control. As in the case of $CaCO_3$, the effectiveness of $Ca(OH)_2$ is limited by the low reaction rate between the VFA formed and the buffer solids.

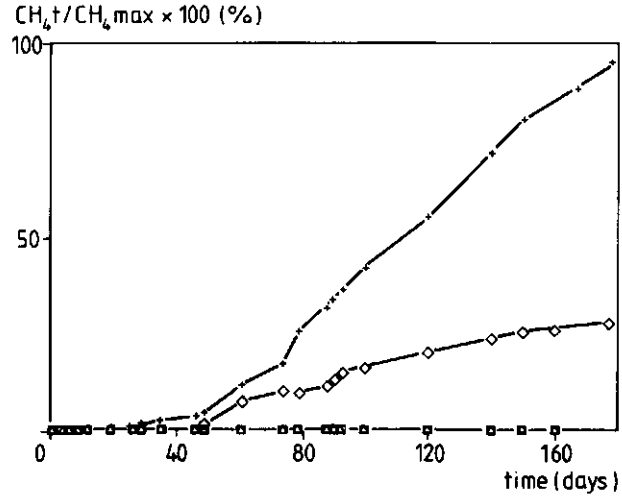


Fig. 9 The influence of pH controlling chemicals on the methane production during dry batch digestion of the organic fraction of MSW. (□) no buffer (+) 60 g $NaHCO_3$/kg TS; (◇) 90 g $Ca(OH)_2$/kg TS; (△) 75 g $CaCO_3$/kg TS.

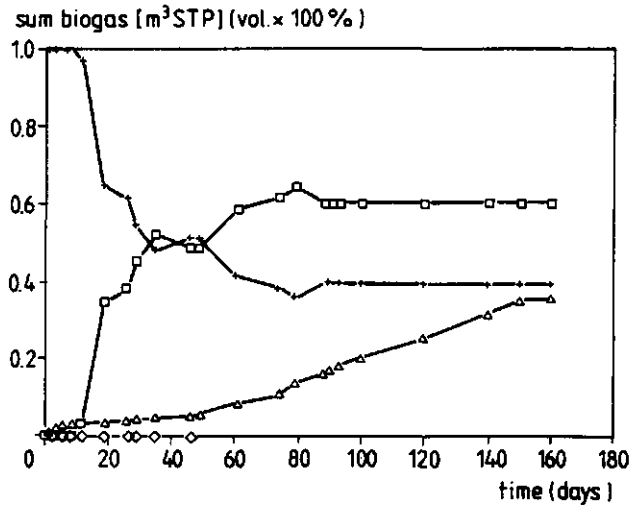


Fig. 10 Biogas production and biogas composition during the balanced dry batch digestion of the organic fraction of MSW with addition of 60 g $NaHCO_3$/kg substrate solids. (△) biogas production; (□) vol. % CH_4; (+) vol.% CO_2; (◇) vol. % H_2.

The effect of the type of buffer, i.e. the extend to which the pH is controlled is also reflected in the methane production pattern found in the dry digestion (Fig. 9). Apparently a greatly balanced process is achieved between acid formation + hydrogen formation and the methane formation in the experiment with $NaHCO_3$ as a buffer at a minimum buffer/substrate solids ratio of 0.06 $kg.kg^{-1}$ TS (0.71 eq/kg TS), (see also Fig. 10). Any lactic acid could not be detected and the hydrogen content of the biogas was nihil during the course of the experiment.

The time needed to reach the maximum methane yield (80 l CH_4 STP.kg^{-1} organic fraction of MSW) amounted to 6 months, which is longer than reported by De Baere et al. (1985) for experiments with continuous dry anaerobic digestion of OFMSW. When using the continuous dry digestion was applied, a digestion time of 21-28 days at 35 °C is required. However, these figures are based on experiments with a reactor that had already been started up with digested OFMSW.

The lower methane production rate found in dry anaerobic batch digestion of OFMSW with $NaHCO_3$ addition compared to results reported in the literature could be a result of the toxicity of the excessive amount of Na^+-ions (10.2 g/l) present in the liquid phase. Na^+-ions inhibit the methane formation at concentrations exceeding 7 g/l (De Baere et al. 1984) when a shock load is applied. The degree of inhibition depends on the type of methanogen which is present in the anaerobic bacterial population. Methanogens of the genus *Methanothrix* which normally predominate granular sludge digested sewage sludge and sludge from UASB-reactors are less tolerant to high Na^+ concentrations than methanogens of the genus *Methanosarcina sp.* (De Baere et al., 1984; Rinzema et al., 1988). Since *Methanothrix sp.* was the predominant methanogen in the inocula, the methane formation in the experiments with $NaHCO_3$ is strongly inhibited. At concentrations above this level an adaptation period is necessary before any methane production can occur. Adaptation in this case presumably means the development of *Methanosarcina sp.* in the bacterial population. Inhibition due to of high Ca^{2+} concentrations is likely to be found in the same order of magnitude as Na^+ inhibition, although there are indications that Ca^{2+} is less toxic to methanogens (McCarthy and McKinney, 1961; Kugelman and Chin, 1971).

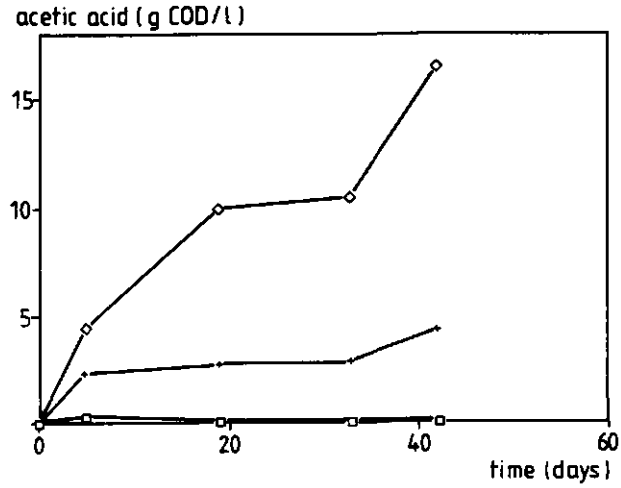


Fig. 11 The acetic acid buildup during dry anaerobic digestion of precomposted organic fraction MSW with various buffer additions (0.8 eq/kg TS). (□) no buffer; (◇) $NaHCO_3$; (+) $CaCO_3$. (*concentrations other VFA's < 100 mg COD/l*).

The influence of high Na^+ and Ca^{2+} concentrations, applied in the present study on the methane production, was studied in dry anaerobic digestion experiments with aerobically pretreated organic fraction (see also next paragraph of this chapter). In the partial composting the easily degradable compounds were converted. When a seed/substrate solids ratio of 0.08 $kg.kg^{-1}$ is applied, the dry digestion will proceed balanced because of the absence of easily degradable material. The acid formation + hydrogen formation rate is distinctly lower in that case. The effect of high concentrations cations on the methane production can in this way be distinguished from the inhibition by organic acids at low pH values. The results show that with the non-buffered substrate, only low concentrations (< 1 g COD/l) of acetic acid are found, whereas in the experiments with $CaCO_3$ and $NaHCO_3$ increased concentrations of acetic acid are found (Fig. 11).

As was mentioned in Chapter 1, acetic acid is the main precursor for methane formation during the anaerobic digestion of organic compounds. The inhibition by compounds which are more toxic to the acetoclastic methanogenic bacteria (methanogens which form methane from acetic acid) than the hydrolytic and acidogenic bacteria which form acetic acid from other organic compounds will result in an increasing acetic acid concentration.

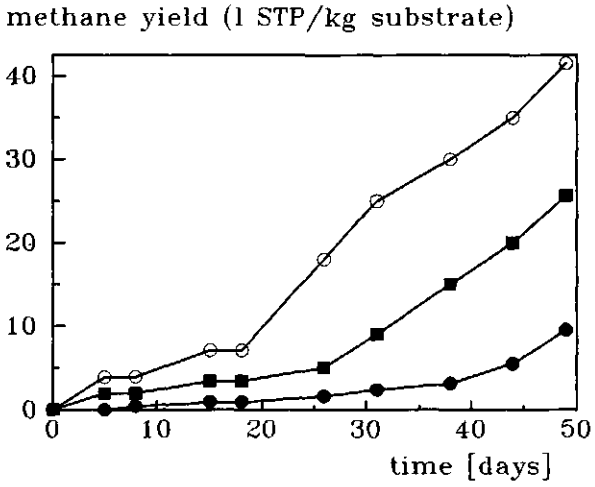


Fig. 12 The infuence of buffer addition (0.8 eq/kg TS) on the methane yield in dry digestion of precomposted organic fraction of MSW. (○) no buffer; (■) $NaHCO_3$; (●) $CaCO_3$.

This might be true for both Na^+ and $CaCO_3$ as can be abstracted from Fig. 11. Both $NaHCO_3$ and $CaCO_3$ inhibit the digestion process which is indicated by the amount of methane produced and the total COD converted (sum of methane COD plus VFA COD) during the experiments (Figs. 12 and 13). From Figs. 12 and 13 it appears also that Ca^{2+} also affects the digestion process. There is not as much information about the effect of high Ca^{2+}-concentrations during anaerobic digestion as for Na^+. Early research does not clearly differentiate between Ca^{2+} and Na^+ inhibition of the methane formation (Kugelman and Chin, 1971). Methane production after 50 days amounted to 40 litres (STP) without buffer addition, 29 litres when $NaHCO_3$ was added (0.8 eq.kg^{-1} TS) and 10 litres when $CaCO_3$ was added (0.8 eq.kg^{-1} TS) (Fig. 12). In Fig. 13 the total COD concentrations are presented for these experiments. The VFA concentrations (Fig. 11) together with the total COD converted (Fig. 13) indicate that in the case of $CaCO_3$ the biogas production rate is both limited by the hydrolytic + acidogenic processes and the methanogenic step. In the case of NaHCO3 methanogenesis is the limiting step. In both experiments with buffer addition, acetic acid was by far the largest fraction of volatile fatty acid build-up.

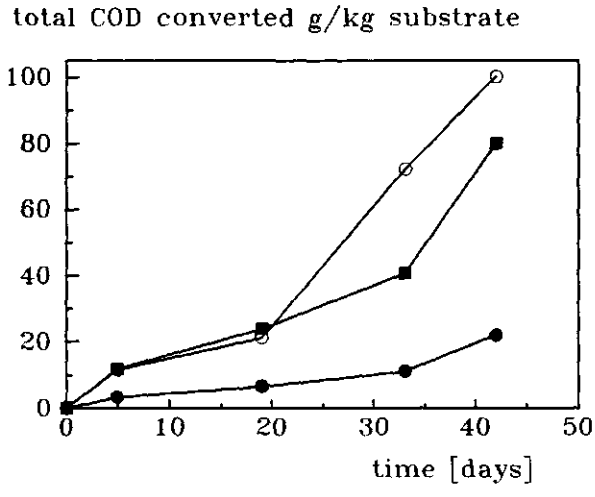


Fig. 13 The infuence of buffer addition (O.80 eq/kg TS) on the total COD conversion in dry digestion of precomposted organic fraction of MSW. (○) no buffer; (■) 0.71 eq/kg TS $NaHCO_3$; (●) $CaCO_3$.

Partial composting

The VS reduction data assessed in the aerobic composting experiments with OFWMS is shown in Fig. 14. In the case c. 20 % of VS had been degraded during the partial composting stage the temperature did not regain thermophilic values after sampling as was observed for the samples with 0 - 20 % VS reduction. Apparently that the easily degradable compounds have been removed in the case of 20 % VS-reduction. The maximum temperature observed during the period where 20-23.5 % VS reduction proceeded was only 42 °C.
The effect of the several precomposting periods on the relative methane yield is presented in Fig. 15. The relative methane yield is defined the sum of the methane produced at time (t) divided by the potential methane yield of the concerning organic fraction, as determined in a batch assay at low solids concentration. The loss in the potential amount of methane due to precomposting was calculated by subtracting the methane yield of the composted VS from the methane yield of the untreated organic fraction. Significant methane production rates occur when 20 % of the VS have been degraded in the precomposting period. At lower VS conversions methane formation is much lower (Fig. 15). The highest methane production rate is found at a VS-reduction of 23.5 %. In Fig. 16 the relation of the initial VS degradation rate (r_{vs}) and the VS-conversion by precomposting is given. The initial (day 0 - day 12) r_{vs} was calculated from the sum of the VS which is degraded to acids, hydrogen and

methane during day 0-day 12. By plotting the sum of the degraded VS against the time the value of the initial r_{vs} is given by the maximum slope of the curve (Fig. 17). The initial VS degradation ($\approx$ initial acid formation rate) decreases due to the partial composting. In particular the formation rate of lactic acid is strongly affected by aerobic treatment. Lactic acid could not be detected at VS reductions exceeding 4 %. The hydrogen content of the biogas was negligible. These results suggest that soluble sugars which are the precursors for lactic acid in an unbalanced dry anaerobic digestion of MSW were degraded during the aerobic period. The initial amount of methanogenic activity of the seed sludge (0.5 g CH_4-COD.l^{-1}.day^{-1}) suffices when 23.5 % of the VS is aerobically degraded. The initial acid formation rate was still higher than the total methanogenic activity of the inoculum, while the digestion starts immediately. The reason for this is not clear. In Fig. 18 the organic acids and pH are shown for the digestion experiment of 23.5 % VS reduction. The pH values and the organic acid concentrations are characteristic for a more or less balanced digestion process, i.e. pH values around 7, and the total organic acids and hydrogen are readily converted without an excessive build-up as was found under unbalanced conditions.
The aerobic pretreatment decreases the initial VS removal rate, which appears from the lower initial acid formation rate (Fig. 17).

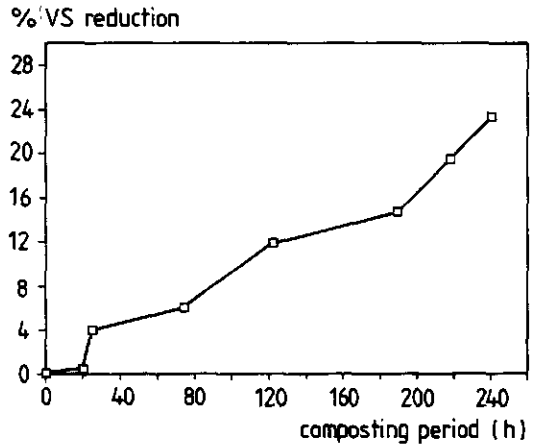


Fig. 14 Volatile Solids reduction during the precomposting of the organic fraction of Municipal Solid Waste.

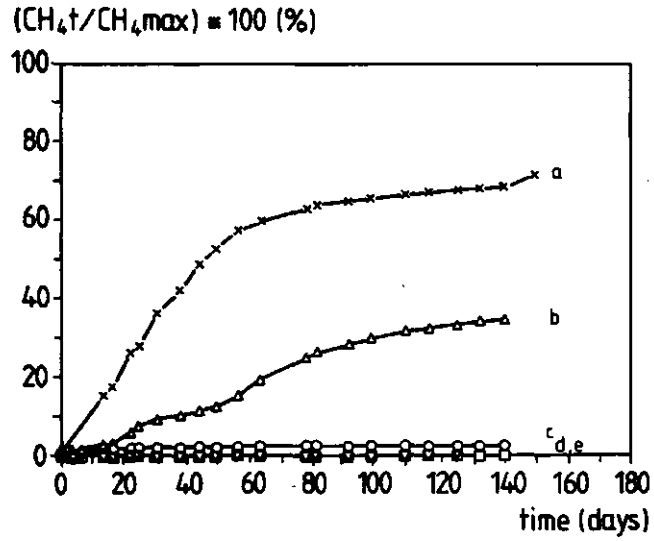


Fig. 15 Relative methane yield curves of the organic fraction of MSW at several VS reduction grades in the precomposting treatment. (**a**) 23.5 % VS-reduction. (**b**) 19.5 % VS-reduction. (**c**) 14.5 % VS reduction. (**d**) 11.9 % VS reduction. (**e**) 4 % VS reduction.

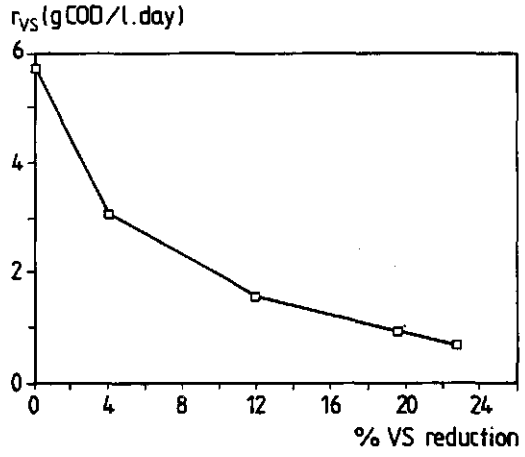


Fig. 16 Effect of the VS reduction by precomposting of the organic fraction of Municipal Solid Waste on the removal rate r_m during subsequent dry anaerobic batch digestion.

The easily degradable part of the substrate apparently is degraded during the composting period as was presumed above. It can be concluded that the start-up of the dry anaerobic batch digestion of the organic fraction of MSW can be enhanced by using an aerobic pretreatment step. However, the amount of VS which has to be degraded during the partial composting results in a loss of 40 % of the potential methane yield. The composting time (artificial aeration) needed for such an amount of VS reduction amounts to 2 weeks. The long composting period and a significant loss of a potential amount of methane obviously represent major drawbacks for the implementation of the such precomposting step in the BIOCEL-process as the treatment costs increase. Also the net energy production drops down distinctly. Therefore a shorter precomposting period, which results in increased temperature in combination with a another start-up procedure might be more feasible. The heat which is released during the composting period then is used for heating the waste before the digestion process.

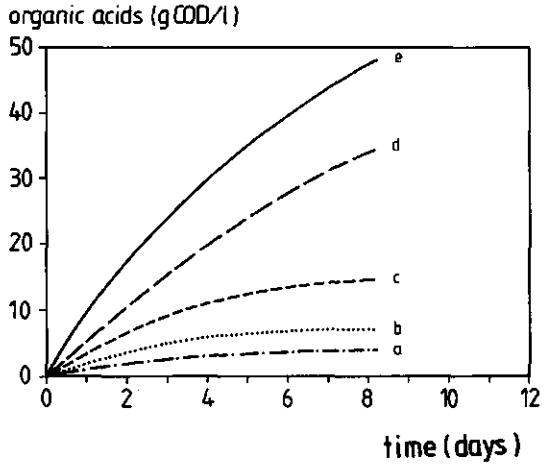


Fig. 17 Effect of the VS reduction by precomposting of the organic fraction of MSW on the initial acid formation rate in subsequent anaerobic digestion; a: 23.5 VS-reduction; b:19.5 VS- reduction; c: 14 % VS reduction; d:11.9 5 VS-reduction; e: 4 % VS-reduction.

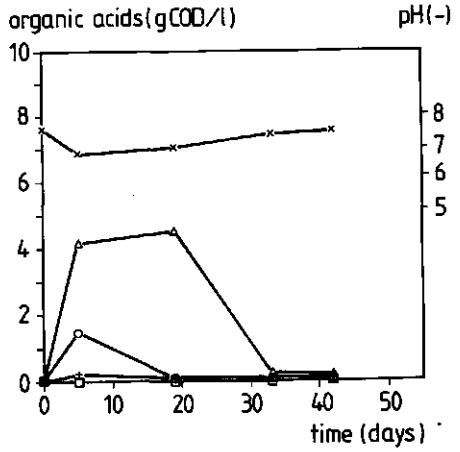


Fig. 18 Organic acid concentration and pH during the dry anaerobic digestion of the precomposted (23.5 % VS-reduction) organic fraction of MSW; (□) lactic acid; (○) acetic acid; (+) butyric acid; (△) total organic acids; (×) pH.

The effect of spatial separation of substrate and seed sludge when applying leachate recycle

The digestion experiments dealing with assessment of the effect of partial spatial separation of the substrate (OFMSW) and the methanogenic seed sludge (granular sludge) were carried out using three digesters. The first digester was filled with the mixed OFMSW and inoculum (IN) at 39 % TS; the digestion conducted without leachate recirculation. A second digester was filled as the first one with the mixed OFMSW and inoculum at 31 % TS but the digestion proceeded with leachate recirculation. A third reactor was started with separate layers of OFMSW and inoculum 31 % TS and once again with application of leachate recirculation.

Fig. 19 presents one of the characteristic patterns of the biogas production and biogas composition of these experiments, Figs. 20,21 and 22 the pH and organic acids of the three digesters. It is obvious from the pH values and VFA-concentrations presented, that the three digesters show a very similar pattern. The initial biogas production was 50-100 $l.day^{-1}$ but after 8 days the production rate dropped down to less than 1 $l.day^{-1}$. The methane concentration in the biogas slowly increased from 0 % to a value of 5-30 vol. % after 30

days. The hydrogen concentration in the biogas showed maximum values of 30-40 vol. %. The pH and the organic acids also showed the characteristic pattern of unbalanced anaerobic digestion. The pH decreased from 6.5 to a value of 5.2 within 2 days, then increased again to 5.8-6.0 and decreased again to a value of 5.3. The total organic acids concentration reached a value of 40-50 g COD.l^{-1} within 10 days. The organic acid formation rate plus the hydrogen formation rate of the experiments were in the range 3.5 - 4.5 g COD .l^{-1}.day^{-1}. The initial methanogenic capacity of the seed sludge amounted to 1.3 g COD.l^{-1} reactor.day^{-1}.
From the results of the experiments it can be concluded that the effect of partial spatial separation of methanogenic biomass and substrate (pure OFMSW) combined with leachate recycling anaerobic digestion of the pure organic fraction of MSW is rather small. The observed formation rate of the organic acids + hydrogen means an overloading of three times the maximum methanogenic activity added to the digesters. Since the maximum methanogenic activity was determined in an environment which is more favourable for methanogens than the BIOCEL environment the actual overloading even was larger. This overloading results (Figs. 20,21,22) in high organic acid concentrations (40-50 g COD.l^{-1}) and low pH values (5.1-5.4). Ethanol and methanol concentrations were below 0.1 g/l. The methane production rate (r_{CH4}) 30 days after the start of the experiment, viz. 0.004 l CH_4/l_r/day, is still very low compared to the methane production rate obtained with addition of buffers, viz. 0.11 l CH_4/l_r/day, as is described earlier in this Chapter.

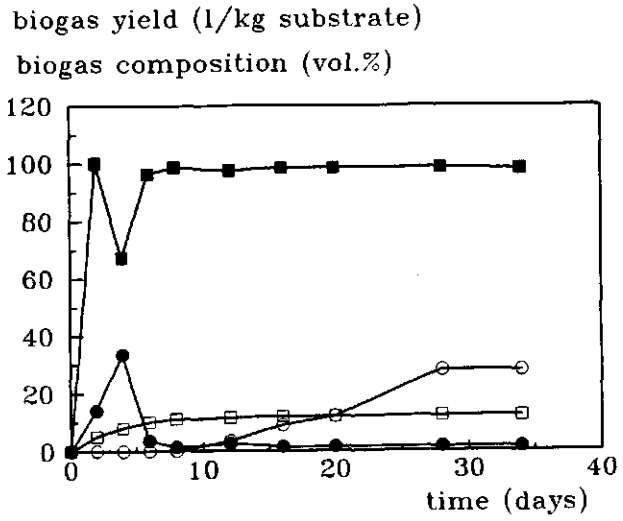


Fig. 19 Characteristic pattern of the biogas production biogas composition concentration in the dry anaerobic digestion of the organic fraction of MSW with spatial separation of seed sludge and with applying leachate recycle. (□) cumulative biogas production; (○) vol. % CH_4;(■) vol.% CO_2; (●) vol.% H_2.

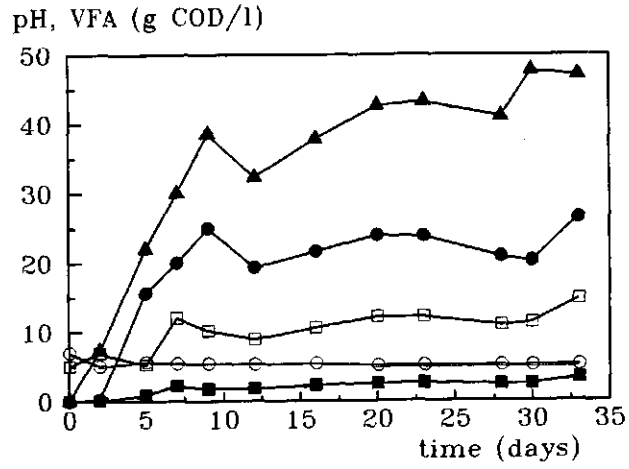


Fig. 20 The course of the pH and VFA's in anaerobic digestion of OFMSW with application separate layers of granular seed sludge; (○) pH; (□) acetic acid; (■) propionic acid; (●) butyric acid; (▲) total VFA's. *(ethanol < 0.1 g/l).*

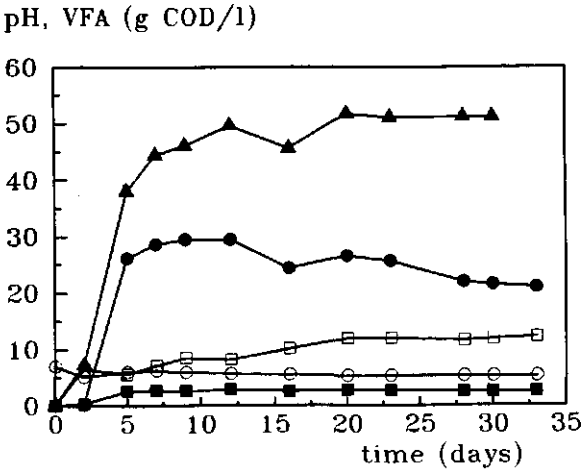


Fig. 21 The course of the pH and VFA's in anaerobic digestion of OFMSW with application of leachate recycle; (○) pH; (□) acetic acid; (■) propionic acid; (●) butyric acid; (▲) total VFA's. (*ethanol,methanol < 0.1 g/l*).

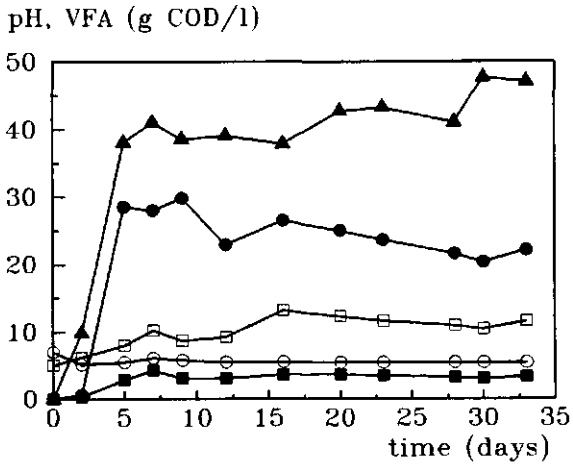


Fig. 22 The course of the pH and VFA's in anaerobic digestion of OFMSW with application separate layers of granular seed sludge and leachate recycle; (○) pH; (□) acetic acid; (■) propionic acid; (●) butyric acid; (▲) total VFA's. (*ethanol < 0.1 g/l*).

Addition of compost

TABLE 3 Experimental set up for the start-up of the dry digestion of OFMSW with composted OFMSW or digested OFMSW

PROCESS CONFIGURATION	code	% TS	TS ratio IN/OFMSW	TS ratio compost/OFMSW
mixed OFMSW/compost/IN1 no leachate recycle	1	38	0.04	0.40
mixed OFMSW/compost/IN leachate recycle	2L	31	0.04	0.40
separated OFMSW/CP/IN no leachate recycle	3	38	0.04	0.40
separated OFMSW/CP/IN leachate recycle	4L	31	0.04	0.40
separated OFMSW/Digested OFMSW leachate recycle	5L	31	0.4	0.40

The effect of combined addition of composted OFMSW and methanogenic seed sludge during the first start-up of the dry anaerobic digestion of OFMSW was studied with the experimental set up given in TABLE 3. One reactor was filled with the mixed OFMSW/compost and inoculum at 35 % TS and digested without leachate recirculation. Another reactor was filled with the mixed OFMSW/compost and seed sludge (= inoculum = IN) as described above at 31 % TS with leachate recirculation. A third reactor was started up with the OFMSW and the inoculum in separate layers at 31 % TS applying leachate recirculation. A fourth reactor was filled in the same manner, but leachate recycle was not applied for this reactor. The experiments were carried out with granular sludge as an

inoculum (0.04 kg sludge solids per kg OFMSW solids) and a OFMSW + compost mixture with an initial compost solids/OFMSW weight ratio of 0.40 $kg.kg^{-1}$. The course of biogas production and biogas composition of experiment 2L, is presented in Fig. 24. The curves of experiment 1, 3 and 4L that are not presented here, showed a very similar pattern. The course of the pH and VFA concentrations are presented in Figs. 24, 25, 26 and 27. The methane content of the biogas increased to a value of 60 % in the period 0-20 days. The hydrogen content reached a maximum value of 3.5 % after two days and decreased rapidly zero after 4 days. This pattern was typical for all four experiments in which compost addition to the OFMSW was applied. The cumulative methane yield curves are presented in Fig. 28. The curves show that the dry digestion process proceeds more or less similar in the experiments with compost addition and under the various process configurations applied, viz. leachate recycle, mixing fresh OF solids and inoculum solids and spatial separation of OFMSW and inoculum prior to start-up. Fig. 27 shows the organic acid concentrations of the experiment with compost addition, leachate recycle and separation of OF and inoculum in layers.

The values of the first order reaction rate constant k_{vs} (see for definition, equation 7 & 8, Chapter 1) and of the organic acid + hydrogen formation rate k_{ac} during the first 13 days for these experiments are summarized in TABLE 4.

It is obvious that the addition of compost on the start-up the dry anaerobic digestion of OFMSW is very positive. Leachate recycle and partial spatial separation have only a small additional positive effect. When 40 % of the initial solids consists of compost solids, the most rapid start-up is found when applying leachate recirculation and spatial separation. The organic acid concentrations decrease to values of 1 COD $g.l^{-1}$ within 36 days. In the other experiments with compost addition this low VFA-COD value is reached after 50 days. From these data it can be concluded that in the first period of the dry digestion spatial separation of inoculum and OFMSW combined with leachate recycling enhances the start-up.

When combining merely spatial separation (without leachate recycle) the methane yield does not differ from the case with leachate recycling. This result is more or less surprising, regarding the several implications leachate recycle can have. If the distribution of methanogens, acids and moisture in de solid waste bed is assumed to be not homogenous due to the bad mixing of the solid bed, leachate recycle can stimulate the homogenous distribution over the solid bed and as a result can accelerate the digestion process. However, the results do not support the hypothesis, that substrate limitation of the methanogens actually took place under the experimental conditions. After 60 days, the relative methane yield of the start-up experiments with compost was still very small.

The dilution of the OFMSW with compost results in high organic acid concentrations (30-40 g COD l^{-1}) and low pH values (4.9-5.5). Despite that, the digestion process proceeds rather well. Commonly such highly suboptimal conditions are detrimental for an anaerobic reactor.

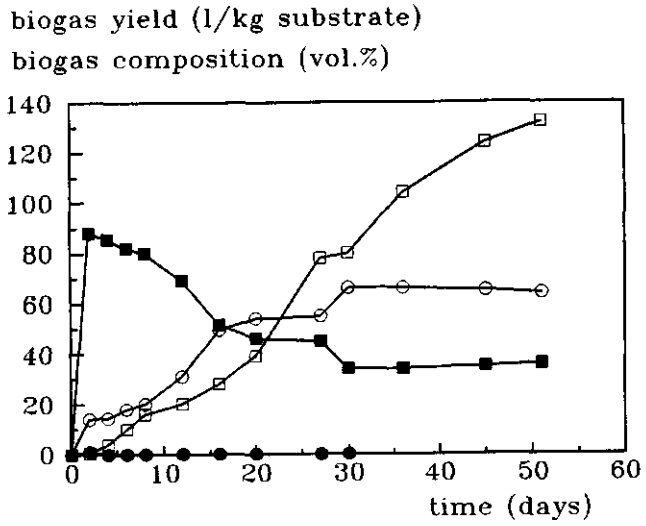


Fig. 23 Characteristic pattern of the cumulative biogas production, biogas composition concentration in anaerobic digestion of OFMSW with compost addition (experiment nr. 2L, 40 % of the initial total solids. (□) cumulative biogas production; (○) CH_4; (■) CO_2; (●) H_2.

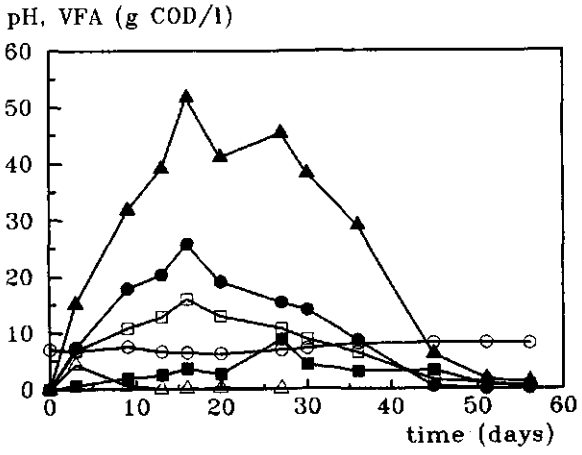


Fig. 24 Pattern of the organic acid concentrations during dry anaerobic digestion of an organic fraction with addition of 40 % compost total solids (exp. 1); (□) acetic acid; (●) butyric acid; (△) lactic acid; (▲) total organic acids; (●) pH.

The toxicity of the non-dissociated organic acids is generally thought to be the main reason for reactor failure under these conditions (Chapter 1, Kroeker et al. 1979; Anderson et al., 1982; Atal et al., 1988). The calculated maximum concentration of non-dissociated organic acids was 0.2 $mol.l^{-1}$ in the experiments with addition of composted OFMSW, which is significantly higher than the range were inhibition of the methane formation is reported to prevail for the non-dissociated volatile fatty acids i.e. 0.005-0.010 $mol.l^{-1}$ (Kroeker et al., 1979).

That nevertheless the dry digestion process still proceeded may be the result of:

a) a selection of a methanogenic population predominated by *Methanosarcina sp* induced by the high organic acid concentrations and the low pH values. The predominance of this type of methanogen was confirmed repeatedly microscopic observation of the digested OF. In general the methanogenic biomass in an anaerobic reactor (e.g. UASB reactor, sludge digester) is predominated by *Methanothrix sp.* (Huser et al. 1982; Huser, 1982). Anaerobic digesters are generally maintained at low organic acid concentrations, especially acetic acid, the main precursor for methanogenesis. At low acetate concentrations *Methanothrix sp.* is kinetically in advance over *Methanosarcina sp.* (Zehnder et al., 1982). The pH growth optimum is more narrow for *Methanothrix sp.* than for *Methanosarcina*. *Methanosarcina sp.* shows methanogenic activity in the pH range 5-8, while *Methanothrix sp.* shows methanogenesis in the range 6.7-8.0 (Zehnder et al., 1982). Apart from the pH and the acetic acid concentration the total salt concentration plays a role in the selection. In Chapter 5 experiments are described which attempt to elucidate these obscurities. Acetic acid degradation will be studied at high concentrations and at low pH values and also at high salt concentrations by an enrichment culture from digested OFMSW. The fact that the inoculum was UASB sludge which is predominated by *Methanothrix sp.* supports the idea of a population shift. However, the environmental conditions during the first period of the process exclude the rapid commencement of the methane production as was observed during our experiments.

b)The existence of zones (micro environments) where lower acid concentrations and higher pH values prevail, may play a role during the first critical period of the process. The suboptimal mixing conditions in the reactors, which is characteristic for the BIOCEL process can enhance the formation of these zones. In Chapter 4 of this thesis the actual existence and the possible role of these zones will be investigated. In Chapter 7 a simple scheme will be presented to account for the effect of these zones on the rate of the digestion process in a BIOCEL digester.

Start-up with a digested organic fraction as inoculum

The digested residue remaining from experiment with compost addition (4L, TABLE 3), separation of inoculum and substrate and leachate recycle was used for a start-up experiment. The objective of this experiment was to clear up whether or not the digested residue would be a better inoculum, viz. to provide a faster start-up of the dry digestion. The methanogenic activity of the digested OF amounted itself 0.003 kg CH_4-COD kg^{-1} residue.day^{-1}. The seed solids amounted to 40 % of the initial total solids, which amounted to 30 %. Fig. 19? shows the assessed organic acid concentrations during the experimental period. Fig. 20 allows a comparison of the methane production rate in this experiment with that in the experiment with the addition of compost solids and UASB sludge with identical process set up (experiment 4L). The value for the first order reaction rate constant k is given in TABLE 4.

TABLE 4. Values of k_{vs} and r_{vs} for the start-up of the dry digestion of OFMSW with compost or digested OFMSW

process configuration	r_{vs} (g COD/l.d)[1)]	k_{vs} (d^{-1})	r^{2} [2)]	σ[3)]
mixed OFMSW/compost/IN no leachate recycle	1.81	-0.038	0.76	0.0060
mixed OFMSW/compost/IN leachate recycle	1.84	-0.048	0.79	0.0083
separated OFMSW/CP/IN no leachate recycle	1.81	-0.031	0.97	0.0022
separated OFMSW/CP/IN leachate recycle	1.99	-0.044	0.89	0.0033
separated OFMSW/Digested OFMSW leachate recycle	2.17	-0.032	0.97	0.0016

[1]: time interval:day 0-day 13 [2]: number of observations: n = 14 [3]: standard deviation

The experiment with the digested residue as inoculum gives identical results as the experiment with compost addition, spatial separation of methanogenic biomass and substrate combined with leachate recycle. From Fig. 30 it can be concluded that a slightly shorter lag phase of the methane production is found in the experiment with the digested residue. It should be noted, that the r_m is higher because of the higher biodegradable VS content of the OFMSW used in this experiment. The amount of methanogenic biomass added with the digested OFMSW was lower than in the experiments with compost addition and UASB sludge as inoculum. Per digester volume the initial methanogenic capacity of the biomass amounted to 1.3 and 1.8 $COD.l^{-1}.day^{-1}$ respectively. The methanogenic biomass added was calculated on the basis of the specific activity standard test which does not discriminate between types of methanogen. However, because as stated above, it is likely that the larger portion of the methane was produced by Methanosarcina sp. present in the UASB sludge. Considering their higher tolerance for low pH and high volatile fatty acid concentrations, only a fraction of the methanogens will be really active.

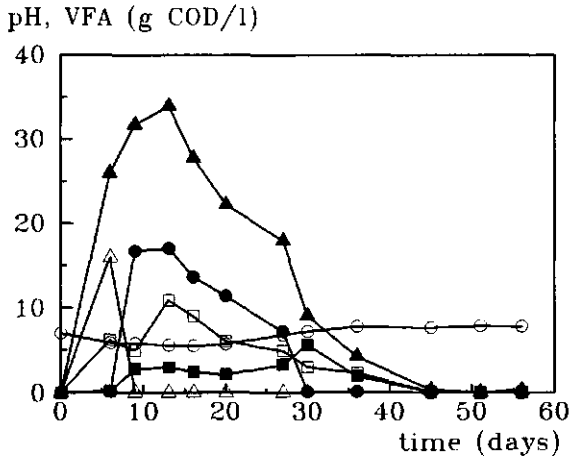


Fig. 25 Pattern of the organic acid concentrations during dry anaerobic digestion of an organic fraction with addition of 40 % compost total solids and leachate recycle (exp. 2L); (□) acetic acid; (●) butyric acid; (△) lactic acid; (▲) total organic acids; (○) pH.

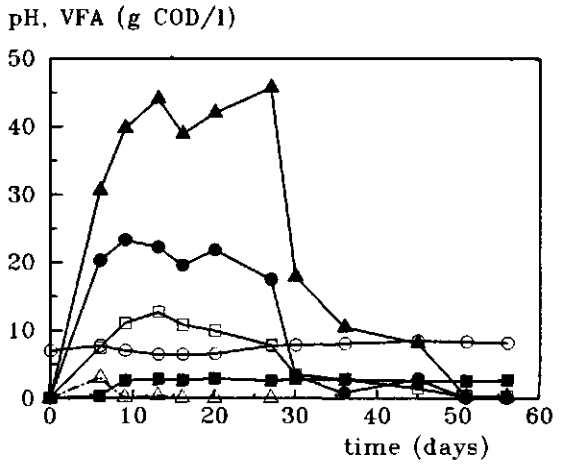


Fig. 26 Pattern of the organic acid concentrations during dry anaerobic digestion of an organic fraction with addition of 40 % compost total solids and partial separation of substrate and inoculum (exp. 3); (□) acetic acid; (●) butyric acid; (△) lactic acid; (▲) total organic acids; (○) pH.

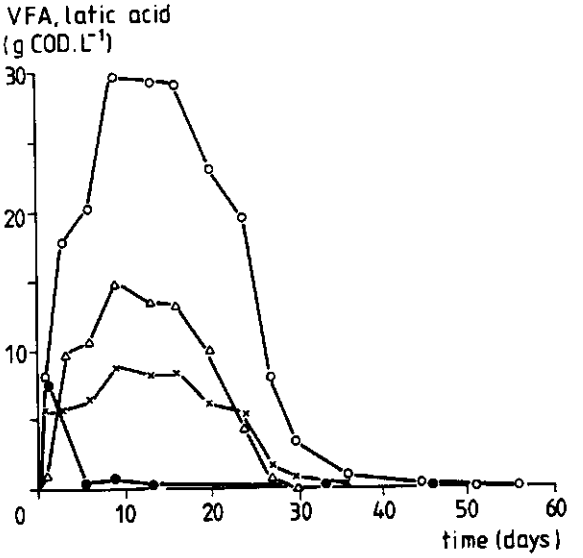


Fig. 27 Pattern of the organic acid concentrations during dry anaerobic digestion of an organic fraction with addition of 40 % compost total solids and partial separation of substrate and inoculum + leachate recycle (exp. 4L); (×) acetic acid; (△) butyric acid; (●) lactic acid; (○) total organic acids.

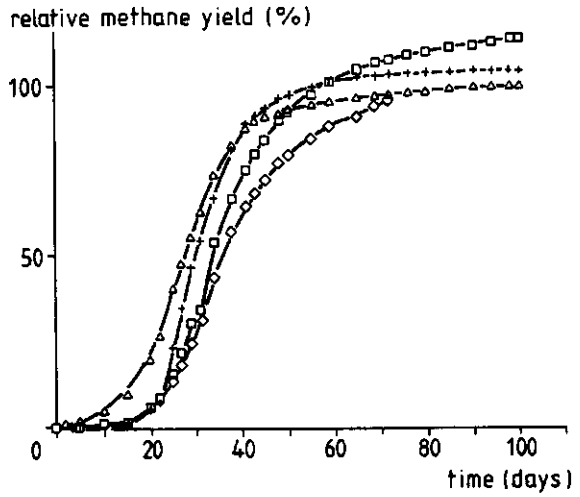


Fig. 28 Methane yield (related to maximum of 80 l/kg OFMSW) for dry anaerobic digestion experiments with compost addition; ( ) mixed substrate- /inoculum, no leachate recycle; (+) mixed substrate/inoculum, leachate recycle; (◇) separated substrate/inoculum, no leachate recycle; (△) separated substrate/inoculum, leachate recycle.

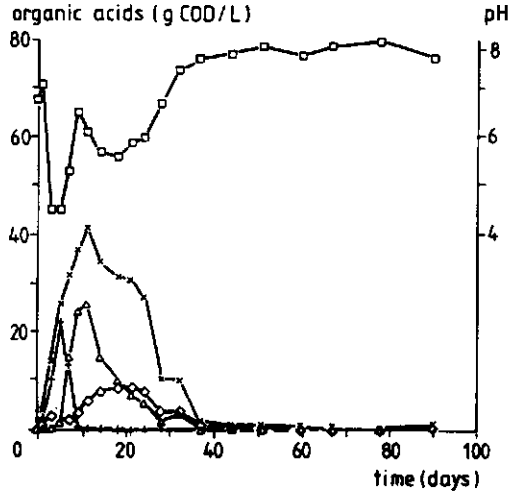


Fig. 29 Pattern of the organic acid concentrations during the dry anaerobic digestion of the organic fraction of MSW and digested organic fraction (40 % of the initial total solids) as the methanogenic inoculum, with spatial separation of inoculum/substrate and leachate recycle; (◇) acetic acid; (△) butyric acid; (+) lactic acid; (×) total organic acids; (□) pH.

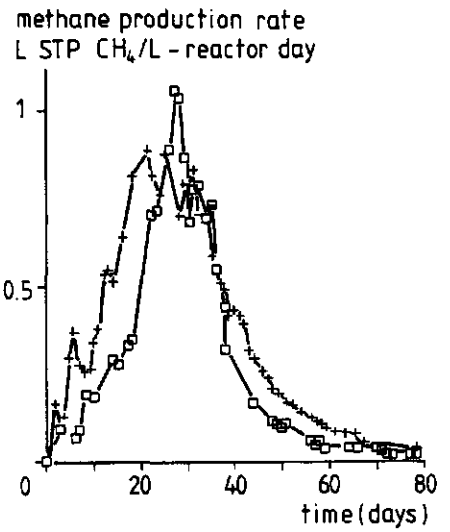


Fig. 30 Comparison of the methane production rate during the dry anaerobic digestion of an organic fraction of MSW with different methanogenic inocula. (□) granular UASB sludge; (+) digested organic fraction.

Some authors suggest, that merely compost not using any additional methanogenic seed would be sufficient for rapid start-up of the dry anaerobic digestion process (Stegmann and Ehrig, 1980; Stegmann, 1982). Apart from dilution of the substrate, as is aimed at in our experiments, the main effect of compost may be the presence of methanogenic organisms in compost. Further investigations are necessary to assess the presence of such organisms in medium.

CONCLUSIONS

Several methods were investigated to enhance the start-up of the dry anaerobic batch digestion of the organic fraction of Municipal Solid Waste. Addition of digested sewage sludge or sludge (0.4 kg per kg OFMSW) from a UASB reactor alone does not result in a balanced digestion process within 60 days, since the methanogenic capacity of the amount of seed sludges added was tenfold lower in all cases compared to the initial formation rate of hydrogen and organic acids from the substrate.

The addition of 0.71 equivalents of a pH buffer per kg OFMSW total solids stimulated the methane production to a great extent, at least when applying $NaHCO_3$. In that case a period

of 6 months at 30 °C was needed for maximum methane yield (80 l CH_4 STP/kg organic fraction). $Ca(OH)_2$ showed a minor effect on the methane production due to a negligible effect on the pH. $CaCO_3$ gives no pH buffering effect; in fact $CaCO_3$ inhibited the hydrolysis and acidogenesis of the volatile solids of OFMSW to acids and hydrogen. Although addition of $NaHCO_3$ buffers the pH around 7 and, as a consequence, stimulates methane production, the high Na^+-concentrations (10 $g.l^{-1}$) decrease the rate of the methane production. The practical applicability of buffer addition in enhancing the start-up of dry anaerobic digestion therefore is limited.

The start-up of the dry digestion process can be accelerated by applying an aerobic pretreatment step. However, since the amount of VS which has to be degraded in such partial composting step implies a loss of 40 % of the potential methane yield, the efficiency of such a procedure is questionable. Moreover, the composting time (artificial aeration) needed for such a degree of VS reduction amounts to 2 weeks, which also is a major drawback of such a pretreatment step. Therefore a shorter precomposting period which results in an elevated temperature of the mixture combined with another start-up procedure presumably is more feasible. Anyhow, the fact that the temperature can be elevated by applying some precomposting might be attractive in practice, despite the fact that the methane yield will become lower.

The start-up of dry anaerobic digestion of OFMSW can not be accelerated by applying partial spatial separation of the inoculum and the substrate nor by applying leachate recycling. However, when 40 % of the initial total solids consist of composted OFMSW solids or in the case of digested OFMSW solids, the start-up proceeds rapidly. When employing partial spatial separation of substrate and inoculum it is necessary to apply leachate recycle in order to prevent substrate limitation, which would result in a prolonged digestion time. A digestion time of 36 days was observed under these conditions, with a methane yield of 65 l (STP) kg^{-1} OFMSW added (200 $l.kg^{-1}$ VS), despite the fact that the methanogenic biomass is overloaded initially due to rapid acid formation from the easy degradable part of the OFMSW. Apart from a population shift in the methanogenic biomass from *Methanothrix sp* to *Methanosarcina sp* the formation and/or existence of zones (micro environments) with more optimal conditions for methane formation probably can explain that the methane formation during the period of overloading still proceeds rather satisfactory. A slight acceleration of the start-up of the dry digestion can be achieved by using the digested OFMSW as inoculum instead of granular UASB sludge and aerobically stabilized OFMSW (compost).

Of all methods investigated in this Chapter application of compost addition together with a seed sludge, or seeding with the digested substrate, give the best results. The digestion time can be reduced to 36 days, while with the other procedures five months or more are needed.

In Chapter 3 of this thesis other limiting factors of the dry digestion process such as the

temperature and the total solids concentration will be studied using the start-up procedure with compost + methanogenic seed sludge.

NOMENCLATURE

CH_4/CH_{4max}	-	relative methane yield after t days
COD	-	Chemical Oxygen Demand
CP	-	compost
DOF	-	digested organic fraction
IN	-	methanogenic inoculum
k_{VS}, k_{AC}	-	first order reaction rate constants (day^{-1})
L	-	leachate recycle
l	-	litre reactor
MSW	-	Municipal Solid Waste
OFMSW	-	organic fraction of Municipal Solid Waste
r_{VS}	-	removal rate of volatile solids (g COD.l^{-1}.day^{-1})
$r_{CH4,VS}$	-	methane formation rate (g COD.l^{-1}.day^{-1})
TS	-	total solids (weight %)
VS	-	Volatile Solids (converted to g COD)
VS_0	-	total initial amount of volatile solids (g COD)
VS_t	-	total amount of volatile solids in reactor after t days (g COD)
[VS]	-	concentration volatile solids (g COD.l^{-1})

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CHAPTER 3

THE INFLUENCE OF TEMPERATURE AND OF THE TOTAL SOLIDS CONCENTRATION ON DRY ANAEROBIC DIGESTION

(Submitted for publication)

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ABSTRACT

The effects of temperature and of the total solids concentration on the rate of the dry anaerobic batch digestion of the organic fraction of Municipal Solid Waste in a BIOCEL-reactor were investigated. The effect of temperature was determined by calculating the first order rate constant k_{CH4} (day-1) for the degradation of the volatile solids to CH4 at a specific temperature and subsequently plotting the values of k_{CH4} against the temperature according the Arrhenius law. The highest value for k_{CH4} was found at 40 °C. At 55 °C a much lower value was found. At 14 ° and 20°C the rate of the digestion was low and not completed, because the initial acid formation rate was higher than the methane formation rate of the inoculum. The initial acid formation rate showed a much smaller response towards an increasing temperature than the methane formation rate. The effect of the total solids concentration on the rate of digestion depended highly on the start-up conditions. Start up at a ratio of compost solids to total initial solids (compost solids plus organic fraction solids) of 0.5 showed decreasing values of k_{CH4} with increasing total solids concentrations. This decreasing rate of the digestion was due to high organic acid concentrations (up to 30 g/l) and low pH values (5.5-6.0) that were abundant in the digesters after 7 days. When a ratio of compost solids to total initial solids of 0.8 was applied any inhibition of the digestion could not be observed up to a total solids concentration of 50 %.

Key words: Dry anaerobic batch digestion; biogas; municipal solid waste; temperature; total solids concentration; reaction rate constants.

1 Introduction

Anaerobic digestion of the Organic Fraction of Municipal Solid Waste (OFMSW) meets increasing interest nowadays (1). Up to now most experience in practice exists with digestion of OFMSW at low solids concentrations (< 15 % TS), but essentially the process can be applied at higher solids concentrations (20 % w/w or higher) without significantly lower decomposition rates as compared to lower total solids concentrations (2,3). In fact even higher loading rates can be applied as a result of the higher substrate concentration in the reactor feed (3). In chapter 2 of this thesis and in an earlier publication (4) we described several methods for start up of batch type dry anaerobic digesters. These methods concern different types and amounts of methanogenic inoculum, buffering and pretreatment of the substrate. Precise data concerning the physical factors which determine the rate of the dry anaerobic digestion of OFMSW in batch reactors are not yet available in the literature. However, from experiments with simulated landfills it can be concluded that the decomposition rate of the organic matter by anaerobic digestion in a landfill is highly affected by the temperature and the total solids concentrations (moisture level) (5,6,7). Similar findings were reported for dry batch digestion of agricultural wastes (2,8).

The purpose of the investigations described here is to assess the influence of temperature and of the total solids concentration on the overall rate of the anaerobic digestion process in a batch reactor. Both factors will be studied under balanced conditions, i.e. at a stabilized solids to substrate solids ratio of 1 or higher. The investigations should lead to certain strategies for the optimization of the reactor start up.

2 Experimental materials and methods

2.1 Organic fraction

The substrate that was utilized consisted of an organic fraction of MSW obtained from the Recycling Zoetermeer separation plant. The chemical composition of the organic fraction is given in chapter 2 of this thesis.

2.2 Apparatus

The dry digestion experiments dealing with the influence of the temperature and the total solids concentration on the rate of the digestion were carried out using the same type of digesters as described in chapter 2 of this thesis. The reactors used in the experiments at temperatures other than 20 and 30 °C were equipped with a water jacket. The temperature in these reactors was controlled by thermostated recirculation water baths which were connected to the water jacket of the reactors.

2.3 Seed sludge

The seed sludge used originated from an Upflow Anaerobic Sludge Blanket reactor treating waste water from a potato processing factory. The total solids concentration of the sludge was 9.6 % TS and its maximum methanogenic activity, determined according to the methods described by De Zeeuw (9), amounted to 0.3 kg CH_4-COD/(kg VSS.day) (= 0.05 m^3 STP CH_4/(kg TS.day)) at 30 °C.

2.4 Procedure

The batch reactors were filled with a mixture of organic fraction, aerobically stabilized organic fraction (compost), methanogenic inoculua and tap water. The mixture was prepared in a dough mixer. In this way differences in homogenity between the experiments could be avoided.

The initial density of the mixture amounted 0.25 kg TS/l achieved by manual compression.

2.5 Analyses

Biogas. Biogas composition (CO_2,CH_4,H_2) was determined with a gas chromatograph (Packard 407), equipped with a TCD detector. CO_2 and CH_4 were determined with two parallel columns: a column of 1.5 m x 1/8", teflon packed chromosorb 108, 60-80 mesh and a 1.2 m x 1/8" mol. sieve 5A, 60-80 mesh. The column split ratio was 1:1. Hydrogen was analysed separately with an other column (mol sieve 5A 1.00m x 1/4"). Samples of 100 μl were taken with a glass gas tight syringe. The measurement of the

biogas volume was carried out by pumping the biogas at intervals out of the gas bags (maximum volume 10 l) through a wet test gas meter. The volume was corrected to the volume at STP (0 °C, 1 bar).

Organic acids and pH. In the determination of acids the contents of the 0.5 l reactors was extracted with 1.5 liters of tap water during 30 minutes. From the extract samples were taken and analysed for organic acids. The overall concentrations were calculated from these data together with the initial moisture amount of the reactor contents.

pH, Volatile Fatty Acids and lactic acid were determined as described in chapter 2 of this thesis.

2.6 Experimental set-up

The experimental set-up is summarized in TABLE 1. In the experiments concerning the temperature variation the total solids concentration was 35 % TS. Anaerobic granalar sludge was applied as seed material at a ratio of 0.08 kg sludge solids to total inital solids (symbol: S), which is sufficient for a more or less stable digestion at a compost solids to total initial solids ratio (symbol: I) of 0.4 or higher. (chapter 2, this thesis).

The experiments concerning the effect of the total solids variation were carried out in two different set ups. The first set up was at I = 0.5. In order to assess the effect of a more balanced digestion, the process was investigated at I = 0.8. As seed material anaerobic granular sludge was applied at S = 0.08.

The anaerobic degradation of the Volatile Solids (VS) of the organic fraction of Municipal Solid Waste can be described with first order kinetics (Chapter 2, this thesis). The influence of total solids concentration and the temperature on the digestion process was determined by evaluating the assessed values of the overall first order rate constants k_{CH4} for degradation of the VS. This was also done for non methanogenic conditions. i.e. with unseeded substrate, to obtain the first order constant k_{AC} under these conditions.

TABLE 1 Experimental set-up in the batch experiments at different levels of temperature (°C) and total solids concentration (w/w %)

type experiment	temperature	compost solids[1] : total solids	Total Solids concentration
temperature variation	14, 20, 30, 35, 40, 55	0.50	35
total solids variation (1st set-up)	30	0.50	12.5, 23, 35, 40, 50
total solids variation (2nd set-up)	30	0.80	12.5, 21, 30 40, 50

[1]: in all experiments: inoculum solids/total initial solids ratio (S) 0.08

3 RESULTS AND DISCUSSION

3.1 Effect of temperature

The observed cumulative methane productions during the experiments conducted at different temperatures are presented in Fig. 1. Considering the results obtained at 14 °C and 20 °C, the methane production showes a longer lag phase and proceeds at a much lower rate as compared to the higher temperatures (Fig. 1). The biogas production at 14 °C stopped 30 days after the start of the experiment, although only 20 % of the potential biogas yield (220 l STP) had been produced. The organic acids concentration determined at this point was 50 VFA-COD/l, the concentrations of lactate and ethanol were lower than 0.01 g COD/l, and the pH was 5.8. The pH and the VFA concentrations remain constant upon continuation of the experiment. The potential CH_4 yield at 20 °C is twice as high compared to 14 °C and was 40 % of the potential methane yield (Fig. 1).

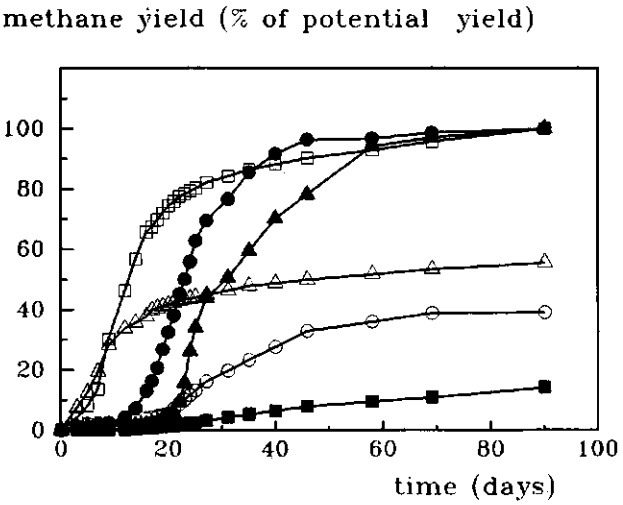

Fig. 1 Methane yield (% of potential yield) in dry anaerobic digestion (35 % TS) of the organic fraction of MSW at different temperatures; (■) 14 °C; (○) 20 °C; (▲) 30 °C;(●) 35 °C; (□) 40 °C; (△) 55 °C.

The pH and organic acids concentrations were very similar as those obtained at 14 °C. A more detailed course of biogas production and biogas composition during the experiment at 20 °C, is given in Fig. 2. As was reported in Chapter 2, unbalanced digestion becomes manifest from the high content of hydrogen in the biogas. Apparently this is merely the case during the first period of the digestion at 20 °C. In the experiment at 40 °C little if any hydrogen could be detected in the biogas. As also the organic acid content was low (< 1g COD.l^{-1}), it can be concluded that we are dealing with a balanced digestion at this temperature.

For all temperatures investigated, the highest value of k_{CH4} is found at 40 °C (TABLE 2). In the experiment at 40 °C any organic acids build up was not observed during any phase of in the process, and the pH was 7.0-8.0. Surprisingly, digestion at 55 °C did not proceed at the highest rate. Fig. 3 shows the course of the pH and the VFA concentrations of this experiment. From this figure it can be concluded that the digestion process could have been detiorated neither by a high VFA concentration nor a low pH. A low hydrolysis rate of the volatile solids seems a more likely reason for the lower digestion rate at 55 °C compared to the digestion rates observed at 35 °C and 40 °C.

A similar temperature optimum at 40 °C is found by other authors (6,16). It can be

around 40 °C.

However, our results and the results from the literature as well conflict with those found by De Baere et al. (3), reported 2-3 times higher decomposition rates in the anaerobic fermentation at high total solids concentrations at 55 °C as compared to mesophilic conditions. This is in contrast with the results of our experiments and those of many other researchers, which show a faster and more complete digestion at mesophilic temperatures (5,6). Latter experiments were carried out with solid waste samples from a methanogenic landfill with mixed MSW, while the experiments described by De Baere concerned the dry anaerobic digestion of the organic fraction of MSW. In the experiments of De Baere et al. the methanogenic biomass was already adapted to thermophilic conditions. The methanogenic biomass grown in their system contains sufficient thermophilic methanogens for a rapid start-up of the digestion. It can be concluded from these findings, that the digestion process can be accelerated, when an appropriate thermophilic methanogenic inoculum is employed. This certainly is not the case for the granular sludge used in our experiments because this sludge was cultivated under mesophilic conditions. As was shown recently (17), mesophilic sludges greatly loose their methanogenic activity when exposed to temperatures exceeding 42 °C for periods exceeding approximately 30-60 minutes.

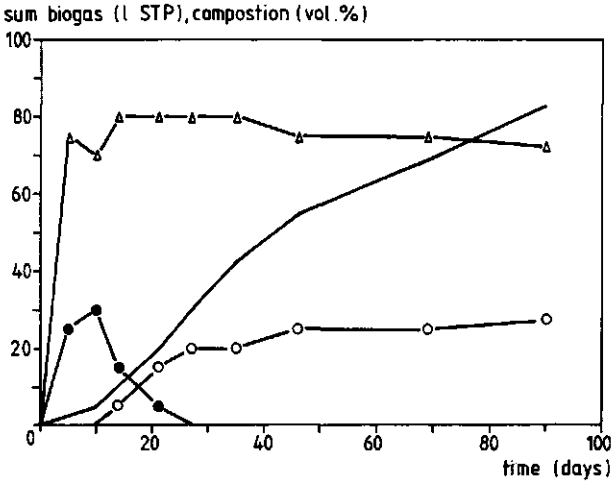

Fig. 2 Biogas production and biogas composition in dry anaerobic digestion (35 %TS) of the organic fraction of MSW at 20 °C; (————) cumulative biogas production; (○) vol.% CH_4; (●) vol.% CO_2; (△) vol. % H_2.

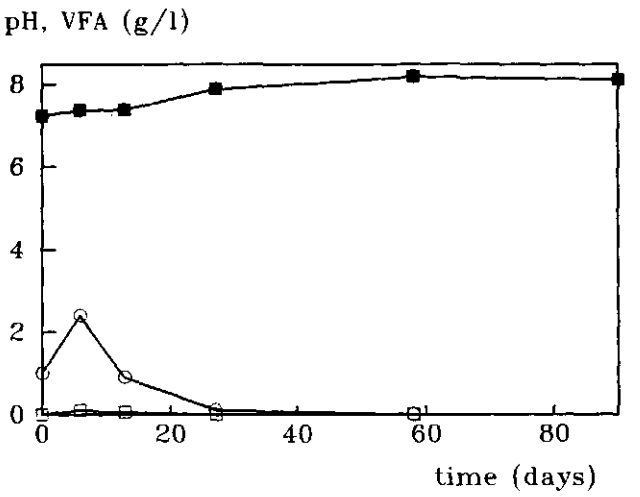

Fig. 3 Course of volatile fatty acids concentration and the pH in dry anaerobic digestion (35 % TS) of the organic fraction of MSW at 55 °C; (■) pH; (○) acetic acid; (□) propionic acid.

The effect of the temperature on the methanogenic activity of the biomass was further evaluated by application of Arrhenius relation in the integrated form (14,15):

$$LNk = LN(A) - E/RT \qquad (5)$$

were A is the 'collision factor', (to be considered as a constant), T is the absolute temperature, R is the universal gas constant and E is the activation energy. The Arrhenius equation also describes satisfactorily the influence of the temperature on the rate of methane production in samples from landfills (5,14,15).

According to equation (5) a plot of the natural logarithm of the k versus 1/T should give a linear relationship. A plot of the calculated experimental values of $LN(k_{CH4})$ and $LN(k_{ac})$ versus 1/T values is shown in Fig. 4. Apparently a linear relationship for k_{CH4} versus 1/T is only exists for mesophilic temperature range. Moreover, a clear effect of the temperature on k_{ac} apparently does not exist. Fig. 4 shows that the values of k_{ac} exceeded the values of k_{CH4} below a temperature of 30 °C. From these results it therefore can be concluded that the during the initial phases of start up temperatures lower than 30 °C the acids formation rate plus hydrogen formation rate exceeded the methane production rate

at a temperature below 30 °C for speeding up the start-up. In this way a balanced digestion can be obtained under these lower temperature conditions. The amount of seed sludge which shoud be added to achieve a well balanced digestion process depends on the methanogenic activity of the seed and the initial acid plus hydrogen formation rate from the substrate. Since the values of these parameters show a great variation, this should be calculated for each specific case.

From our results it can be concluded that the methane formation is definitely more affected by the temperature than the acid plus hydrogen formation rate. This implies that the start up temperature should be around the optimum value and remain rather constant, since a suboptimal temperature will greatly affect the balance of the digestion process. As the acid formation is less influenced by the temperature, a suboptimal temperature can lead to a build up of acids and hydrogen, which in in turn will cause a pH drop. Similar observations on the effect of temperature between the acid formation and the methane formation were reported by Speece and Kem in experiments concerning sludge digestion (19). They investigated the effect of temperature on sludge digestion using sludge from a 'sour' digester operated at 35 °C. The digesters were operated at 35 °C and 45 °C respectively. The digester operated at 35 °C showed a lower methane production rate than the acid formation rate in comparison to the digester operated 45 °C. The acid formation rate and methane production rate are balanced at 45 °C as a result of a lower response of the acid forming bacteria to the temperature increase.

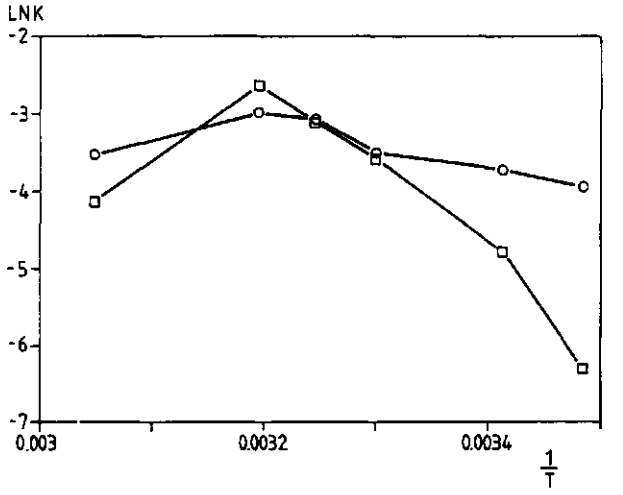

Fig. 4 Arrhenius plots of first order reaction rate constants for dry anaerobic digestion of the organic fraction of MSW at several temperatures; (□) k_{CH4};(○) k_{AC}.

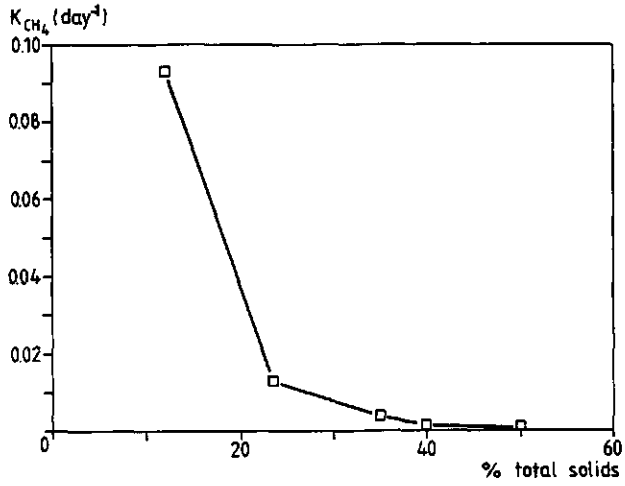

Fig. 5 First order reaction rate constants for dry anaerobic digestion of the organic fraction of MSW at different total solids concentrations and I = 0.5 and S = 0.08; (□) k_{CH4}.

TABLE 2 First order reaction rate constants (day^{-1}) for dry anaerobic digestion of the organic fraction of MSW at different temperature levels

Temperature (°C)	k_{CH4} (day^{-1})	k_{AC} (day^{-1})
14	-0.002	-0.016
20	-0.008	-0.024
30	-0.028	-0.030
35	-0.045	-0.047
40	-0.072	-0.050
55	-0.016	-0.029

3.2 The effect of the Total Solids concentration

The effect of the TS concentration in the dry anaerobic digestion of OFMSW was investigated at 30 °C merely for practical reasons. The first series of experiments was carried out at I = 0.5 and S = 0.08 (see TABLE 1).

Fig. 6 shows the course of the total the organic acids concentrations and Fig. 7 shows the the VFA concentreations, ethanol concentrations and the pH.

A plot of the calculated first order rate constant k_{CH4} and the TS concentration is presented in Fig. 8. Compared to the methane production rate found at the experiment at 12.5 % TS, methanogenesis is highly inhibited at (semi) solid conditions, viz. TS concentrations exceeding 23 %. The initial acid formation rate plus hydrogen formation rate (as calculated from the organic acids concentration) is signifiantly less effected by the TS concentration. High concentrations of organic acids were found at TS values exceeding 23 % (Fig. 6).

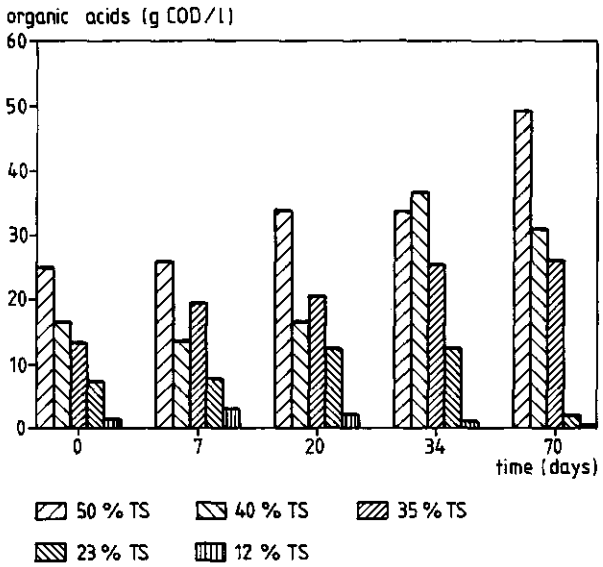

Fig. 6 Total organic acids concentrations during the anaerobic digestion of the organic fraction of MSW at different total solids concentrations and at I = 0.5, S = 0.08.

Total VFA-COD concentrations were in the range of 32-62 g COD/l, the pH values under these conditions varied between 5.5 and 6.0. Fig. 7 shows the course of the VFA cocentrations and ethanol concentrations at several TS concentrations. The main products built up at all TS concentrations were acetic acid and butyric acid.

Lactic acid was detected up to concentrations of 20 g COD/l at 35 % TS and 50 % TS, but after 10-15 days it was converted to butyric acid. Ethanol concentrations, analysed only at 35 % and 50 % TS, were always lower than 0.1 g COD/l.

The negative effect of high total solids concentrations on the overall decomposition rate (≡ methane formation rate) in dry anaerobic digestion can attributed to factors such as a lower water availability for the micro-organisms involved, a higher concentration of inhibiting compounds at higher total solids concentrations or by substrate limitation due to insufficient mixing of substrate and bacteria at higher total solids concentrations. The availability of free water for microorganisms is determined by the total amount of dissolved substances (20). In the experiments concerning the effect of the TS concentration on the rate of the digestion process discussed earlier in this chapter, the water availability very likely was not the only important rate limiting factor.

Although a detrimental effect of a suboptimal water avalilability can not be excluded, also the high acids concentration affects the osmotic pressure of the liquid phase, and consequently, the assessment of any possible effect of the low water availability on the dry digestion process has to be studied under more balanced conditions. The high concentration of organic acids in combination with the low pH values must have been detrimental to a rapid start-up of the methane formation. This was already shown in chapter 1 and 2 of this thesis. We investigated the effect of the level of total solids at I = 0.8 (instead of 0.5), S = 0.08 and TS concentrations ranging from 12.5 to 50 % TS (see TABLE 1 for experimental set up). Fig. 8 presents the characteristic pattern of the biogas production and biogas composition of experiments at a compost solids/initial organic fraction solids plus compost solids ratio of 0.8. Any hydrogen could not be detected throughout the experiments at I = 0.8. The methane yield was 100 % of the potential yield (80 l/kg OFMSW) for all total solids concentrations. Fig. 9 shows a plot of the calculated first order reaction rate constants k_{CH4} as a function of the total solids concentration. Although after 14 days still high concentrations of organic acids could be detected (up to 20 g COD/l, Fig. 10, Fig. 11), the pH values always exceeded values of 7.0. The main products were acetic acid and butyric acid, which are similar to the products formed at I=0.5. In fact inhibition of the methanogenesis by organic acids plays a less important role because after 24 days the organic acids were very similar for all TS levels investigated and was approximately 0.5 g COD/l. The first order rate constant k_{CH4} shows a slightly positive correlation with the total solids concentration (Fig. 9) up to 30 % TS and it declines slightly beyond TS values of 40 %.

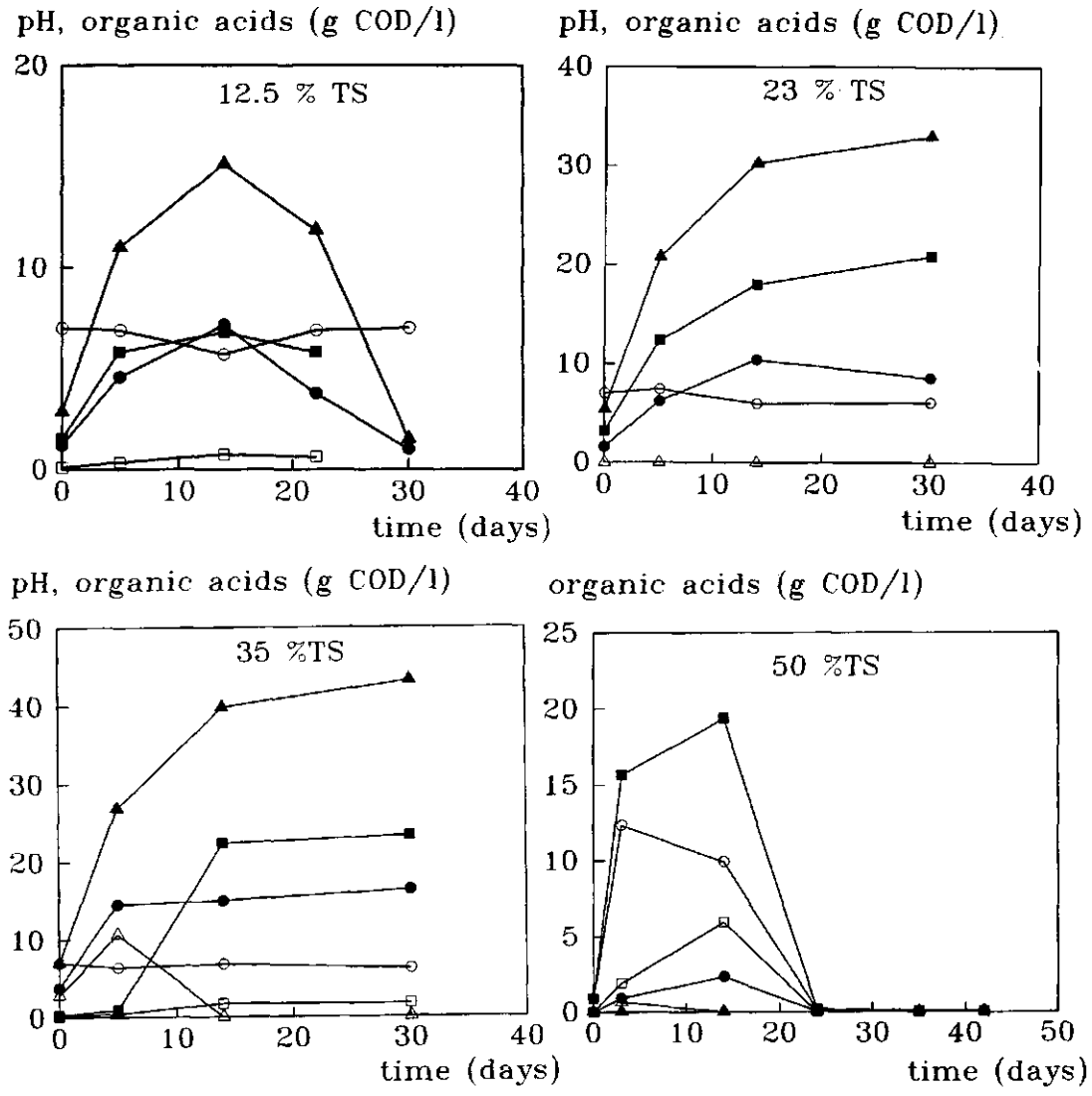

Fig. 7 Course of the organic acids concentration in dry anaerobic d gestion at I = 0.5 and S = 0.08 at different TS concentration levels; (○) pH; (●) acetic acid; (□) propionic acid; (■) butyric acid; (△) lactic acid; (▲) total acids; ethanol < 0.1 g/l.

At 50 % TS about the same value for k_{CH4} is found as at 12.5 % TS. For values found for k_{ac} were very similar to those for k_{CH4}. These findings indicate, that the digestion process is balanced for the experiments carried out with I = 0.8. Since at TS concentrations exceeding 30 % TS the biodegradable VS concentration (kg VS per liter reactor) is 2.0 times higher than at 12.5 % TS, the TS content is 250 g/l instead of 125 g/l. The higher TS concentration means, that the mean VS removal rate (in kg VS per reactor volume per day) is a factor 2.0 lower in the 12.5 % TS experiment compared to the 50 % TS experiment. Hence, a reactor run at TS concentrations exceeding 25 % is in favour compared to a reactor operated at lower TS concentrations, because of its higher VS degrading capacity.

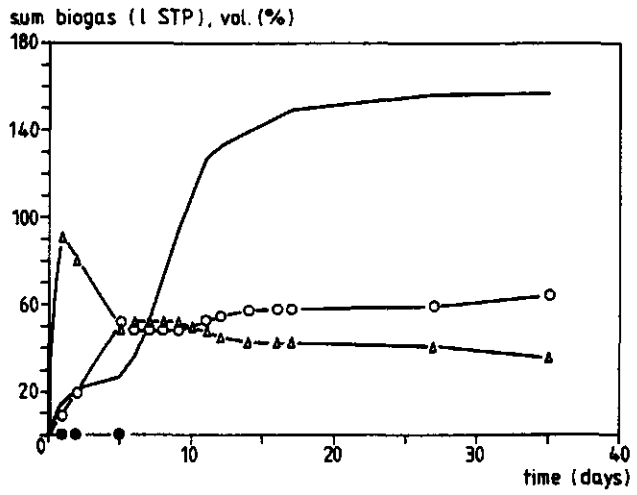

Fig. 8 Characteristic pattern of the biogas production and biogas composition in dry anaerobic digestion (40 %TS) of the organic fraction of MSW in the experiments at I = 0.8 and S = 0.08; (—) cumulative biogas production; (○) vol.% CH_4; (△) vol. % CO_2;(●) vol. % H_2.

In the literature dealing with landfilling experiments more pronounced negative correlations are reported between the total solids concentration and the methane production rate. In landfills where the methane production proceeds at very high solids concentrations (21,22,23), the poor contact between bacteria and substrate is the rate limiting factor with respect to the methanogenesis.

In landfill simulation experiments it was observed that at moisture contents below 20 %, the methane production improves, presumably because of a dilution of toxic compounds, although the authors attribute it to the type of waste (6,22).

Several researchers found a negative correlation between the total solids concentration and the methane production rate in their studies concerning the dry anaerobic digestion of agricultural wastes (10,26). Wujcik and Jewell (2) reported a drop in the methane production rate at total solids concentrations exceeding 30 % TS, while they found that the VS degradation did not reach its maximum value within a period of 120 days at TS concentrations exceeding 40 %. At a certain total solids concentration in the range of 20-40 % TS they found a higher overall VS degradation rate at higher inoculum/substrate solids ratios.

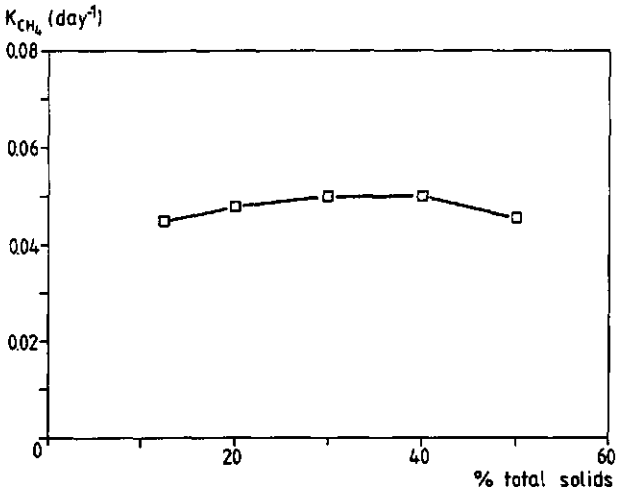

Fig. 9 First order reaction rate constants for dry anaerobic digestion of the organic fraction of MSW at I = 0.8 and S = 0.08 ; (□) k_{CH4}.

Moreover, they also observed that the VFA concentrations increases at increasing total solids concentrations increasing VFA concentrations. The acid formation rate became inhibited at a total solids concentration exceeding 56 %. These results suggest that the methane formation may become retarded at total solids concentrations exceeding approximately 30 % TS due to a reduced contact of substrate and the methanogenic inoculum and due to high fatty acids concentrations as well. Unfortunately, any information about the pH values in these specific experiments were not provided.

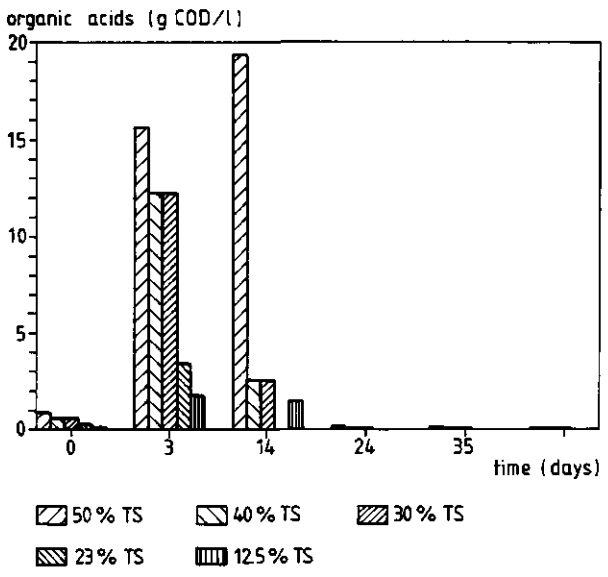

Fig. 10 Total organic acids concentrations during anaerobic digestion of the organic fraction of MSW at different total solids concentrations and at I = 0.8 and S = 0.08.

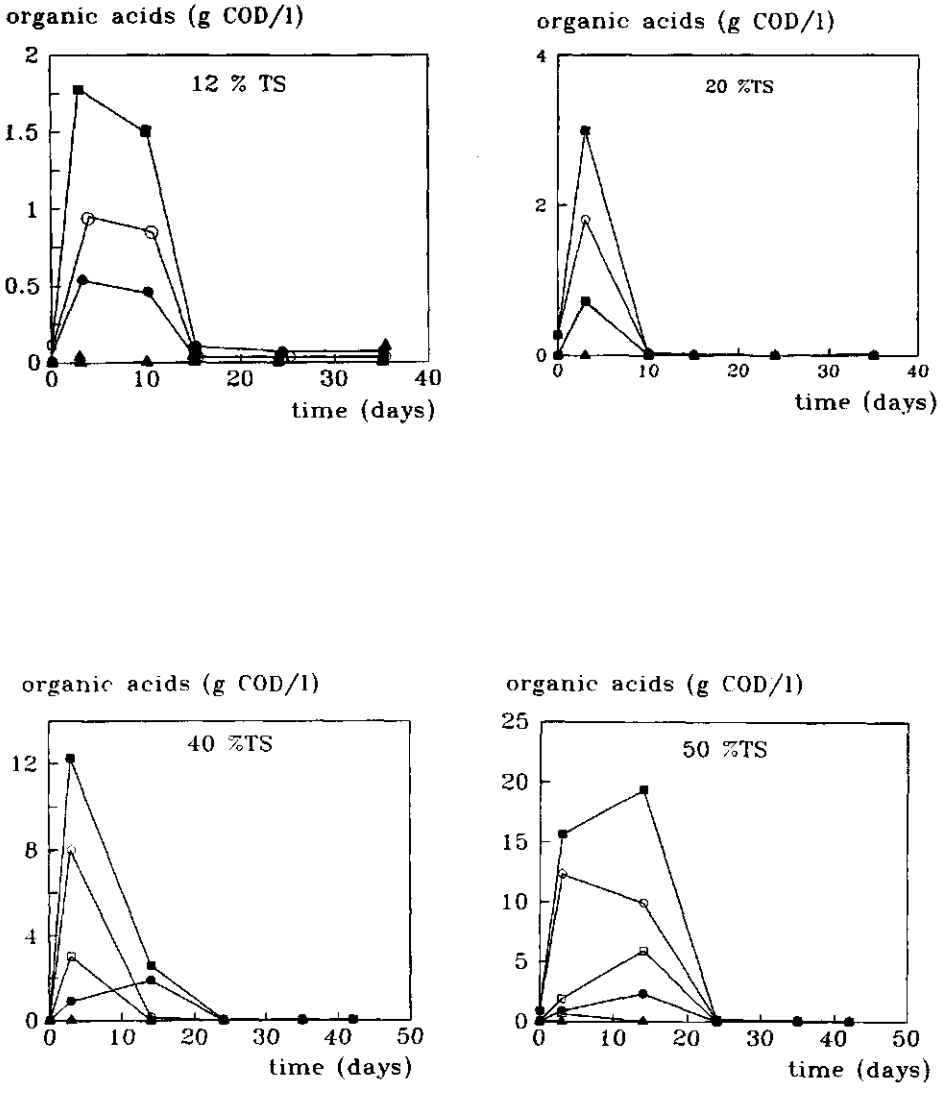

Fig. 11 Course of the organic acids concentrations in anaerobic digestion of the organic fraction of MSW at different total solids concentrations and at I = 0.8 and S = 0.08; (○) acetic acid; (●) propionic acid; (□) butyric acid; (▲) lactic acid; (■) total acids.

In the practice of dry anaerobic batch digestion of organic solid wastes generally the concentration of methanogenic organisms is elevated by adding a proper inoculum; the acid forming bacteria already are present in sufficient amounts in the raw substrate, while these organisms also grow rapidly (Chapter 1).

At high total solids concentrations, the initial amount of mixing of the substrate and inoculum will determine the extent in which substrate and methanogenic seed material are spatial separated because under these conditions there is little if any free water to improve the required contact in the system. In slurry digestion systems , substrate and bacteria can be brought in intensive contact very easily. It can not be excluded that at higher total solids concentrations mixing is less intensive than at low TS concentration. Presumably a paste with a high viscosity needs a longer period of mixing for proper mixing of the substrate and inoculum.

From our experiments it can be concluded that dry anaerobic digestion of the organic fraction of MSW is feasible up to a total solids concentration of 50 % TS in a batch reactor and under mesophilic conditions. According to Baere et al. (3) the maximum feasible TS concentration in continuous dry anaerobic digestion of the organic fraction of MSW is 40 %. However, they did not prove this with experimental data, while they also did not provide any information about the concentrations of organic acids occurring in their system, nor about the pH. Therefore it is not possible to draw conclusion about the occurrence of inhibition due to a reduced contact of substrate and inoculum or to high concentrations of of organic acids resulting from an imbalance of the digestion in their system in particular.

4. Conclusions

Dry anaerobic digestion of the organic fraction of MSW at 35 % TS when seeded with mesophilic methanogenic sludge (I= 0.5, S=0.08) proceeds at the highest rate at 35-40 °C. Reactor start-up at temperature lower than 30 °C and 35 % TS is impossible because the acid formation proceeds too rapid in that case relative to the methane formation rate. When start-up is carried out at 55 °C methane production rate is lower and the methane yield as well, compared to start up at 35-40 °C. This is due to the small amount of thermophilic methanogens in present in the seed sludge applied.

At I=0.5 and S=0.08 total solids concentrations exceeding 23 % result in a distinct inhibition due to organic acids and to suboptimal pH values. At I=0.8, dry anaerobic digestion still proceeds well at TS concentrations up to 50 % TS, i.e. almost similar degradation rates (in kg VS per kg reactor volume per day) occur in the TS-range of 30-50 %. The water availability and the amount of contact of substrate and (methanogenic) bacteria is sufficient up to a total solids concentration of 50 % TS.

5 References

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CHAPTER 4

THE ROLE OF METHANOGENIC ZONES DURING DRY ANAEROBIC BATCH DIGESTION OF THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

(submitted for publication)

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ABSTRACT

Dry anaerobic batch digestion of solid organic wastes can proceed at total solids concentrations up to 50 % and pH values as low as 5.2 and organic acid concentrations of 40-50 g COD/l in the reactor environment. Anaerobic digestion at low total solids concentrations (< 5 %) under similar conditions is not possible. The existence of methanogenic zones where optimal conditions (higher pH, lower concentrations of organic acids) prevail during dry anaerobic batch digestion might explain this discrepancy. It was tried to detect methanogenic zones in dry digestion experiments by determining pH profiles over the height of a reactor at different stages of the digestion. During the initial stage of the digestion process gradients could be observed, but methanogenic zones, if present were too small to be detected with our equipment. After 90 days the methanogenic zones could be visualized by the pH profiles. The pH which was determined with the normal sampling procedure amounted to 5.7, while the pH in the reactor enviroment varied between 5.38 and 6.8. The organic acids concentration was 60 g COD/l. After the start of leachate recycle the methane production rate increased immediately, which formed an indirect proof for the existence of methanogenic zones. The formation of methanogenic zones during an imbalance of the dry digestion was due to heterogenous mixing characteristics of the reactor contents.

INTRODUCTION

The organic fraction of Municipal Solid Waste (MSW) can be converted into methane-rich biogas and a compost-like end product with a dry digestion process, in this case teh so-calle BIOCEL-process (Chapter 2). The BIOCEL-process is characterized by a batch-wise operated digester, maintained under mesophilic conditions. The reactor is started-up with a mixture of 'fresh' waste and digested residue. The digesting mass remains static, viz. any mechanical mixing is not applied. Recirculation of leachate is optional for the process.

Stable anaerobic digestion processes are characterized by the absence of high concentrations of intermediary products such as hydrogen and acids in the digester environment. However, during the initial stage of a dry anaerobic batch digestion process of solid wastes typical characteristics of imbalance between acid formation/hydrogen formation and methane formation generally prevail. The imbalance can lead to high organic acid concentrations and concomitant low pH values. Nevertheless, in preliminary experiments we found that the digestion process could proceed at organic acids concentrations as high as 40 g COD/l and at a pH as low as 5 (Chapter 2).

Fig. 1 shows a typical example of the relative biogas composition as observed during dry anaerobic digestion of the organic fraction of MSW with digested sewage sludge as seed, and diluted with compost (ratio compost solids/substrate solids: 0.67).

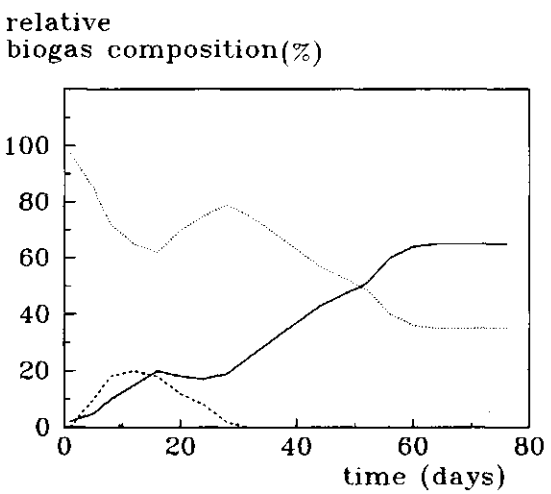

Fig. 1 Relative biogas composition during dry anaerobi mesophilic batch digestion of the organic fraction of Municipal Solid Waste. (---) vol. % CH4; (....) vol.% CO2; (- - -) vol.% H_2

The hydrogen peak suggests that the hydrogen consumption by methanogens is lower than the hydrogen formation rate, which is in fact a symptom of overloading.
Wujcik and Jewell (1980) reported maximum VFA concentrations of 20 g under conditons of concomittant methane production in dry anaerobic digestion experiments of organic agricultural waste. pH values during their experiments were not reported. Stegmann (1982) reported maximum total organic acid concentrations of 25-30 g COD/l and pH values around 6, in controlled digestion experiments with MSW. The digestion proceeded under these extreme conditions. These findings conflict with results of anaerobic digestion experiments at low solid concentrations (< 5 % TS). Hoeks and Borst (1982) reported that anaerobic digestion of leachate from a landfill with a volatile acid concentration of 29 g COD/l and a pH of 5.7 was not possible. For anaerobic reactors treating waste waters the maximum organic acids concentration level which can be tolerated for a satisfactory treatment process obviously should be much lower than found in dry anaerobic digestion (Duarte and Anderson, al., 1982; Attal et al., 1988). Generally the pH in anaerobic waste water treatment should be kept above 6 in order to avoid conditions leading to a "sour" digester (viz. a digester in which methanogenesis is completely absent, and only hydrolysis and acidogenesis remains). Some authors report a higher tolerance for low pH values of methanogenic biomass which is growing in agglomerates of macroscopic size (Attal et al., 1986; Ten Brummeler et al., 1985). The relatively high methanogenic activity in these systems at low pH (5.0 - 6.0) values could be explained by the existence of a pH gradient in the agglomerates of biomass, although no experimental proof was given. Similarly the occurence of methanogenesis in a solid waste batch digester could be attributed to the existence of environments (zones), in which conditions prevail that allow methane formation, even during the period of a low pH and extreme high organic acids concentrations. The existence, i.e. the formation of these zones can be the result of the non-mixing conditions in a BIOCEL reactor or other dry digestion systems where stirring is not applied (or impossible).

The investigations described in this chapter intend to determine to what extent the methane formation during dry anaerobic digestion of solid organic waste at low pH values and high organic acid concentrations can be due to the existence of methanogenic zones.

MATERIALS AND METHODS

Substrate and methanogenic inoculum

The substrate for the experiments described in this paper was an organic fraction obtained from the Recycling Zoetermeer shredding/separation plant for MSW. The chemical composition of the organic fraction (OF) and digested OF as used in the present study are described elsewhere (chapter 2, this thesis). The methanogenic inoculum was obtained from a 78 liter batch digester. The Total Solids (TS) concentration of the inoculum amounted to 27.4 % (w/w). The maximum methanogenic activity of the inoculum which was determined according to De Zeeuw (1984) amounted to 0.014 STP m^3 STP CH_4/(kg TS.day) (= 0.011 kg CH_4-COD/(kg TS.day)) at 35 °C. The determination of methanogenic activity of the inoculum at different pH values at a low TS-concentrion (1.38 % TS) were carried out according to the same method. HCl was used for correcting to the initial pH values: 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0.

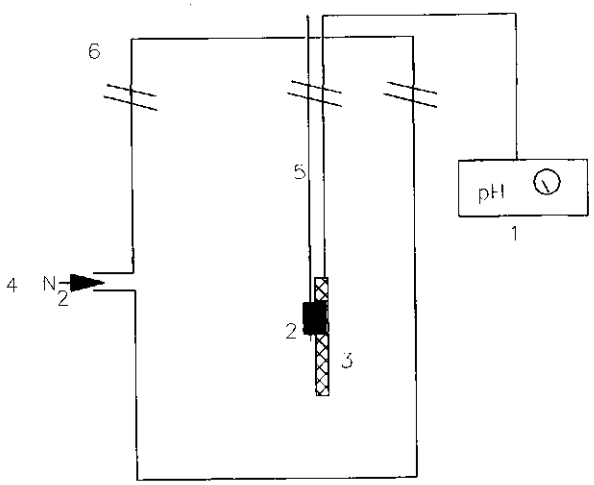

Fig. 2 Schematic diagram of the apparatus applied during the pH profile determinations in the dry digestion experiments. (1) pH/mV meter; (2),(3) pH electrode + attaching device;(4) nitrogen flow;(5) extendable iron rod with indication scale;(6) reactor

Apparatus

The experiments were carried out in batch reactors made of PVC with an internal diameter of 0.19 m and a total height of 3.00 m. The reactors are described in detail elsewhere (Chapter 2). Between the reactor and the water lock a biogas sampling device with a septum was placed. Where noted, leachate recycle was applied by collecting the leachate under a sieve plate at the bottom part of the reactor and pumping it with a peristaltic pump at a continuous flow (0.1 l/h) to the top of a reactor. The reactors were maintained at a temperature of 35 °C (± 1 °C).

pH profiles over the height of the reactor were determined with a pH electrode (Broadly James, gel electrode, epoxy jacket) which was 4 mm in diameter. The pH-electrode was attached to an iron bar (Fig. 2) which was 50 cm in length and was connected with a mV-meter. The total length of the bar could be extended to 3.00 m with extension pieces of 50 cm. The pH-electrode was moved downwards from the top of the reactor at intervals of 5 cm. After every step of 5 cm the pH-meter was read after one minute, in order to allow the establishment of a constant signal. During a pH profile measurement the reactors were kept under pressure with nitrogen gas to prevent diffusion of air into the reactors.

Start-up of the batch reactors

The reactors were filled manually with mixed digested OFMSW and fresh OFMSW using different ratio's of inoculum solids and total solids (inoculum solids plus OFMSW solids). The ratio inoculum solids/substrate solids had to be low enough in order to obtain a significant build-up of organic acids so that the effect of the non-mixed conditions in a BIOCEL reactor can be demonstrated and high enough to have a distinct (well-measurable) methane production. Calculations based on previous results (chapter 2, this thesis) showed that the initial rate of acid plus hydrogen formation would be in balance with the methane formation at an "inoculum factor" (= ratio of inoclum solids/fresh waste solids plus inoculum solids) of 0.67. It was expected that at a relatively low inoculum factor of 0.30 a significant organic acids build up and concomitant pH drop would occur. At the start the Total Solids concentration of the inoculum plus substrate mixture was 36 % (w/w).

Analyses

Biogas. The biogas composition (CH_4, CO_2 en H_2) was determined as described in Chapter 2.

Organic acids and pH. At regular intervals two samples of the digesting mass were taken from each reactor for determination of the organic acids (lactic acid, acetic acid, propionic acid, butyric acid, capric acid, valeric acid). The pH of the samples was determined with a mV-meter and a combined glass electrode directly after sampling.

Samples were extracted with tap water on a shaking table during 30 minutes before analysis of the organic acids was carried out. Volatile Fatty Acids (VFA) and lactice acid were determined as described earlier (Chapter 2, this thesis).

RESULTS AND DISCUSSION

The results in Fig. 3 and Fig. 4 reflect the reactor performance of a start-up experiment at 36 % TS and an inoculum factor of 0.3. The biogas composition showed a pattern which is more or less identical to the pattern which was discussed earlier in this Chapter (see Fig. 1). An initial increase of the methane content in the biogas was followed by a slight decrease. During the next phase of the process a steady increase of the methane content to a value of 55 vol. % was found. The measured total organic acid concentrations and pH values in this experiment (Fig. 4) are characteristic for an overloaded dry digestion system. Within 10 days the reactor pH decreased to a value of 5.6 while the total organic acids increased to a value of 60 g COD/l, which corresponds to a concentration of undissociated organic acids of 4 g/l at pH 5.6. The toxicity level of the undissociated organic acids for the methanogens reported in the literature is far lower (Duarte and Anderson, 1982, Kroeker et al., 1979). At this very high VFA concentrations (acetic acid: 14 g COD/l, propionic acid: 1.5 g/l, butyric acid: 22 g COD/l, capric acid: 5 g COD/l) even the formation rate of acids slows down to a very value (Fig. 4). However, methane production was still found under these conditions (Fig. 3). So far never before methane production under such extreme conditions has been reported. Comparing our resultes with data from the literature it can be concluded that we found methane formation at lower pH values and higher acid concentrations than generally is found in anaerobic digestion systems at low total solids concentrations.

The tolerance for low pH values/high acid concentrations very likely has to be attributed to the presence or the development of an adapted microbial population. In order to get more relevant information about this matter the inoculum used in these experiments was tested for its pH tolerance. The relative maximum specific methanogenic activity at different pH values is shown in Fig. 5. It appeared that even after an adaptation period of 30 days the activity at low pH values (4.5-5.5) remained almost zero. The pH tests were carried out at a concentration of 50 mg undissociated organic acids. From Fig. 5 it may be concluded that the methane formation during the dry digestion experiment which is discussed above could not be explained by an adapted methanogenic population in the seed sludge.

From the results in Fig. 5 the methane production rate of the inoculum at pH = 5.6 could be calculated. The actual methane production rate in the reactor exceeds the maximum potential methane production rate of the inoculum at pH 5.6 four times. Considering this discrepancy, it was tried to locate methanogenic zones by measuring pH profiles at different stages of the dry digestion process.In such locations very likely higher pH values and lower organic acid concentrations will prevail than can be detected with a regular sampling procedure. In the regular sampling procedure the pH is detected in one sample from the sampling port of reactor. In order to obtain non-disturbed profile samples for the determination of organic acids concentrations were taken. The determined pH profiles are shown in Fig. 6. From these profiles it follows that the pH varies significantly in a dry digestion system over the height of the reactor, particularly when the methanogenic biomass is severly overloaded as is the case during the first phase.

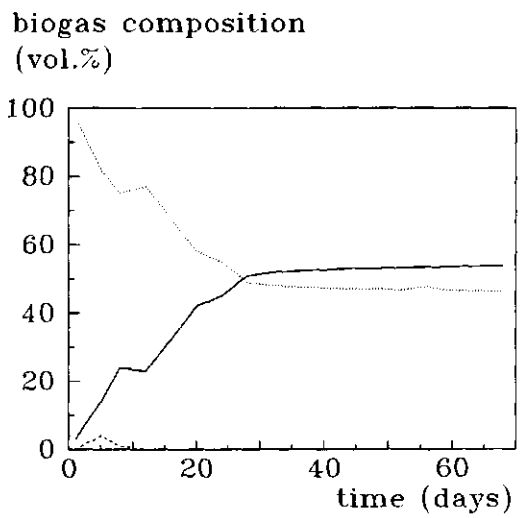

Fig. 3 Biogas composition during dry anaerobic mesophilic batch digestion at 36 % total solids with an inoculum factor of 0.3.(—) vol. % CH_4; (....) vol. % CO_2;(- - -) vol. % H_2 vol.%.

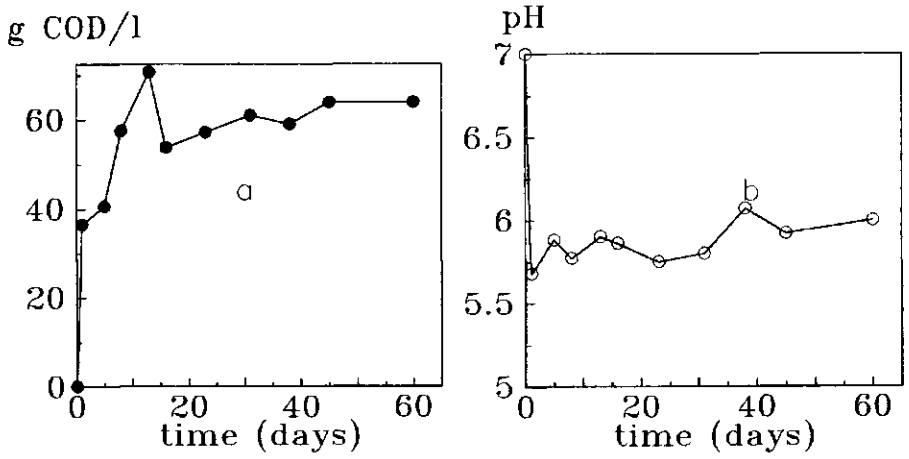

Fig. 4 Total organic acids concentration and pH during dry anaerobic batch digestion at 36 % total solids with an inoculum factor of 0.3.(a) total organic acids; (b) pH.

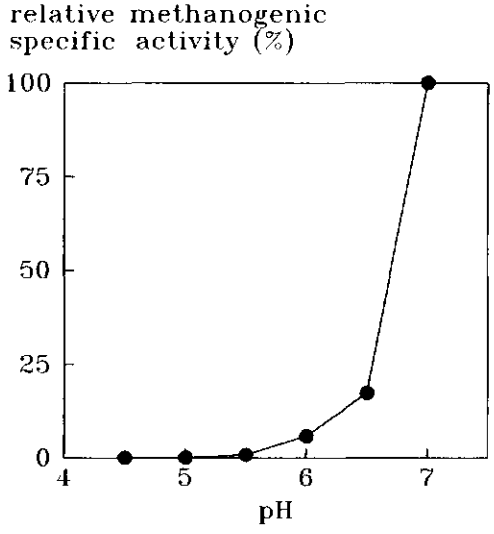

Fig. 5 Relative maximum specific methanogenic acivity of the inoculum as used in the dry digestion experiments.

From the pH profile determined after 2 days (Fig. 6a) it follows that any extended methanogenic (macro) zones with pH values exceeding 6 could hardly be detected. Nevertheless such zones very likely were present, but presumably they were smaller than the size of the pH electrode, so that they could not be located. In the pH profile determined after 60 days of operation (Fig. 6c) the presence of methanogenic zones was more pronounced. From the profile found after 90 days of operation (Fig. 6d) it appears that then already the major part of the reactor was methanogenic, because throughout the reactor zones with pH values around 7 are present.

TABLE 1 pH-values during dry anaerobic batch digestion as calculated from pH profiles or obtained by sampling

days	pH-profile	σ[1]	pH min.[2]	pH max.[3]	pH-sample
2	5.46	0.21	5.05	5.93	5.68
30	5.56	0.08	5.37	5.79	5.80
60	5.65	0.28	5.38	6.55	6.07
90	6.75	0.49	5.8	7.30	7.30

[1]:standard deviation, number of samples: 22
[2]:minimum pH value in the pH profile
[3]:maximum pH value in the pH profile

In TABLE 1 the mean pH values of pH profile measurements and the pH values of the regular sampling procedure are given. The formation, or perhaps better, further development of the methanogenic zones is clearly demonstrated by the increase of the pH and by the value found for minimum and maximum pH in a profile.

Very likely the development of methanogenic zones is stimulated by the fact that mixing is not applied in dry digestion batch reactors as used in the present study. A completely mixed batch reactor at a total solids concentration of 1.4 % at pH 5.6 and an initial carboxyl acid concentration of 60 COD/l (15 g acetic acid, 5 g propionic acid, 25 g/l butyric acid, 15 g n-caproic acid) showed a methane production rate of zero. The course of the concentration of the VFA is shown in Fig. 7.

Indirect proof for the existence of the methanogenic zones was obtained by recirculating leachate form the bottom of the reactor to the top.

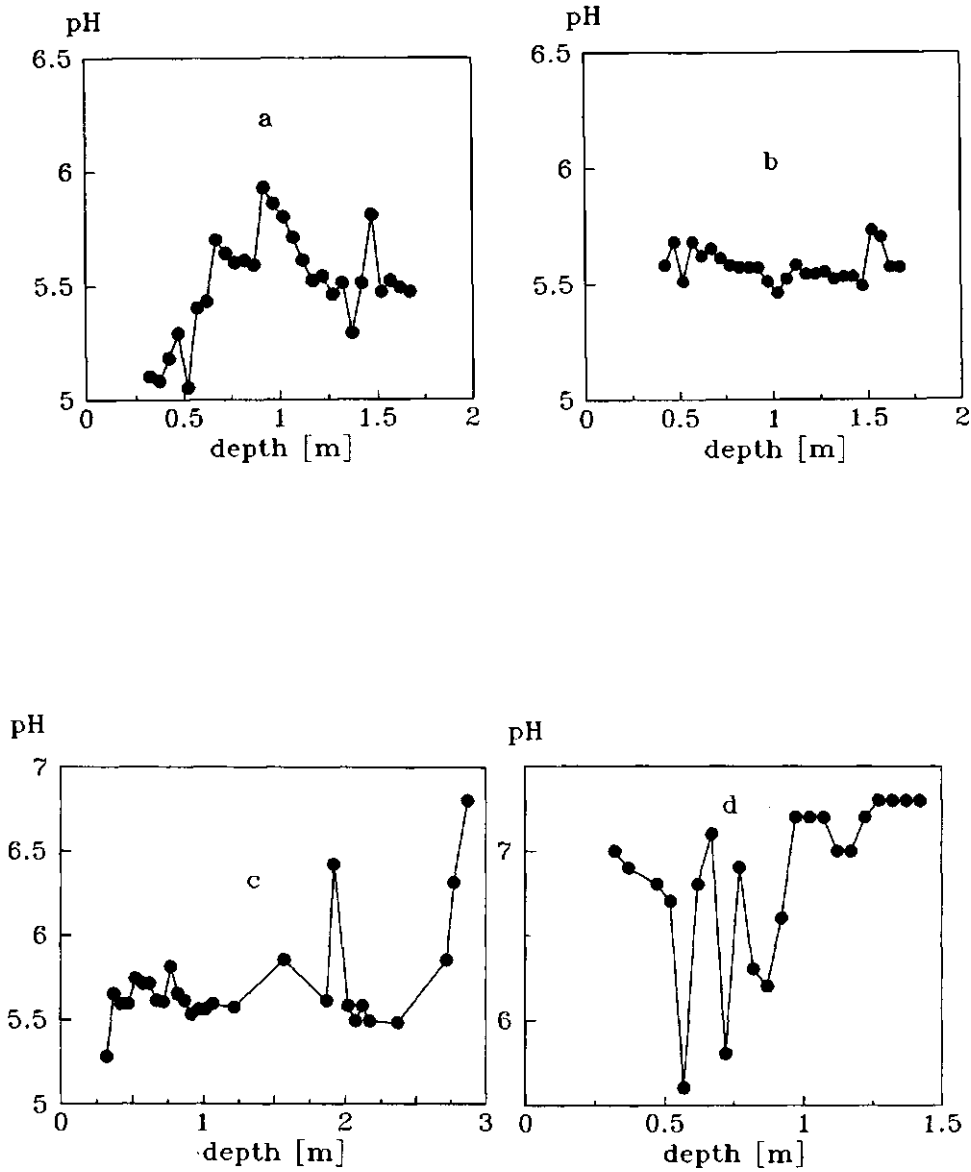

Fig. 6 pH profiles during dry anaerobic mesophilic batch digestion at 36 % total solids of the organic fraction of MSW. pH profile after: (a) 2 days; (b) 30 days; (c) 60 days;(d) 90 days

The results, viz. the methane productionrate against time, are shown in Fig. 8. After starting the leachate recycling there was an immediate respons , viz. an increase of the methane production rate. The leachate recycle apparently caused an acceleration of the transport of substrate (organic acids) to the substrate limited zones and a colonization of methanogens over the reactor. From these findings it can be concluded that in a non-mixed dry digestion reactor leachate recycle is essential for the desirable rapid start up and a prosperous course of a dry batch digestion process. The non-mixing conditions during the digestion will result in a heterogeneous distribution of organic acids and methanogenic bacteria in the reactor. Such a pronounced spacial separation of substrate and active biomass can be minimized by leachate recycle, resulting in a significant enhancement of the digestion process.

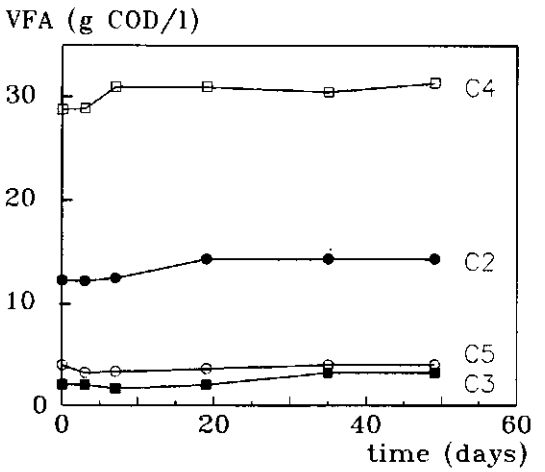

Fig. 7 Organic acids concentrations in anaerobic mesophilic digestion at 1.38 % total solids, (●) acetic acid;(■) propionic acid; (□) butyric acid; (○) valeric acid.

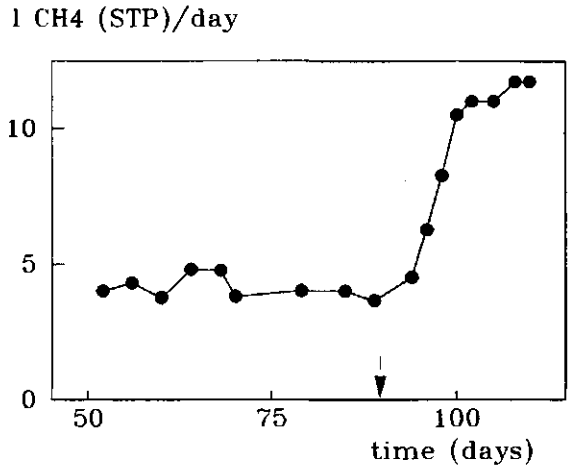

Fig. 8 Methane production rate during dry anaerobic batch digestion of the organic fraction of MSW and an inoculum factor of 0.3 before and after leachate recycle. (●) methane production rate; *(arrow indicates start of leachate recycle).*

On the other hand non-mixed conditions are favorable if an initial overloading of the methanogenic biomass occurs, because this then will not necessarily result in a soured biomass. As a part organic acids are formed in an area different from the methanogenic biomass, methane production can proceed although the conditions in the acid zones may exclude this. Due to this spacial separation a lower overall methane production rate is found. The decrease of the overall degradation rate depends on the degree of overloading. In Fig. 9 the pH and the course of the organic acids concentration are shown during a dry digestion experiment in which an inoculum factor of 0.40 and leachate recycle was applied. A strong initial increase of the total organic acids (up to 40 g COD/l, pH = 4.8) was followed by a strong decrease within 36 days. The initial local overloading of the methanogenic biomass did not result in a competely soured reactor. As was shown earlier, a completely mixed reactor would not recover from these highly unfavourable conditions within a period of 36 days.

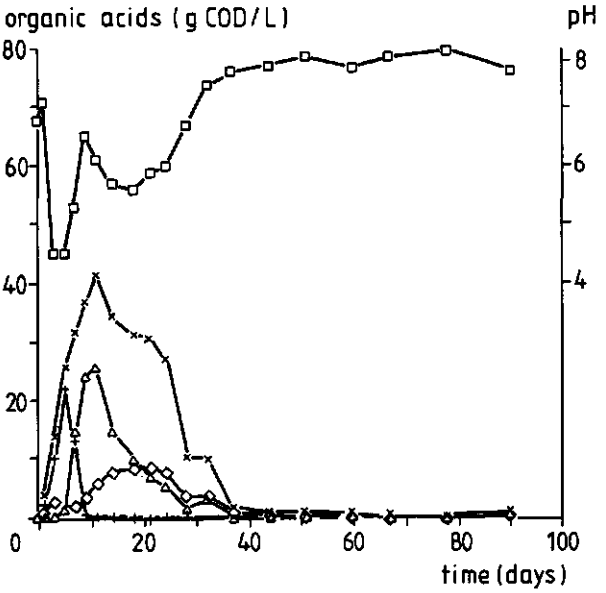

Fig. 9 Organic acids concentrations and pH in dry anaerobic digestion at 30 % TS with an inoculum factor of 0.40 and application of leachate recycle; (□) pH;(◇) acetic acid; (△) butyric acid; (+) lactic acid; (×) total organic acids.

CONCLUSIONS

Dry anaerobic batch digestion (36 % Total Solids) of the organic fraction showed a period of overloading of the methanogenic biomass at an inoculum factor (inoculum solids/organic fraction solids plus inoculum solids) of 0.30 which resulted in a build-up of organic acids (up to 60 g COD/l) and a pH of 5.6. The inoculum used for the digestion experiments did not show a high tolerance for pH values as low as 4.5, as appeared from batch activity tests at different pH values. The methane formation that still could be detected under the extreme conditions during dry anaerobic digestion is a result of the existence of methanogenic zones, where the conditions for methanogenesis are more favourable. In pH profile determinations over the height of the reactor methanogenic zones could be detected. In these zones the pH was 6-7, while in other zones the pH was 5.0-6.0. Indirect proof for the existence of methogenic zones was obtained the immediate response of the methane production rate to leachate recycle. Leachate recycle can minimize the degradation rate limitation caused by the heterogenous distribution of methanogenic biomass in a digester at high total solids concentrations

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CHAPTER 5

METHANOGENESIS AT LOW PH AND HIGH ACETATE CONCENTRATIONS

(submitted for publication)

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ABSTRACT

The phenomenon of methanogenesis in dry anaerobic digestion of solid wastes under extreme conditions, such as high salt concentrations, and pH values below 6, was studied in relation to the methanogenic biomass present in these environments. The tolerance of an enrichment culture from a solid waste batch digester for low pH values and high acetate concentrations was tested in separate batch experiments. The maximum specific methanogenic activity of the enrichment culture dropped considerably at pH values down to 4.5. The maximum specific growth rate of an enrichment culture at initial acetate concentrations of 167 mM and 517 mM amounted 0.54 d^{-1} and 0.23 d^{-1}, respectively. Methanogenesis still proceeded at an initial acetate concentration as high as 583 mM and pH = 7.0. Microscopic observations of enriched cultures showed that the predominant organisms resembled the genus *Methanosarcina*.

INTRODUCTION

The rate of anaerobic digestion of complex organic matter is related to the rate of the methanogenesis, and therefore the optimum environmental conditions for a digestion therefore is determined by the methanogens. It is well known that in anaerobic digesters the pH and volatile organic acid concentrations are important environmental factors to be controlled (1,4,5). Methanogenesis proceeds optimally in the interval of 6.7-7.4 (26) and the maximum allowable concentration of organic acids depends on the pH of the system. The concentration of undissociated volatile fatty acids, which are inhibiting the methane formation is related directly to the pH in a digester (1,5,12,13).

Dry anaerobic mesophilic digestion in of solid wastes in batch systems shows typical characteristics of imbalance between acid formation/hydrogen formation and methane formation during the first part of the digestion (chapter 2 of this thesis, 21). The imbalance leads to relatively high organic acid concentrations and to low pH values. Notwithstanding the initial build up of volatile organic acids and the concomitant pH-drop, batch-wise anaerobic digestion of solid organic waste can be conducted operated at economically viable loading rates. The start up of a dry digestion process proceeds even successful at volatile fatty acids plus lactic acid concentrations as high as 0.37 M and at a pH as low as 5.2. (chapter 2, this thesis). Wujcik and Jewell (23) reported that methanogenesis is possible up to volatile fatty acids concentrations of 0.33 M during dry anaerobic batch digestion experiments. Unfortunately, they did not report on pH values in their experiments. Stegmann (19) reported methanogenesis at total organic acid concentrations of 0.42-0.5 M and pH values of 5.5-6 during controlled batch digestion of Municipal Solid Waste. From these data it can be concluded that methanogenesis still can proceed rather well at extreme conditions.

In anaerobic digestion of complex organic matter acetate is in terms of electron flow the most important precursor of methane (9,16,17). Labelling studies indicated that 70 % of the methane is derived by the splitting of acetate, while 30 % is formed from carbon dioxide reduction with hydrogen (9). The acetoclastic methanogens are found to be more sensitive to low pH values than the hydrogenotrophic methanogens (3). According to Williams (22) methane formation from hydrogen is found at a pH as low as 3.1 in peat lands, although growth of the methanogens in these environments at a pH lower than 5.3 is unlikely.

Several species of mesophilic and thermophilic acetoclastic methanogens have been obtained in pure culture (10,25,27). However, so far cultures that were grown under the extreme conditions, such as pH values 3-5.5, and acids concentrations of 0.5 M, have not been isolated.

In the present work acetoclastic methanogenesis has been studied at low pH and high acetate concentrations which are typical for some anaerobic digestion systems, such as dry anaerobic digesters.

MATERIALS AND METHODS

Inoculum, medium and growth conditions

The inoculum for the batch experiments consisted of completely digested (viz. volatile fatty acids absent) organic fraction of Municipal Solid Waste, obtained from a 78 l laboratory scale dry batch digester. This reactor was originally started up with a mixture of methanogenic sludge from an anaerobic waste water treatment reactor and aerobically stabilized organic fraction of MSW (40 % of the initial total solids). After completion of the first digestion the next start up was carried out with the digested organic fraction. The solids ratio of digested organic fraction and fresh organic fraction solids amounted to 0.67.

The inoculum for the experiments described in this chapter was obtained after completion of the third digestion. The maximum volatile fatty acid concentration in the laboratory-scale reactor was 0.32 M, with a lowest pH of 5. As is described in chapter 4 of this study, these conditions were very likely not fully representative for the entire digester. In the digesting period very likely a certain part of the digester functioned at pH values above 6 and at lower acids concentrations, another part may have functioned at lower pH values and higher acids concentrations. The total solids content (TS) of the inoculum amounted to 27.1 % and its volatile solids content (VS) amounted to 31.0 % of the TS. The inoculum was added to the batch reactors with an initial total solids concentration of 1.4 %. The stirred batch reactors had a volume of 5 litres and were maintained at 35 °C with a temperature controlled water bath, which was connected to the water jacket of the reactors. The reactors were mechanically stirred every 5 minutes during 5 seconds (100 rpm). The methane produced was collected in gas tight bags after removing the CO_2 from the biogas by CO_2 scrubber. The volumetric methane production was measured daily by pumping the methane from the gas bags through a wet test gas meter. The basal medium for the determination of the growth rate and pH tests consisted of acetate which was supplied in an increasing amount as is indicated in the results section. Nutrients and race elements were added in relation to the initial acetate concentration; 0.3 ml of trace elements solution according to (25) per g acetate was added. Per g acetate the following compounds were added: 0.034 g NH_4Cl, 0.056 g KH_2PO_4, 0.056 g $(NH_4)_2SO_4$, 0.05 g $MgCl_2.6H_2O$, 0.09 KCl. The initial pH of the basal medium was brought to 7.0 by $CaOH_2$ addition. The pH was measured daily using a glass electrode (Schott) and a Knick mV meter, and subsequently corrected with 6 N HCl to

pH = 7.0 if the pH was increased above this value.

The enrichment culture elaborations were done according to Houwen et al. (8) in a medium well described by the same authors. The enrichment medium contained an initial acetate concentration of 250 mM, and had an initial pH of 7.0.

Acetate analysis

Samples were taken from the batch reactors and after centrifuging analyzed for acetate with a gas chromatograph (Hewlett Packard, model 402, flame ionization detector FID 200 °C chromosorb column [200 by 0.2 cm]); carrier gas was N_2 saturated with formic acid), equipped with a computing integrator (Spectra Physics 4100). Peak areas were measured and compared with a standard VFA mixture.

Determination of specific growth rate μ

The regular technique for the estimation of the specific growth rate (μ) in mixed cultures from a batch experiment is the integrated Monod equation, which is discussed in chapter 1 of this study. However, accurate determination of the growth rate is possible, if the initial acetate concentration is several times higher than the Ks (Monod saturation constant, chapter 1 of this study). At high initial concentrations of acetate a certain growth of the biomass will occur, but in the Monod equation this growth will be neglected. By close analysis of the results obtained with this method, it appeared that a more accurate method was needed for determination the specific growth rate in our experiments. In this study a recently developed method is used to calculate μ (7). μ was estimated with a relative least squares method with the following equation:

$$S = S_0 + X_0/Y^*(1-\exp(\mu_{max}{}^*t) \qquad (1)$$

where S is the acetate concentration, S_0 the initial acetate concentration, X_0 the initial biomass concentration and Y the yield factor. Accurate determination of K_s from the same set of experiments was not possible.

RESULTS

pH tolerance

The pH tolerance of the digested organic fraction of Municipal Solid Waste the methanogenic activity on acetate was determined during batch tests at several pH values. In order to be able to distinguish between the influence of the pH on the methanogenic activity from the combined effect of a low pH and a high concentration of undissociated acetic acid the initial concentration of undissociated acetic acid was kept at 0.83 mM during the pH tests, assuming a K_a of 1.728×10^{-5} mol/l at 35 °C. Fig. 1 shows the methanogenic activity at several pH values as percentage of the specific activity at pH 7.0 after the second addition of acetate.

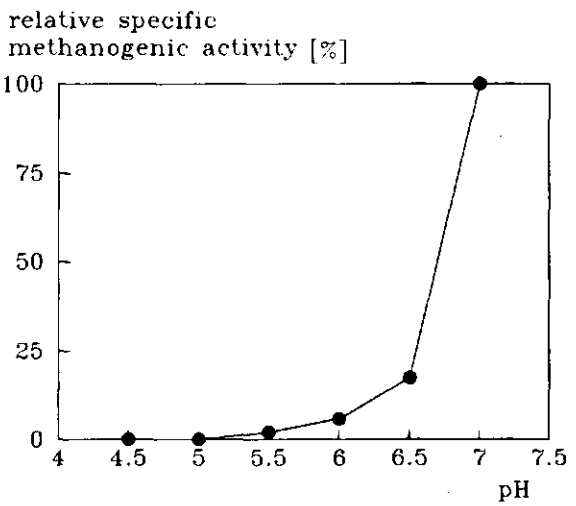


Fig. 1. Relative specific methanogenic activity of an acetate degrading inoculum obtained from a dry anaerobic digester as a function of the pH.

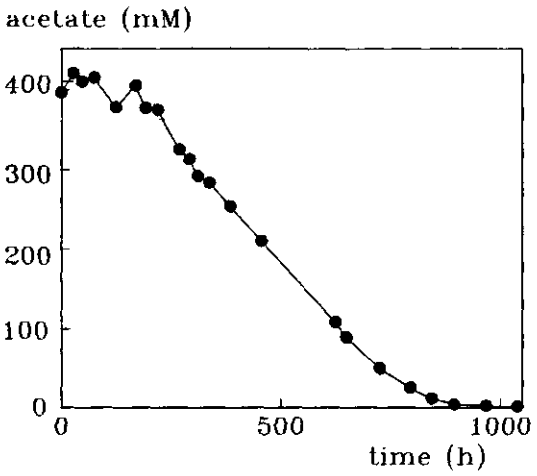


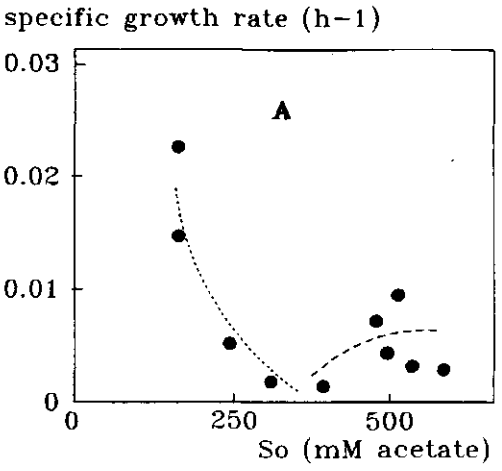
Fig. 2. Acetate degradation of the methanogenic enrichment of the present study; (●) acetate.

The relative specific activities given in Fig. 1 are mean values from duplicates. The maximum specific activity at pH 7 amounted 0.4 mMol CH_4 g^{-1} $VS{\cdot}day^{-1}$. In Fig. 2 the methane production is shown as was observed at the specific activity test at pH = 5.5.

Toxicity of undissociated acetic acid

The tolerance of the enrichment culture for high concentrations of undissociated acetic acid was determined by calculating the maximum specific growth rate at increasing initial acetate concentrations at pH 7. The cultures used during the pH test at pH 7 and 167 mM acetate were exposed to increasing initial acetate concentrations, being 583 mM the highest concentration tested. After completion of the acetate degradation, 1 litre of the batch reactor contents was removed after settling of the biomass. Then the subsequent feeding was added with one litre of basal medium with the proper ratio of nutrients. Fig. 2 acetate degradation shows the results of the for a batch experiment with an initial concentration of 417 mM acetate.l^{-1}. Methane production proceeded in equivalent amounts to the acetate degradation. From the assessed acetate concentrations during each feeding the maximum specific growth rate μ was calculated according to the method described in the Materials and Methods paragraph. The accuracy of the calculated values of μ follows from the standard deviations shown in Fig. 3a. After the experiment with an initial concentration of 500 mM acetate, an enrichment of the culture was made from the batch

reactor in order to assess the predominant microorganism in the biomass, using enrichment medium that contained 250 mM acetate. It should be noticed here that $Ca(OH)_2$ was used instead of NaOH for neutralizing acetic acid, as microscopic observations were useless otherwise due to precipitation of $CaCO_3$. In Fig. 4 light micrographs of the enrichment culture grown at 250 mM acetate are shown. The enrichment culture was predominated by *Methanosarcina*-like organisms, growing in aggregates.



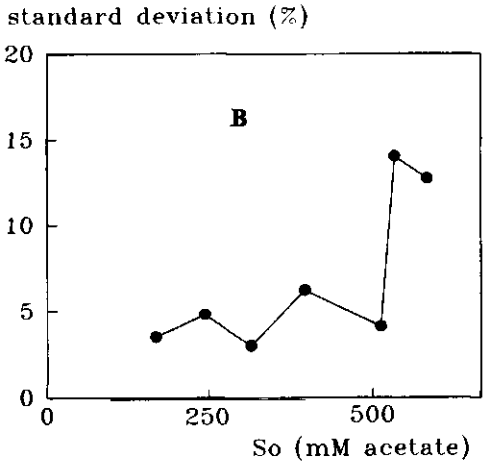
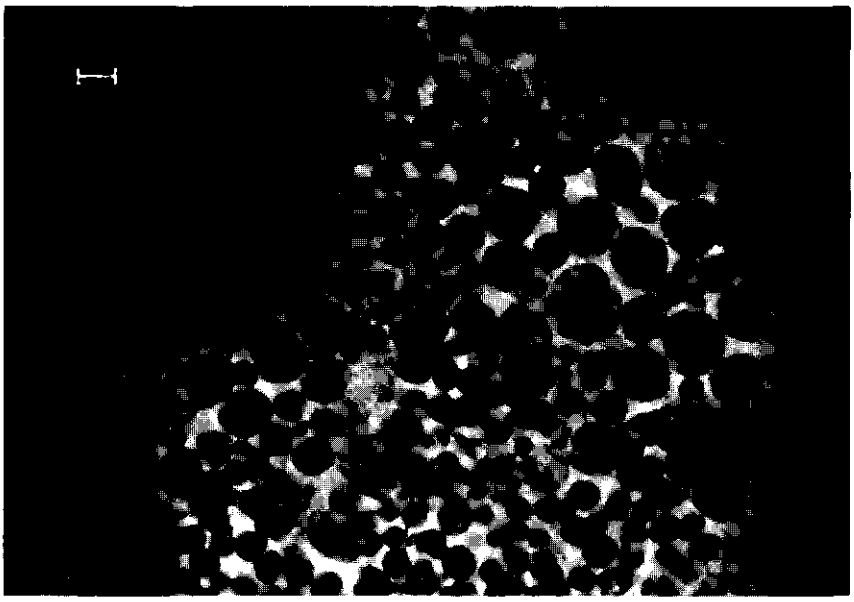


Fig. 3 Specific growth rate (a) and standard deviation (b) of the specific growth rate (a) as a function of the acetate concentration.



A

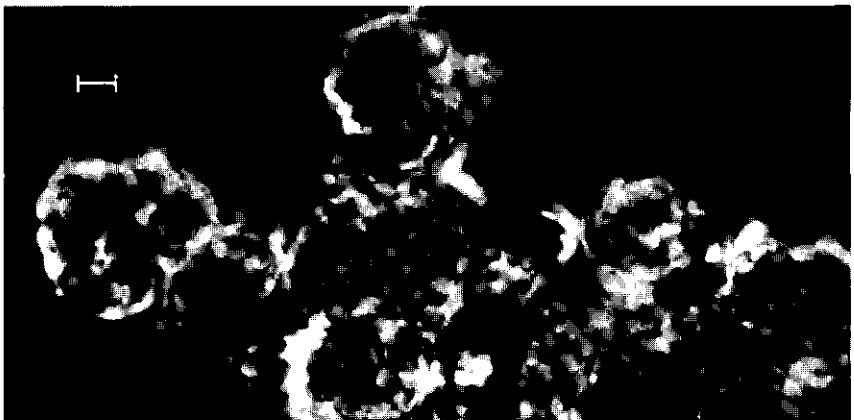


Fig.4 Light micrographs (a,b) of an methanogenic enrichment culture grown at 500 mM acetate; (a) bar=5 μm; (b) bar =0.5 μm.

DISCUSSION

The decreasing specific methanogenic activity at pH < pH 7 (Fig. 1) suggests, that the pH tolerance of the methanogens in the residue from the batch digestion of the organic fraction of Municipal Solid Waste is lower than would be expected from the results of dry digestion experiments, because here methane production was still found at pH = 5.2 and at 0.4 M VFA + lactic acid (chapter 2,4, this thesis). The pH tolerance limit for the dry anaerobic batch digestion of MSW refers to the pH of the bulk liquid, whereas the environmental gradients, as is described in chapter 4 of this thesis, cause regions with a higher pH in which the actual methane production takes place.

Greater tolerance of the enrichment culture was found for high acetate concentrations and high salt concentrations compared to the tolerance for low pH tolerance. Methane production from acetate could still be detected up to an initial concentration of 583 mM, the highest value tested in our experiments. At this high acetate concentration the assessed specific growth rate amounted to 0.17 d^{-1}. Apart from the increasing concentration of undissociated acetic acid, the observed decreased growth rate

might be due to the increasing salt concentrations (here: $CaCl_2$) which are the result of the neutralization of acetic acid. The calculated the specific growth rate showed an increase at an acetate concentration of 500 mM. This increase might be the result of a population shift towards an organism that prefers high concentrations of undissociated acetic acid concentrations and high salt concentrations (290 mM $CaCl_2$). It is known, that halophiles show optimum growth at 3 % NaCl, that decreases at lower concentrations of this substance (2). Since both factors are coupled it is not possible to decide which is the most important one. The value of the specific growth rate detected at 167 mM acetate (TABLE 1) indicates that the acetate degrading methanogenic enrichment is predominated by a *Methanosarcina sp* or by *Methanothrix concilii*. However, the former type of acetoclastic methanogen is mostly found in extreme environments such as sub-optimal pH values, high acetate concentrations and high salt concentrations (6,18,24,26), while the latter type of organism is found in environments with low acetate concentrations and neutral pH values (24,25). The maximum value tested (583 mM) is far beyond the previously reported tolerance of level of 0.5-1.0 mM undissociated acetic acid methanogenesis (12,13). At 583 mM acetate and pH 7 the as at this concentration the undissociated concentration of acetic acid amounts to 3.3 mM. The lower tolerance of anaerobic reactors treating waste waters for high acetic acid can be explained by the fact that the biomass in these rectors is predominated by *Methanothrix soehngenii*-like organisms (17). As appears from the microscopic observations in Fig. 4 indeed *Methanosarcina*-like organisms are predominant in the enrichment culture grown at an initial concentration of 250 mM acetate.

TABLE 1 Specific growth rates of methanogenic cultures degrading acetate

culture	temp (°C)	initial concn (mM)	μ (d^{-1})	reference
Methanosarcina acetivorans	35	20	0.69	(16)
Methanosarcina barkeri	35	150	0.23-0.69	(11)
Methanothrix soehngenii	37	n.r.[1]	0.16	(22)
Methanothrix concilii	40	75	0.69	(12)
enrichment culture	35	100	0.40	(10)
enrichment culture	35	167	0.54	this thesis (Ch. 5)
enrichment culture	35	517	0.23	this thesis (Ch. 5)

[1]: not reported

The specific growth rate that is found at an initial acetate concentration of 517 mM was 43 % of the value at 167 mM. The standard deviation also tended to increase at the/ concentrations higher than 500 mM. This result indicates that indeed it is uncertain, whether the organisms are actually reproducing at high acetate concentrations. It might be

that acetate degradation proceeded at sub-optimal rates without growth of the methanogens, till the concentration of undissociated acetic acid decreased below a critical value and then started growing. Adaptation of the kinetics used for the calculation of the maximum specific growth rate will be a major point for further study.

ACKNOWLEDGEMENTS

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CHAPTER 6

START-UP OF DRY ANAEROBIC BATCH DIGESTION OF VEGETABLE, FRUIT AND YARD WASTE

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ABSTRACT

Dry anaerobic digestion of Vegetable, Fruit and Yard (VFY) waste, the organic fraction of source separated Municipal Solid Waste, was studied in BIOCEL-type batch reactors. The first start up, i.e. a start up with another inoculum than the digested VFY, had to be carried out with dewatered digested pig manure. This type of methanogenic inoculum is adapted to the high ammonium-nitrogen concentrations (3.2 g/l) and high concentrations of organic acids (up to 25 g COD/l) which were detected during start-up of the digestion of VFY waste. Granular sludge which was also investigated as inoculum was not suitable since it is not adapted to the stressful environmental conditions during the first stage of batch digestion. During regular start-up with digested VFY as the inoculum a higher minimum inoculum factor (ratio of inoculum solids and total initial solids at start-up) had to be applied for a balanced digestion. A strong correlation existed between the inoculum factor and the solids retention time. An increasing inoculum factor implied that the conditions for methane formation during a batch digestion were more optimal. The total solids retention time at an inoculum factor of 0.50 was 28 days, the mean methane production rate was 0.8 l STP/l.day. These values are in the same order as was found for other systems that are based on continuous dry anaerobic mesophilic digestion.

INTRODUCTION

The organic fractions of MSW which were investigated in anaerobic digestion systems up to now were obtained from a mechanical separation process, where the organic fraction is separated from the non-biodegradable fraction after hammermilling the raw MSW (1). The digested residue can be used as a soil conditioner (compost). However, frequently the heavy metal content of the residue is too high to meet the raising standards for organic soil conditioners (4,5). In principle the contamination with heavy metals can be prevented by applying source separation of MSW (4,5). In the process of source separation both the storage and the collection of the organic fraction of MSW, the so called Vegetable, Fruit and Yard waste (VFY waste) is carried out separately from other contaminating fractions.

The start-up method of a BIOCEL reactor for dry anaerobic digestion of VFY waste may differ from start-up with the organic fractions from a separation process, as described in chapter 2 of this thesis. VFY waste has a more heterogeneous particle size distribution in comparison to the organic fraction of MSW, which can affect the mixing of the inoculum with the VFY waste. The VFY waste does not contain paper, which means that a larger fraction of the biodegradable organic compounds in the waste are non-cellulosic compounds, such as sugars, starch and proteins. As was concluded in chapter 1 of this thesis, cellulose degradation is often rate limiting during anaerobic digestion of cellulose containing wastes. Anaerobic degradation of easy degradable compounds is not rate limiting. To compensate for a relatively higher content of easy degradable compounds in VFY waste, a higher amount of methanogenic inoculum may have to be be added than in the case of a paper containing organic fraction of MSW. Also the relatively higher amount of easy degradable proteins in VFY waste certainly will also affect the start-up of the digestion, because in the anaerobic degradation of proteins NH_4^+ is formed. The concentration of NH_4^+ can increase above the level where inhibition of the methanogenesis will occur (8).

Because of the reasons mentioned above, we believed that the digestion of VFY-waste proceeds differently from the organic fraction of MSW obtained by mechanical separation. This chapter deals with the start-up of a batch reactor for digestion of VFY-waste. Methods will be described for the first start-up, i.e. using methanogenic inocula, other than the digested VFY-waste, and using the digested VFY-waste. Latter start-up is referred to as 'regular start-up'. Dry digestion will be studied at several ratios of inoculum solids and the total amount of solids (inoculum solids + VFY waste solids), to assess the effect on the solids retention time. The necessity of leachate recycling as a part of the start-up procedure will be investigated.

MATERIALS AND METHODS

TABLE 1 Characteristics of the vegetable fruit and yard fraction from source separated municipal solid waste

total solids (w/w %)	36.0
volatile solids (% of ts)	60.7
methane yield l stp/kg[1]	59.0
Particle diameter (d) distribution[2]:	
d > 20 mm	77.6
13.6 mm < d < 20 mm	8.5
6.8 mm < d < 13.6 mm	6.6
d < 6.8 mm	7.3
	100

[1]:determined in a batch test with digested sewage sludge at 3 % TS and 35 °C.
[2]: % of total weight

substrate The substrate for the experiments described in this paper was a source separated organic fraction of MSW, the so called Vegetable Fruit and Yard waste (VFY waste). The mean composition of this fraction as used in the present study is given in TABLE 1.
compost The compost used for the first start-up experiments was obtained from an aerobic composting plant for VFY-waste. The total solids (TS) concentration of the ocmpost was 67 % w/w, and its VS content of the solids was 25 % w/w.
methanogenic inocula Three types of methanogenic inoculum were used during the start-up experiments: granular sludge, dewatered digested pig manure, and digested VFY-waste. The granular sludge was obtained from an Upflow Anaerobic Sludge Blanket reactor treating treating wastewater from a potatoe processing factory. The TS of the sludge amounted to 11.5 %, and its maximum methanogenic activity determined according to (9) was 0.009 CH_4-COD/(kg.day) (= 0.035 m^3 (STP) CH_4/(kg TS.day) at 30 °C. The digested pig manure was obtained from a pig manure digester (plug flow type) in Sterksel, the Netherlands. The TS concentration of the digested manure was 24.5 %, and its maximum methanogenic activity amounted to 0.01 kg CH_4-COD/kg.day) (=0.0142 m^3 CH_4 (STP)/kg TS.day). The TS concentration of the digested VFY-waste was 41.3 %, the methanogenic activity was 0.01 kg CH_4-COD/(kg.day) (=0.0085 m^3 (STP)/kg TS.day).

TABLE 2 Experimental set up of the start-up experiments concerning dry anaerobic batch digestion of Vegetable Fruit and Yard waste

type of experiment	seed	inoculum factor[1]	l.r.[2]
first start-up	UASB sludge + compost	0.012;0.024;0.030; 0.042;0.08;0.09	no
first start-up	pig manure (dewatered)	0.15;0.20;0.25; 0.30;0.35;0.45	no
first start-up	pig manure (dewatered)	0.20	yes
regular start-up	digested VFY	0.20	no
regular start-up	digested VFY	0.25; 0.30; 0.5; 0.77	yes

[1]: ratio of seed solids and compost solids + seed solids + VFY waste solids (I)
[2]: application of leachate recycling

apparatus The experiments were carried out with batch reactors with a working volume of 0.5, 6 and 78 liters. The technical specifications of the reactors are described in detail elsewhere (chapter 2,this thesis).
experimental set-up and procedure The amount of inoculum added, expressed as the ratio inoculum solids/total initial VFY-waste solids plus inoculum solids plus compost solids, depended on the type of experiment and varied in the range 0.012-0.50 in the various experiments. The initial total solids concentration applied was 35 % TS during the experiments with the small scale reactors (0.5 and 6 liters). If needed, tap water was added to obtain this TS-value. The total solids concentration in the reactors of 78 liters varied in the range 30-41% TS. The initial compactness amounted to 0.3 kg TS/l for all experiments. The VFY-waste and the inocula were manually mixed, brought into the reactors and compressed to the required compaction. The experimental set up is given in TABLE 2. In specific experiments (indicated in the **RESULTS**-section) with the reactors of 78 liters leachate recycle was applied with a mean recirculation flow of 0.3 $m^3/(m^2.day)$.
analyses Biogas. The reactors of 6 and 78 liters were monitored for biogas production and biogas composition three times a week. Biogas composition (CO_2,CH_4,H_2,N_2,O_2) was determined with a gas chromatograph equipped with a TCD detector and with two parallel columns: a column of 1.5 m x 1/8", teflon packed chromosorb 108, 60-80 mesh and a 1.2 m x 1/8" mol. sieve 5A, 60-80 mesh. The column split ratio was 1:1. Samples of 100 μl were taken of the reactors with a gas tight syringe. The measurement of the biogas volume was carried out by reading a wet test gas meter once a day. The gas volumes produced were recalculated to standard temperature and pressure (STP), of 0 °C, 1 bar.

Organic acids pH and ammonium-nitrogen. Samples were taken from the extract and analyzed for organic acids. The concentrations were recalculated to the original reactor conditions by taking into account the initial amount of moisture in the reactors and the amount of extraction water applied. Samples were taken from each reactor for determination of the organic acids (lactic acid, acetic acid, propionic acid, butyric acid, capric acid, valeric acid). Sampling of the reactors of 78 liters was carried out by taking 50 g of reactor contents at two different heights. From this point the procedure was similar to the procedure for the reactors of 0.5 liter. Before the analysis the content of the 0.5 l reactors (= 1 sample) was extracted with tap water during 30 minutes. Volatile Fatty Acids (VFA) were determined as described earlier (11). Lactic acid was determined on a HPLC, equipped with a UV detector and an organic acids column (Chrompack, 300x6.5 mm). The injection volume was 10 μl, the eluent 0.01 N H_2SO_4 with a flow of 0.8 ml/min. The wave length during the detection was set at 210 nm, the absorbtion range 0.050. The pH of the samples was determined with a mV-meter and a combined glass electrode directly after sampling, before addition of the extraction water. Ammonium nitrogen was determined with a autoanalyser, equipped with a UV-spectro fotometer detector at 210 nm.

RESULTS

First start-up experiments

The effect of the start-up method on the digestion time (DT, in days), i.e. the time that is needed for maximum achievable methane yield (TABLE 1), was investigated. The first method tested was the combined addition of granular sludge and compost to the VFY-waste. The inoculum solids/total "initial solids" ratio amounted 0.012, the compost solids/total initial solids was varied in the range 20-50 %. These ratios are found to be successful for the start-up of dry anaerobic batch digestion of an organic faction of MSW obtained by mechanical separation (Chapter 2). In Fig. 1 the biogas production and the biogas composition, and in Fig. 2 the organic acids concentrations pH and ammonium-nitrogen concentrations are shown of an experiment with a compost solids/total initial solids ratio of 0.50.

The results in Fig. 1 and Fig. 2 are characteristic for the experiments concerning the first start-up method with granular sludge and compost. Methane production was extremely low and the biogas consisted mainly of CO_2 and H_2, indicating an unbalanced digestion.

The imbalance resulted in high organic acids concentrations and low pH values, which were detrimental to the methanogens present in the inoculum applied in the first start-up experiments.

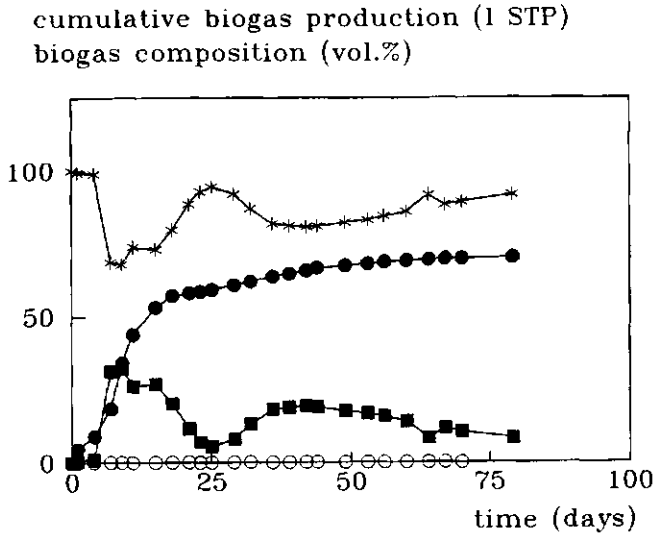


Fig. 1 Biogas production and biogas composition during dry anaerobic batch digestion of Vegetable Fruit and Yard Wastes; inoculum solids/initial total solids ratio 0.012, stabilized (composted) solids/initial total solids ratio: 0.50; (●) sum biogas;(✳) vol. % CO_2; (○) vol. % CH_4; (■) vol. % H_2.

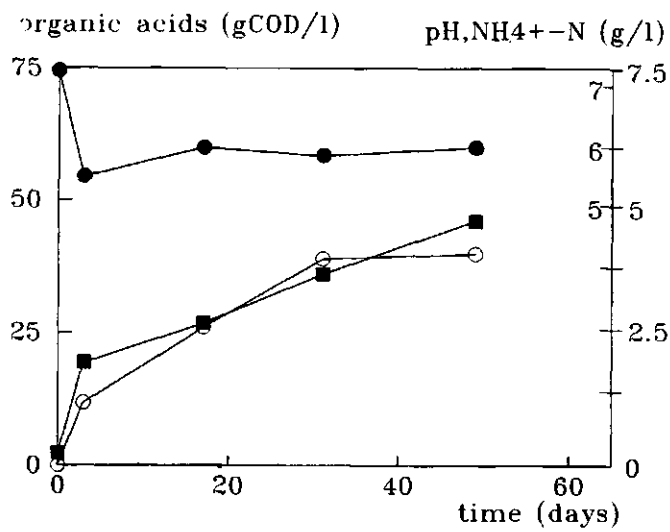


Fig. 2 Organic acids, ammonium-nitrogen and pH during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with granular sludge as inoculum;inoculum solids/initial total solids ratio 0.012, stabilized (composted) solids/initial total solids ratio: 0.50;(○) total organic acids; (■) NH_4^+-N; (●) pH.

The initial (day 0 - day 14) acid formation rate plus hydrogen formation rate amounted to 3.4 g COD/(l.day) at 30 °C. Based on the maximum methanogenic activity determined at pH 7.0, the initial methanogenic capacity was calculated to be 0.3 g COD/(l.day) while the pH during the experiment was 6 or lower, so the actual methanogenic capacity was probably lower.

The ammonium-nitrogen concentration increased rapidly to 2 g/l (liquid phase) indicating a distinct breakdown of organic nitrogen compounds.

In order to obtain a balanced digestion process another reactor was started with granular sludge as an inoculum solids/total initial solids ratio of 0.09. This ratio was the highest ratio possible, as a higher ratio would result in a total solids concentration below 35 %.

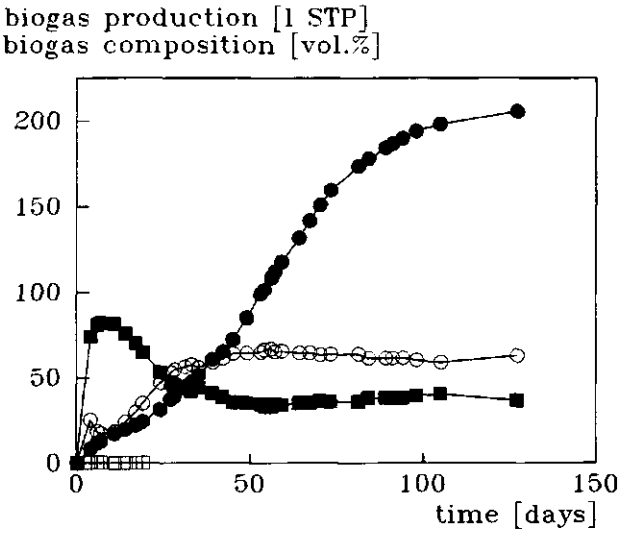


Fig. 3 Biogas production and biogas composition during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with granular sludge; inoculum solids/initial total solids ratio 0.09, stabilized (composted) solids/initial total solids ratio 0.50; (●) cumulative biogas production;(■) vol. % CO_2;(○) vol. % CH_4;(□) vol. % H_2.

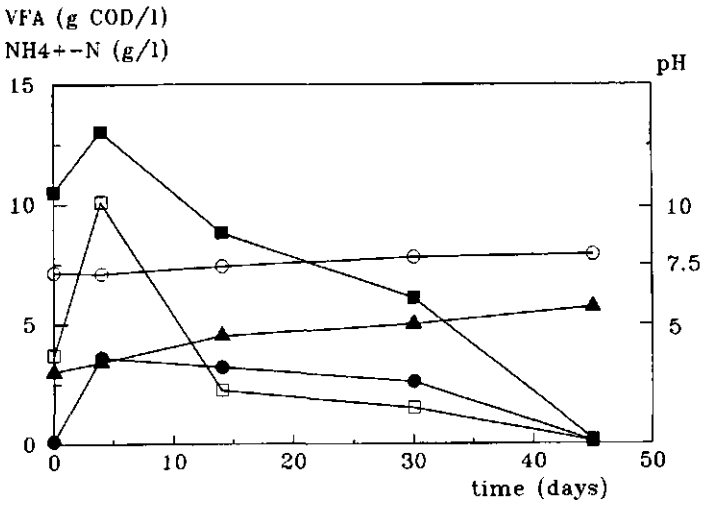


Fig. 4 Organic acids, ammonium-nitrogen and pH during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with granular sludge as inoculum; inoculum solids/initial total solids ratio 0.09, stabilized (composted) solids/initial total solids ratio: 0.50;(■) total organic acids; (⊏) acetic acid;(●) propionic acid;(▲) NH_4^+-N;(○) pH.

In Fig. 3 the biogas composition and the biogas production are shown. Although also here some hydrogen was produced in the very initial stages, the start-up of the methanogenesis proceeded rapidly. The calculated methanogenic capacity added to the reactor amounted to 1.9 g COD/(l.day). The initial acids-COD + H_2-COD formation rate plus hydrogen formation rate amounted to 4.1 g COD/(l.day). The lowest pH measured in the experiment was 5.8, while the maximum organic acids concentrations and ammonium-nitrogen concentrations were similar to those found in the experiments with lower amounts of inocula (Fig. 4). The digestion time needed to obtain the maximum potential methane yield of 59 l STP CH_4/kg VFY-waste added was 125 days.

The second type of inoculum tested for its potentials to enhance the first start-up of dry VFY-waste digestion in a was dewatered digested pig manure. This inoculum was thought to be dominated by a methanogenic population which is adapted to more extreme conditions than granular sludge, i.e. 5-6 g ammonium-N/l, 10 g VFA-COD and a salt concentration of 3 % salts and has a slightly higher methanogenic activity per kg in comparison to granular sludge (0.012 kg CH_4-COD/(kg.day vs. 0.009 kg CH_4-COD/(kg.day) at 30 °C). Another advantage of this inoculum was the higher total solids concentration in comparison to granular sludge, which implies, that per kg VFY-waste a higher amount of dewatered digested manure solids (= higher amount of methanogenic biomass) could be added to reach a total solids concentration of 35 % in the VFY-waste/inoculum mixture. A higher amount of inoculum solids was needed to compensate for the high initial acid formation rate plus hydrogen formation rate. An experiment was carried out with an inoculum solids/total initial solids ratio of 0.20. At this ratio the

methanogenic capacity was calculated to be sufficient. In Figs. 5 and 6 the results of this experiment are shown. The biogas composition and biogas production indicated a balanced start-up of the digestion, i.e. a rapid start of the methanogenesis and no hydrogen in the biogas. After 50 days already 60 % of the potential methane yield was produced. The period needed for the remaining 25 % methane amounted to approximately 100 days. This retarded methane production may result from a poor contact of the methanogenic inoculum and the substrate. The relative large particles of the VFY-waste may hinder a close contact of methanogenic bacteria and substrate (volatile fatty acids) in a non-mixed reactor (Chapter 3 & 4, this thesis). The effect of a certain extent of mixing accomplished by leachate recycle, was investigated during start-up experiments with digested manure also at an inoculum solids/total initial solids ratio of 0.20. but at an initial total solids concentration of 30 %.

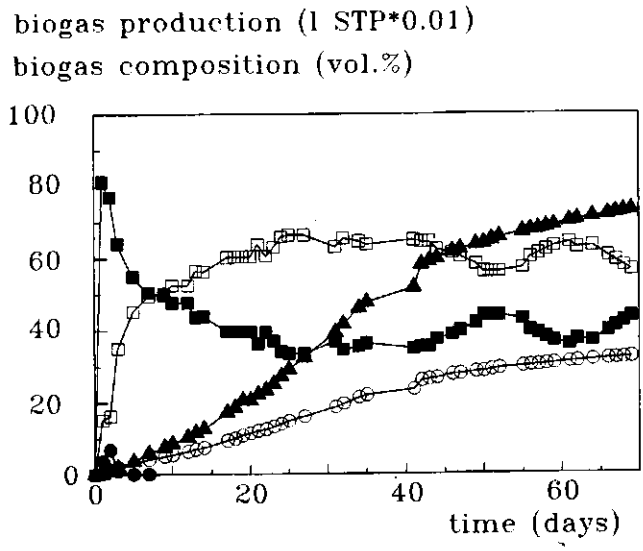


Fig. 5 Biogas production and biogas composition during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with digested dewatered pig manure as inoculum and without leachate recycle; inoculum solids/initial total solids ratio 0.20, (○) sum biogas; (■) vol. % CO_2;(□) vol. % CH_4;(●) vol. % H_2.

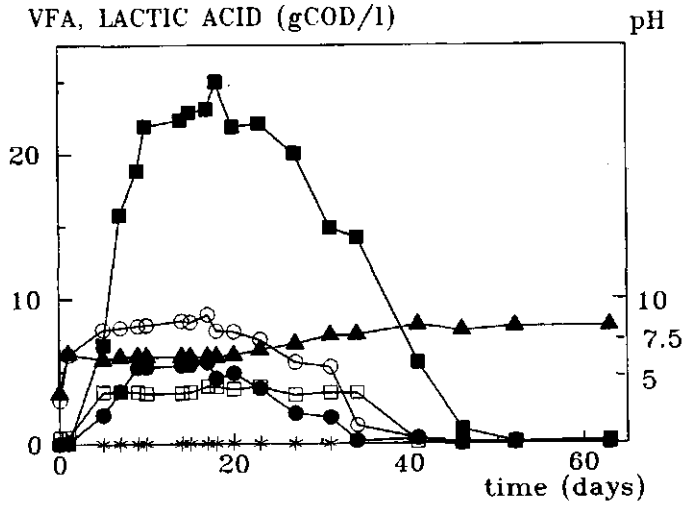


Fig. 6 Organic acids, and pH during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with digested dewatered pig manure as inoculum and without of leachate recycle; inoculum solids/initial total solids ratio 0.20. (■) total organic acids; (○) acetic acid; (□) propionic acid;(∗) lactic acid;(●) butyric acid;(▲) pH.

In Fig. 7 and Fig. 8 the organic acids concentrations and pH are shown of the experiment with leachate recycle. The organic acids concentration increased to a value of 20 g COD/l, but rapidly decreased to 0.5 g/l, within a period of 40 days. At this stage of the digestion the methane production rate decreased dramatically (Fig. 9), despite the fact that the methane yield was only 60 % of the potential yield. This result suggests that methanogenesis was not the rate limiting step during this stage of the digestion. For the experiment without leachate recycle it took 50 days to reach this stage (Fig. 6). The characteristics of the experiments concerning the effect of leachate recycle are summarized in TABLE 3.

TABLE 3 Characteristics of the start-up experiments with VFY waste and dewatered digested pig manure as the inoculum

initial TS (%)	leachate recycle	inoculum factor	DT1 (days)
30	+	0.20	40
30	-	0.20	50
36	-	0.20	79

[1]: digestion time

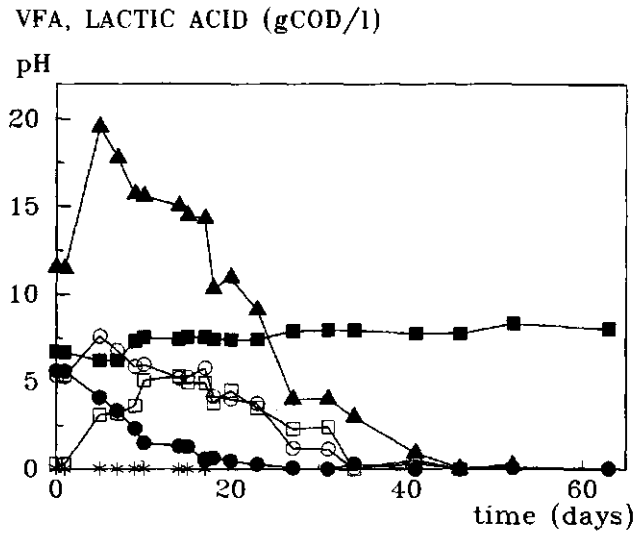


Fig. 7 Organic acids, and pH during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with digested dewatered pig manure as inoculum and with application of leachate recycle; inoculum solids/initial total solids ratio 0.20.(▲) total organic acids; (○) acetic acid;(□) propionic acid;(∗) lactic acid;(●) butyric acid;(■) pH.

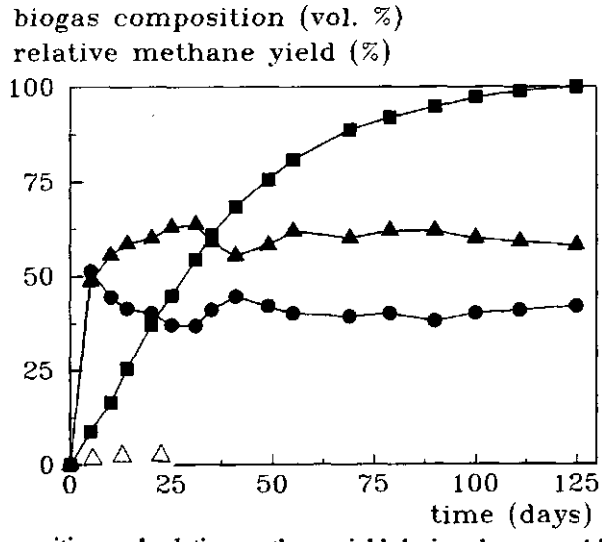


Fig. 8 Biogas composition and relative methane yield during dry anaerobic digestion of Vegetable Fruit ad Yard waste with digested dewatered pig manure as inoculum with application of leachate recycle;(●) % CO_2;(▲) CH_4;(△) % H_2;(■) % relative methane yield.

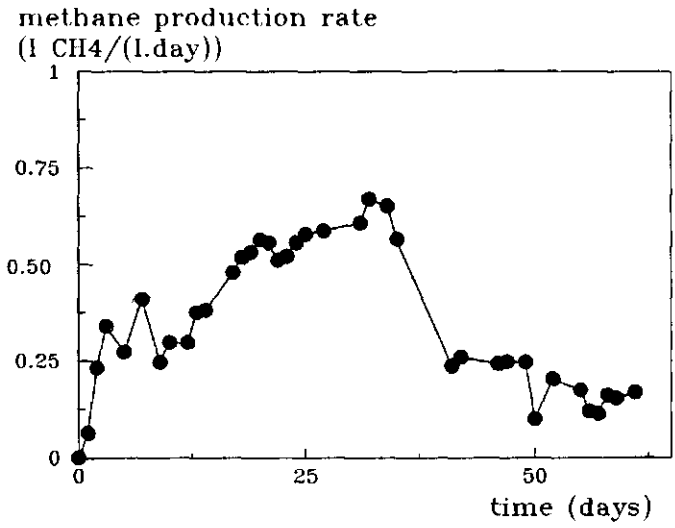


Fig. 9 Rate of methane production during dry digestion of Vegetable Fruit and Yard Waste with digested dewatered pig manure as the inoculum; inoculum factor 0.20. (●) CH_4-production rate

Regular start-up experiments

The second part of the experimental work concerned the determination of optimal ratio of digested VFY waste solids (inoculum) and total initial VFY solids for a so-called regular start-up of batch reactor. This ratio will be indicated in the following as the inoculum factor (I). On the basis of the results obtained in the first start-up experiments with dewatered digested pig manure another series of experiments was carried out (TABLE 2). An inoculum factor of 0.20 was tested with digested VFY waste as inoculum. In fact digested VFY-waste might represent a better inoculum than dewatered digested pig manure, since the bacterial population present in the digested VFY waste is adapted to the conditions during dry anaerobic digestion of VFY waste. Fig. 10 shows the results of the organic acids concentrations values during the experiment with an inoculum factor of 0.20. The methanogenic capacity, calculated with results from the standard methanogenic acitivity test described in the materials and methods section, which was added with the inoculum to the reactor amounted to 3.4 g CH_4-COD/(l.day) which is very similar to the start-up experiment with pig manure. During day 0 - day 50 leachate was not recycled.

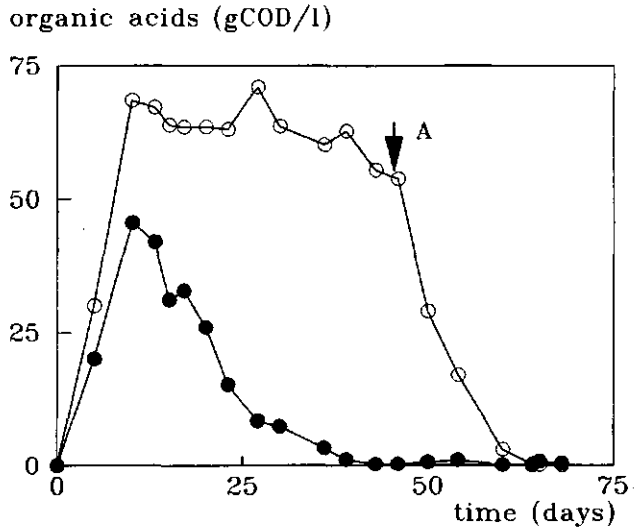


Fig. 10 Organic acids concentrations measured at different heights of the reactor during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with digested VFY-waste as inoculum; inoculum solids/initial total solids ratio 0.20;1(○) total organic acids at 0.5 m; ● total organic acids at 2.5 m. *(arrow indicates start of leachate recycle).*

As is shown in Fig. 10, the organic acids concentration varied within the reactor. In the upper part of the reactor the organic acids concentration remained rather stable from day 10 - day 50, while in the lower part of the reactor the organic acids concentration decreased to a value below 1 g COD/l at day 40. Fig. 11 shows the methane production rate of this experiment. Methane was produced at a constant rate beyond 10 days. Starting from day 50 leachate recycle was applied to assess the effect on the methane production rate and thus on the organic acids concentration over the reactor. From the start of the leachate recycle the methane production rate increased, and the organic acids concentration in the upper part of the reactor decreased concordantly. After 61 days the organic acids concentration was lower than 1 g COD/l. The methane yield amounted then 60 % of its potential methane yield, which amounts of 59 l (STP) CH_4/kg VFY-waste (TABLE 1). Higher values of the inoculum factor were tested in order to assess to what extent this might result in lower maximum values of the organic acids concentrations and higher pH values (TABLE 2).

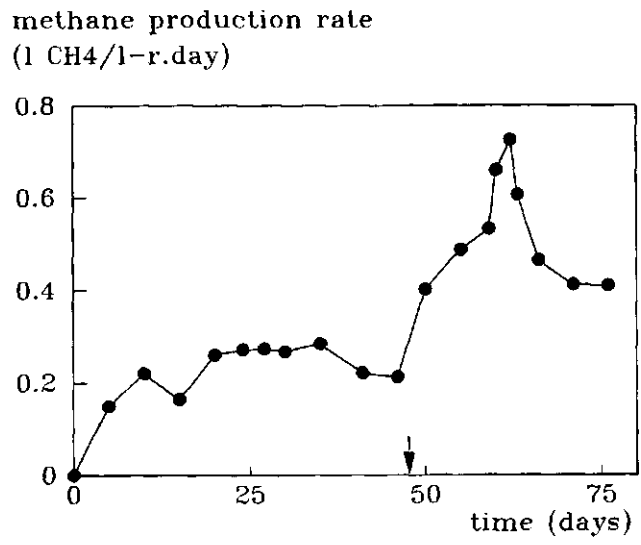


Fig. 11 Rate of methane production during dry digestion of Vegetable Fruit and Yard Waste with digested VFY-waste as inoculum; inoculum factor 0.20;(●) CH_4-production rate. *(arrow indicates start leachate recycle).*

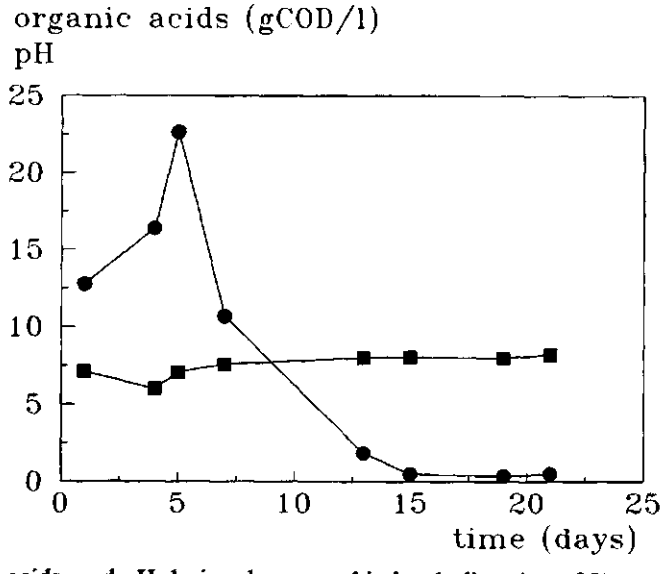


Fig. 12 Organic acids, and pH during dry anaerobic batch digestion of Vegetable Fruit and Yard Waste with digested VFY-waste as inoculum and application of leachate recycle; inoculum solids/initial total solids ratio 0.50;(●) total organic acids;(■) pH.

In the case this can be accomplished, could be achieved, the digestion process could proceed at higher rates, consequently also which means that the VS degradation rate, expressed in g COD/(l.day), would be higher. In the light of the results obtained so far, these experiments were carried out under conditions of leachate recycle from the start of the experiment. As expected, lower maximum concentration of organic acids and higher pH values were measured at I=0.5 in comparison to lower values of the inoculum factor (Fig. 12). Moreover the concentration of organic acids reached a value lower than 1 g COD/l after 14 days over the reactor. The concentration of VFA in the upper part of the reactor was very similar as the concentration of VFA in the lower part of the reactor. The calculated mean loading rate, i.e. from the batch load divided by the digestion time was 7 kg VS/(m^3.day). Assuming that 1 kg VS is equal to 1.4 kg COD, the mean COD loading rate over the digestion was 9.8 kg COD/(m^3.day). Higher values of the inoculum factor, i.e. of 0.77 or higher, don not result in higher mean loading rates. The mean volumetric biogas production rate was 1.3 m^3 STP/(m^3-reactor.day). In Fig. 13 the observed methane production rate during the experiment with an inoculum factor of 0.5 is shown. The methane production rate decreased strongly after 15 days.

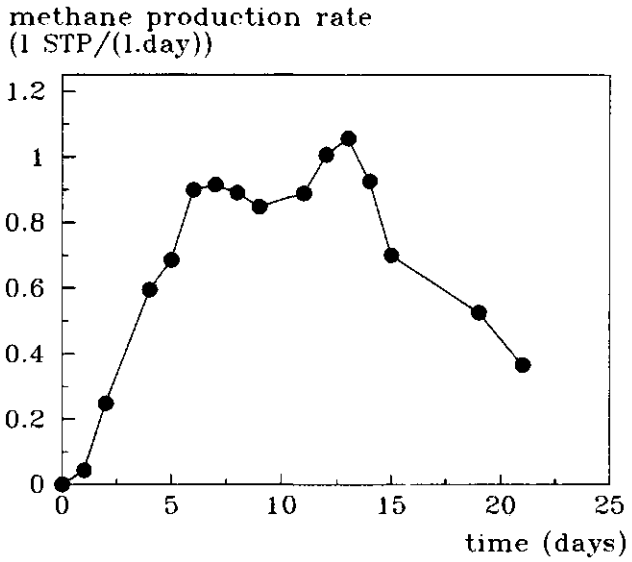


Fig. 13 Rate of methane production during dry digestion of Vegetable Fruit and Yard Waste with digested VFY-waste as inoculum; inoculum factor 0.50;(●) methane production rate.

DISCUSSION

For the first start-up of a digester treating VFY waste granular sludge is not a feasible inoculum. One likely reason for the poor performance of the start-up with VFY and granular sludge as the inoculum is that the NH_4^+-N concentration raises within a short period of time beyond the toxicity level for non NH_4^+-N adapted granular sludge. The methanogenic activity of granular sludge decreases with increasing ammonia concentration above 0.8 g N/l (8). In the case the ammonia concentration exceeds a value of 2 g N/l, an unadapted sludge as was used in the present experiments has to go through an adaptation period of several weeks. Such an adaptation period is characterized by an almost complete temporary cessation of methanogenesis (11). Since ammonia toxicity is related to the free (or: undissociated) ammonia the pH during the digestion is of importance (11,12,13). For our experiments the free ammonia concentration at pH 5.8 and an ammonium-nitrogen concentration of 3.2 g/l amounted to 2 mg/l. This value is much lower than the toxicity level of 80 mg/l free ammonia-nitrogen which has been reported elsewhere for sludge digestion (12,13). However, the tolerance for free ammonia depends strongly on the type of methanogenic bacteria in the sludge. As in granular sludge the predominant acetoclastic methanogen is of the *Methanothrix sp* type (14,15), the tolerance can be much lower in comparison to methanogenic biomass where *Methanosarcina sp* is predominant. In extreme environments, e.g. at high salt concentrations and/or at high organic acids concentrations *Methanosarcina sp* is often reported to be the predominating methanogen (16,17). As dewatered digested pig manure is adapted to an extreme environment, and could be added in higher amounts than granular sludge the start-up of the dry digestion of VFY-waste showed better results than the start-up with granular sludge.

As the results of the regular start-up exeriments are considered, identical results were expected as found in the first start-up experiments with digested dewatered pig manure. It was thought, that the digested VFY waste was predominated by a highly adapted microbial population more or less identical to the one in digested pig manure. The dry anaerobic batch digestion of VFY-waste also takes place at high organic acids concentrations and high NH_4^+-N concentrations (2-3 g NH_4^+-N/l). Digested VFY-waste shows a very similar maximum methanogenic activity (0.01 kg CH_4-COD/(kg.day) under standard conditions compared to digested manure. However, using digested VFY waste as the inoculum, a higher ratio (>0.20) of inoculum solids/total initial solids has to be applied compared to the start-up with dewatered digested pig manure. The reasons for this difference are not clear. The faster start-up of the dry digestion process with digested dewatered pig manure in comparison to digested VFY-waste might be related to the structure of the materials itself. The digested manure kept its sticky structure (probably caused by the use of polyelectrolyte as dewatering aid) when it is mixed with the VFY-waste and tap water prior to the start-up experiment. The impossibility to get a completely mixed substrate and inoculum at a total solids concentration of 30 %, i.e. to have a desintegration of the inoculum particles of several mm in size, probably caused the formation of methanogenic zones during the first phase of the digestion, which was quite severely overloaded at I = 0.20. The existence of these zones during dry anaerobic batch

digestion has been proved elsewhere (Chapter 4, this thesis). This formation of methanogenic zones might have resulted in a limited loss of methanogenic activity due to the pH drop and to the high organic acids concentrations prevailing during the first phase of the digestion. The digested VFY could also not be mixed homogenously with the substrate, which would also result in the formation of methanogenic zones and acidic zones. However, the digested VFY and VFY waste mixture showed a more homogeneous structure than the dewatered digested pig manure and VFY waste mixture. Here also methanogenic zones could be detected, but they were less effective in comparison to the experiment with digested manure.

The effect of leachate recycle on the rate of the digestion process was more distinct for VFY than was reported elsewhere for dry digestion of the organic fraction of MSW from a mechanical separation process (Chapter 2). This substrate has a mean particle size which is smaller than 20 mm. The much larger mean particle size of VFY-waste (TABLE 1) can be responsible for this different response to leachate recycling. It is likely, that in the latter case the inoculum is more spatial separated from the substrate than in the former case. The total solids concentration in a reactor must be low enough in order to have a certain amount of free liquid which is available for recycling. At an initial total solids concentration of 30 %, the maximum possible recycle flow amounted 0.3 $m^3/(m^3.day)$.

At a certain stage of the dry digestion of VFY-waste the nethane production rate decreased dramatically. At this stage of declining methane production rate, 55 % of the potential (=maximum achievable) methane yield was obtained and shortly before this time point the organic acids concentration reached a value below 1 g COD/l. This result suggests, that the hydrolysis of the remaining particles of the VFY-waste becomes rate limiting, and that the hydrolysis of the remaining particles is a rather slow process. The second part of the biogas (45 %) was produced in a twice as long period as the first part (55 %). It can be concluded, that during the digestion of VFY-waste the volatile solids of the VFY-waste are stabilized to a great extent, the moment 55 % of the potential amount of biogas is produced. The digestion time, which was defined above as the period needed for the potential methane yield to be obtained, can become longer than is economically feasible, because it a longer digestion time will increase the reactor volume needed. It is questionable, whether the costs for the higher reactor volume needed for maximum biogas yield can be compensated by the selling of biogas. It is proposed here, that the digestion time for a BIOCEL-reactor should be defined as the period that is needed for the concentration of the organic acids to reach a value below 1 g COD/l. The VFY-waste is sufficiently stabilized at this stage since the rate of hydrolysis, and hence the biogas production rate ($<<0.1$ $m^3/(m^3.dag)$) is very low.

To assess the value of I that can be recommended for a regular start-up of VFY digestion, the criteria for the optimal value of I have to be defined. The value of I must be high enough to prevent strong inhibition due to suboptimal pH values (lower than 6) and high organic acids concentrations ($>$ 10 g/l). These conditions will affect the maximum applicable loading rate of the digester negatively. On the other hand the value of I must be low enough to prevent a too short digestion time which will increase the time needed for filling and drawing the digester per ton of waste. Considering the assessment of the optimal values of I from the results, it should be mentioned here that the value of the optimal value for I cannot directly be determined by simply comparing the digestion times (DT 's) that are observed at certain values of I. The solids retention time (SRT), which determines the treatment capacity of the digester, is not equal to the digestion time,

as will be shown here. To compare the loading rates (treatment capacities) at different values of I, the solids retention time (SRT) must be calculated from the digestion time (DT). A batch reactor, as is used in our experiments, is therefore considered as a reactor with recirculation of the digested VFY-waste (Fig. 14). For such a reactor with recirculation of digested waste DT is defined according to equation (1):

$$DT = V/(Q_{VFY} + R) \quad (1)$$

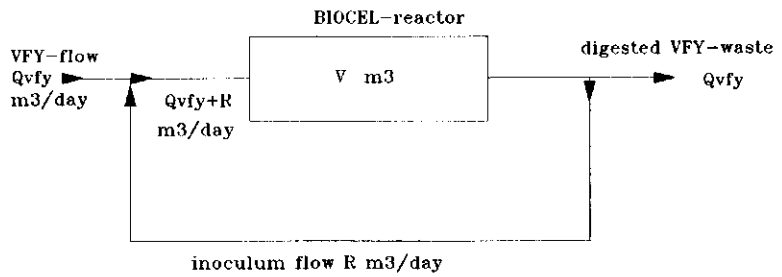
where V is the reactor volume, Q_{VFY} the mean flow of the VFY waste, and R is the recirculation flow of digested VFY waste. For a BIOCEL-reactor Q_{VFY} (m3/day) is the batch load divided by DT, R (m3/day) is the batch load of inoculum divided by the digestion time.

The solids retention time SRT for a reactor which is run with or without recirculation of digested waste is defined as:

$$SRT = V/Q_{VFY} \quad (2)$$

The solids retention time can be calculated from the DT and R by combining equation (1) and (2) to:

$$SRT = DT*(Q_{VFY} + R)/Q_{VFY}) \quad (3)$$



digestion time = DT = V/(Qvfy+R)
solids retention time = SRT = V/Qvfy
inoculum factor = I = R/(Qvfy+R)

Fig. 14 Schematic diagram of the hydraulic characteristics of a BIOCEL reactor

If the assumption is made that the compaction (in kg total solids/m3) of the VFY-waste is equal to the density of the digested VFY-waste, the inoculum factor can be defined as follows:

$$I = R/(Q_{VFY} + R) \quad (4)$$

The SRT can be calculated from DT and the inoculum factor I according to:

$$SRT = DT/(1-I) \quad (5)$$

In Fig. 15 the effect of the inoculum factor on the solids retention time is shown. The solids retention time decreases with the inoculum factor up to I= 0.5. From equation (2) it follows, that with a shorter SRT the value of Q_{VFY} is higher. It can be concluded, that at a higher inoculum factor a higher batch loading rate may be applicable. A shorter period of imbalance, i.e. a shorter period with low pH values and high organic acids concentrations, made this higher loading rate possible. The highest inoculum factor tested (0.77) did not result in a significant shorter solids retention time in comparison to the inoculum factor of 0.50. An inoculum factor of 0.77 means a short digestion time of 7-10 days.

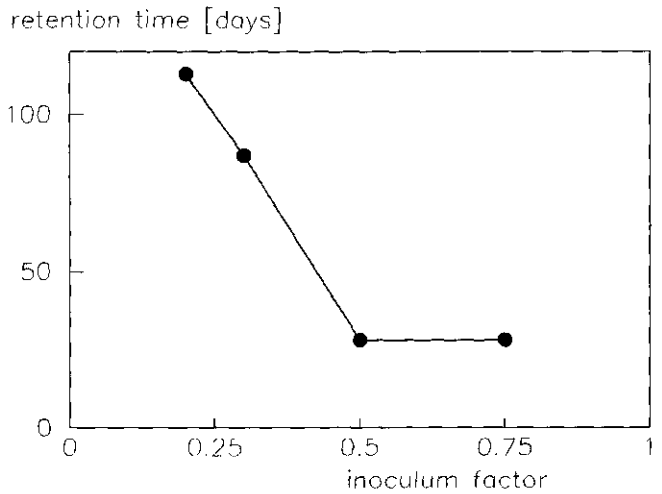


Fig. 15 Effect of the inoculum factor I (ratio digested VFY-waste solids/initial total solids) on the solids retention time during dry anaerobic digestion of Vegetable Fruit and Yard waste in a BIOCEL reactor.

As the BIOCEL concept is based on minimum costs for handling (filling and drawing of the reactor) the inoculum factor which should be applied must result in the shortest solids retention time possible in combination with a minimum of handling. An inoculum factor which is higher than 0.5, implies more handling per ton of waste, while the maximum loading rate is not positively affected.

At an inoculum factor of 0.50 the solids retention time was 28 days. At this solids retention time a stabilization rate (=loading rate) of 7 kg VS/(m^3.day) was obtained which is in the same range as was reported for mesophilic continuous dry anaerobic digestion (19). The low grade of technology which is needed for the BIOCEL-concept in comparison to continuous dry digestion systems, and the same potentials in terms of maximum loading rates makes this concept rather promising as an economic attractive treatment method for organic solid wastes.

CONCLUSIONS

The first start-up of dry anaerobic batch digestion of Vegetable Fruit and Yard (VFY-waste) waste, should be carried out using an inoculum adapted to high ammonia-nitrogen and high organic acids concentrations. Dewatered, digested pig manure is a better adapted inoculum, than methanogenic granular sludge from a Upflow Anaerobic Sludge Blanket reactor in combination with composted VFY-waste. Using the UASB sludge as the inoculum, prolonged digestion times were observed. The ratio of inoculum solids and initial total solids for digested pig manure for a succesful first start-up was 0.20, the digestion time was 43 days.

To obtain a maximum possible loading rate, leachate recycle was proved to be essential. When leachate recycling was omitted, even after 50 days a heterogenous distribution of methanogenic biomass and organics was found over the reactor. The maximum leachate flow that could be applied amounted 0.3 $m^3/(m^3.dag)$.

The ratio of inoculum solids and initial total solids (= I) for a successful regular start-up of a batch reactor is higher than for dewatered digested pig manure. A positive correlation was observed between the inoculum factor and the loading rate. The observed correlation between the inoculum factor and the solids retention time is caused by the shorter period of imbalance of acid formation and methane formation at increasing values of the inoculum factor. The solids retention time at a inoculum factor of 0.50 is 28 days, which is in the same order of magnitude as is reported for continuous dry anaerobic digestion at mesophilic temperatures (19). The loading rate that can be applied is also comparable with that reported for continious dry anaerobic digestion at mesophilic temperatures (19).

Notation:

COD	-	chemical oxygen demand
I	-	inoculum factor
DT	-	digestion time (days)
m3-r	-	m3 of reactor volume
MSW	-	municipal solid waste
Q_{vfy}	-	flow of vegetable fruit and yard waste
R	-	recirculation flow of digested vfy-waste
SRT	-	solids retention time
TS	-	total solids
VFY-waste	-	vegetable fruit and yard waste
VS	-	volatile solids
V	-	volume of the digester

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CHAPTER 7

DRY ANAEROBIC DIGESTION OF VEGETABLE FRUIT AND YARD WASTE IN A BIOCEL REACTOR ON PILOT PLANT-SCALE

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CHAPTER 7

DRY ANAEROBIC DIGESTION OF VEGETABLE FRUIT AND YARD WASTE IN A BIOCEL REACTOR ON PILOT PLANT-SCALE

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ABSTRACT

Dry anaerobic digestion of the source separated organic fraction of Municipal Solid Waste (Vegetable, Fruit Yard waste) was studied in pilot plant scale reactors (5 m^3, 450 m^3). The maximum loading rate that can be applied is 7 kg VS/(m^3.day) which is similar to the loading rate reported for experiments on laboratory scale. Per ton organic waste 90 m^3 (STP) biogas is recovered. A reactor temperature at start-up of 20 °C which was gradually increased to 35 °C results in a prolonged digestion time, while a temperature of 43 °C at start-up with a gradual decrease to 30 °C gave a similar digestion time as start-up at 35 °C. Particle size reduction of the VFY results in a longer solids retention time which is related to the reduced leachate recycle flow that can be applied. The optimum value for the inoculum factor I, i.e. the ratio of inoculum solids and the initial total solids at start-up, is 0.5 - 0.6. At this value of I the solids retention amounts to 30 days. At higher values of I longer retention times are observed due to a suboptimal leachate recycle flow rate. At lower values of the inoculum factor (0.40 or lower) the solids retention time was 50 days or longer due to the relatively long period of suboptimal conditions (low pH, high organic acid concentrations). Thermal drying and aerobic post-treatment (after-composting) as well are applicable to produce compost in the BIOCEL process.

INTRODUCTION

So far, dry anaerobic digestion of the source separated organic fraction of MSW, the Vegetable Fruit and Yard waste (VFY) in the BIOCEL process has been studied in laboratory scale reactors with a maximum working volume of 78 liters (chapter 6, this thesis). The BIOCEL process is based on batch-wise digestion of solid organic wastes materials, which are brought into the reactors as static pile. Due to the batch-wise operation and the absence of mixing in a BIOCEL reactor a characteristic pattern is observed: initially there is a build-up of volatile organic acids with a concomitant pH-drop, followed by a period of decreasing concentrations of volatile organic acids and an increasing pH. The shorter the initial "sour" period, the higher the mean degradation rate of the volatile solids. The maximum (batch) loading rates (averaged over the total period of the digestion expressed as kg VS/m^3.day) which could be applied at 35 $^{\circ}$C were in the same order as those reported for continuous dry digestion systems on pilot plant scale (chapter 6, this thesis). The potentials of the for practical application have to be assessed from results of relevant pilot plant scale experiments and full scale systems. Preliminary experiments with a BIOCEL-reactor on pilot plant scale (5 m^3) gave promising results (Koster et al, 1988).

Apart from the digestion process the heavy metal content of the digested residue plays a role in the applicability of the BIOCEL process, since the production of compost implies a major advantage of the process. Although the heavy metal concentrations are determined by the heavy metal concentration of the input, the digested residue is analysed on these components. The compost produced from the process has to meet certain meet standards for the application as soil conditioner. The actual heavy metal content of the residue will be compared to the Dutch future standards for compost.

The digested residue needs further processing because the total solids concentration is not high enough (c. 40-45 % TS) for additional treatment such as sieving and removal of inert solids (metals, glass) to produce a valuable compost. In this chapter several post treatment techniques are investigated such as thermal drying and aerobic composting. The present study deals with several aspects of up-scaling of the dry anaerobic digestion process in a BIOCEL reactor. Important process factors, such as leachate recycle, temperature regime and the optimum inoculum factor (ratio of inoculum solids and initial organic waste solids plus inoculum solids) will be investigated.

The objectives of the present study are:

- the upscaling of the process from 78 l to 5 m^3 and 450 m3 to determine the effect of leachate recycle and the minimum flow needed
- effect of several values of I (inoculum factor)
- the effect several ways of heating the process
- post treatment and quality of the residue.

MATERIALS AND METHODS

Apparatus

The experiments were carried out in spherical tank reactors made of stainless steel, which were 2.40 in height and 1.75 in diameter for the 5 m^3 reactor. The 450 m^3 reactor was 4.5 m in height and 12 m in diameter. A schematic diagram of the digesters used is shown in Fig. 1. A perforated plate (holes of 1 cm) was placed 30 cm above the reactor bottom to prevent clogging of the outlet during leachate recycle. Leachate was recycled to the top of the reactors with peristaltic pumps. The flow rate was monitored by registrating the rounds of the pump with a magnetic counter. Leachate recycle was carried out intermittently, dependant on the amount of leachate that was collected in the leachate chamber. A level indicator which was placed 5 cm above the reactor bottom switched on the pump when the leachate level reached this height. One round of the pump corresponded to a certain volume of leachate. The lid of the reactor was placed in a water lock. The reactors were isolated with glass wool with a thickness of 10 cm.

The reactor was placed on a plate of glass foam. The mean reactor temperature of 35 $^{\circ}C$ ($\pm$ 2) was maintained by pumping hot water from a boiler through a metal coil, which was placed inside the reactor. The temperature was measured on three points in when the level the reactor with detectors which were 40, 75 and 1.25 m respectively.

Gas production was measured with dry gas meters, which indicated the volume of the gas produced at a certain temperature as the volume of the gas at 15 $^{\circ}C$. Before the gas meters a bypass was installed for gas sampling.

Samples for analysis of organic acids, ammonium nitrogen and pH were taken at three points of the reactors, i.e. from the leachate collection chamber and from two sample ports where samples were taken at a depth of 0.25 m inside the reactors.

The mixture of raw solid waste and inoculum (digested solids) was brought into the reactor with a conveyor belt. For each experiment the weight of the raw solid waste and the weight of the inoculum was determined with a balance. After termination of an experiment the reactor was emptied with a crane.

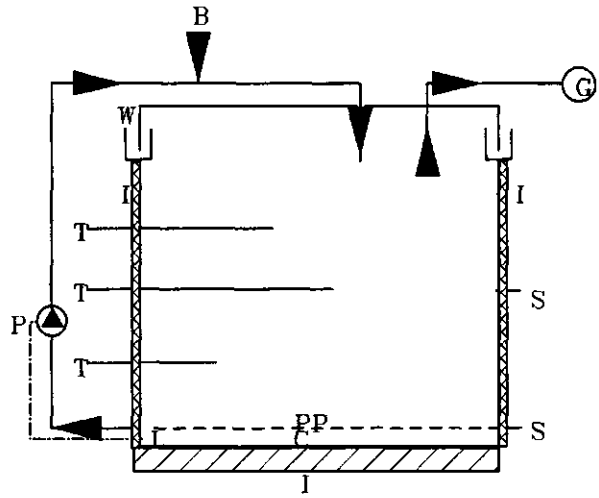

Fig. 1 Schematic diagram of the pilot plant reactors (working volume: 5 m^3) as used in the present study; C: leachate collection chamber, G: gas meter, I: insulation material, L: level indicator, P: peristaltic pump, PP: perforated plate, S: sample ports, T: temperature sensors, W: water lock B:Boiler.

Procedures

A series of digestion experiments was conducted at different values for the inoculum factor I the ratio of digested solids and total amount of solids at the start of the experiment. The VFY waste was obtained from a source separation of Municipal Solid Waste from the city of Apeldoorn, the Netherlands. The mean total solids concentration of the VFY amounted to 36 % TS (w/w) and the volatile solids content amounted 65 % of the total solids. The inoculum for each experiment was obtained from the former digestion experiment. The total solids of the digested VFY amounted to 42 % TS. After weighing the fresh waste and the digested waste were roughly mixed and brought into the reactor (without further compression) using a conveyor belt. The initial density amounted to 280 kg total solids per m^3_r. Tap water was added when the initial total solids of the mixture exceeded 35 % w/w. At total solids concentrations exceeding 35 % TS, because leachate recycle is not possible by lack of free moving water.

Gas production and reactor temperature were registrated 2-3 times a week. Samples of biogas and reactor contents were taken with the same frequency.

Analyses and calculations

Samples of the biogas were analyzed for CH_4, CO_2 and H_2 using a gas chromatograph equipped with a TCD detector and with two parallel columns: a column of 1.5 m x 1/8", teflon packed chromosorb 108, 60-80 mesh and a 1.2 m x 1/8" mol. sieve 5A, 60-80 mesh. The column split ratio was 1:1. Samples of 100 μl were taken from the reactors with a glass tight syringe. The volume of the biogas produced was measured by reading a dry gas meter three times a week. The gas volumes produced were recalculated to standard temperature and pressure (STP: 0 °C, 1 bar). The samples taken from of the reactors were analyzed for pH, total organic acids concentration, and ammonium-nitrogen as described in chapter 2. Digestion was considered to be completed when the concentration organic acids was dropped below 1 g COD. The period required to reach this value is defined as the digestion time (DT) (Chapter 6). To compare the experiments at different values of I, the solids retention time was calculated from DT as is descibed in Chapter 6. For a reactor with recirculation DT, SRT is defined according to equation (1):

$$SRT = DT*(Q+R)/Qw) \quad (1)$$

where Qw the average amount of the solid waste fed to the reactor, and R is the amount of recirculated digested solid waste. For a BIOCEL reactor Qw (m^3/day) is the load of the reactor divided by the digestion time, R (m^3/day) is the average amount of the inoculum fed to the system per day divided by the digestion time.

The minimum value of SRT was assessed by determining the time needed for maximum gas production from the VFY waste at standard conditions, i.e. pH = 7, and the VFA concentration is below 1 g COD/l at a temperature of 35 °C. The SRT determined at this condition was 15 days.

RESULTS AND DISCUSSION

Effect of up-scaling and leachate recycle

To investigate the effect of up-scaling (from 78 l to 5 m^3/400 m^3) and the effect of leachate recycle (0.3 m^3/(m^3.day)) two reactors were started up with an inoculum factor value I of 0.35. This first-start-up was carried out with digested dewatered pig manure as methanogenic inoculum. The second and following series of experiments were carried out using digested waste as inoculum. In Figs. 2,3,4 and 5 the results are shown of the experiments concerning the efffect of leachate recycle. The reactor with leachate recycle

showed a digestion time (DT) of 42 days, which corresponds to a solids retention time (SRT) of 63 days (Fig. 3). After 42 days the organic acids concentration was lower than 1 g COD/l. Then 50 % of the potential methane yield was obtained, which means a yield of 35 m^3 (STP)/ton solid waste, or 70 m^3 (STP) biogas. The biogas production rate decreased significantly at this point, indicating that the hydrolysis of the organic compounds in the VFY waste became rate limiting. In fact the VFY has a high grade of stabilization at this stage.

The value of DT is quite similar to what has been reported for dry digestion of VFY in a 78 liter BIOCEL reactor (Chapter 6). Apparently, as far as the volume is concerned, scaling-up does not affect the rate of the process, provided that leachate recycle is applied at a rate of 0.3 $m^3/(m^3.day)$.

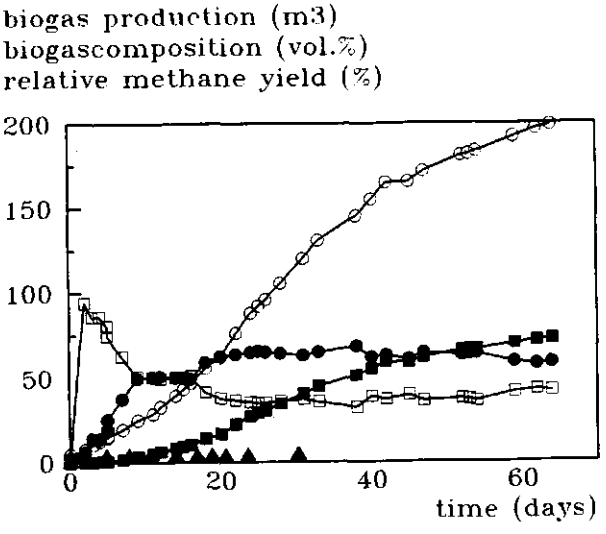

Fig.2 Biogas production and biogas composition in dry digestion of VFY waste in a pilot plant scale BIOCEL digester with leachate recycle;(○) sum biogas; (●) vol. % CH_4; (□) vol. % CO_2; (▲) H_2; (■) relative CH4 yield.

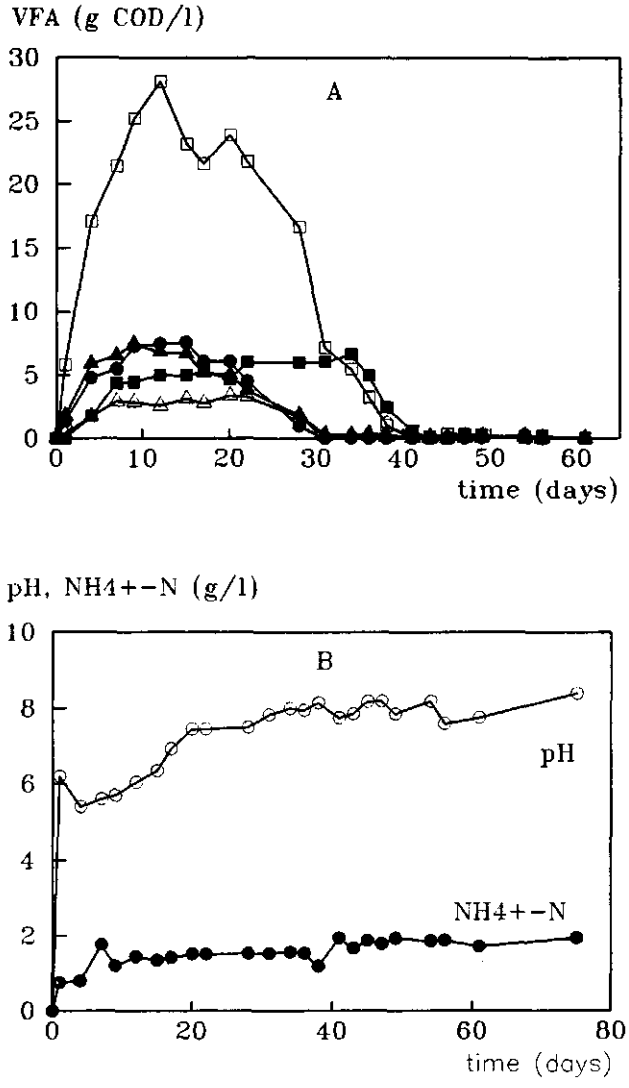

Fig. 3 The course of the VFA concentrations (A) and ammonium nitrogen concentrations and pH (B) in dry anaerobic digestion of VFY waste in a pilot plant scale BIOCEL reactor with leachate recycle; (□) total VFA; (▲) acetic acid; (△) propionic acid; (●) butyric acid;(■) valeric acid

Even after 180 days the reactor without leachate recycle did not show a completed digestion. At that stage leachate recycle (0.3 $m^3/(m^3.day)$) was started in this reactor and resulted in a completed digestion within 20 days additionallly (Fig. 5A). Although the VFA concentration did not decrease until the leachate recycling started, the pH increased from pH = 6.3 up to pH = 8. As the ammonium-nitrogen concentration is considered, a concomitant increase of this parameter is found (Fig. 5B). Presumably the buffering action of the ammonium is responsible for this phenomenon. The effect of leachate recycle in a laboratorium scale reactor of 78 liters was much less pronounced (Ten Brummeler et al., 1991b).

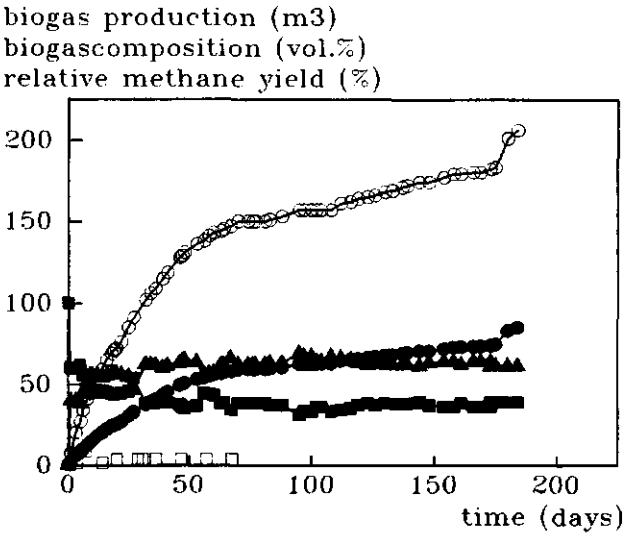

Fig. 4 Biogas production and biogas composition in dry digestion of VFY waste in a pilot plant scale BIOCEL-reactor without leachate recycle;(○) sum biogas;(▲) vol. % CH_4;(■) vol. % CO_2;(●) relative methane yield (□) H_2

Effect of the inoculum factor on the solids retention time

As was reported elsewhere (Ten Brummeler et al., 1991, Chapter 6), the rate of the digestion process in a BIOCEL-reactor is determined by the extent of imbalance between acid formation and methane (acid consuming) formation. A higher amount of inoculum will result in a decreasing retention time (SRT) because the period of severe imbalance becomes shorter than at lower inoculum factors. Fig. 6 shows the effect of the inoculum factor (I) on DT. It is clear that a relation exists between I and DT. At I = 0.55 a retention time of 30 days, which corresponds to a mean VS (batch) loading rate of 7 ($kg/m^3.d$), is found.

The calculated STR at I=0.55 is in accordance with the SRT of 28 days which has been found in experiments on 78 liters scale, but is much longer than the SRT under standard conditions which amounts 15 days. The inhibition at I=0.55 or higher by a low pH and high VFA concentrations was less relevant, so other limiting factors determined a further improving SRT at increasing I. At I= 0.77 and 0.9 a longer solids retention time is required, which amounts 47 days and 60 days respectively. As the concentrations of the organic acids during the experiments with different values of I are considered (Fig. 7), the reason for a longer retention time is not clear, since significantly lower concentrations at I=0.77 and 0.9 were detected than at I = 0.3 and I = 0.5.

A likely reason might be the lower applicable initial rate of leachate recycle which can be applied at higher values of I. The increasing value of I affects the initial porosity of the waste/inoculum mixture negatively, because the digested solid waste has a higher density (kg solids/m^3) than the raw waste.

To describe the influence of I on SRT it was tried to develop a simple model. The following assumptions are made: the initial methanogenic activity of the inoculum is 0.02 (kg COD/kg.d), the pH is higher than 6.5, the inoculum and solid waste are initially spatially separated in the reactor, and the methanogenic biomass and the VFY waste are completely mixed. In fact the reactor is subdivided in acid-containing compartment and an acid-consuming methane producing compartment (Fig. 8). In this model the leachate transports the organic acids to the degrading organisms of the inoculum and stimulates colonization of the fresh waste with methanogens.

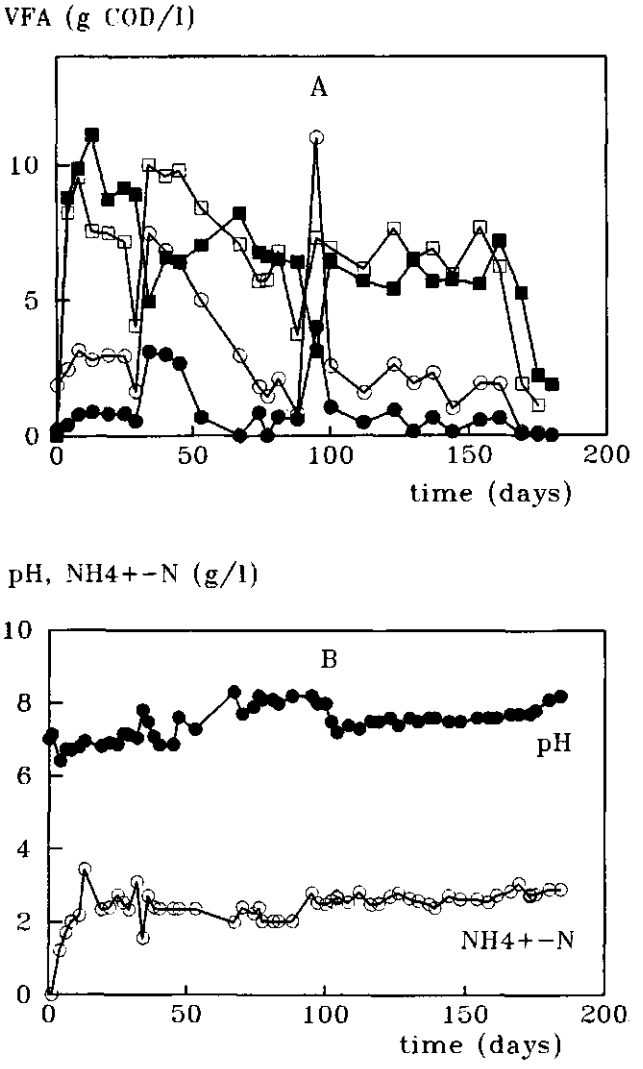

Fig. 5 The course of the VFA concentrations (A), and ammonium nitrogen concentrations and pH (B) in dry anaerobic digestion of VFY waste in a pilot plant scale BIOCEL reactor without leachate recycle; (□) acetic acid;(○) propionic acid; (■) butyric acid; (●) valeric acid.

The minimum flow that is needed for an optimal methane production rate can be calculated from the following equation :

$$Q = M/Cvfa \qquad (2)$$

where Q is the leachate recycle flow (m^3/day), M the total methanogenic capacity (kg COD/day) and Cvfy the concentration of Volatile Fatty Acids (kg COD/m^3). In Fig. 9 the minimum leachate recycling flow rate is shown as a relation of I at 5, 15 and 25 g VFA-COD/l respectively. From Fig. 9 can be concluded, that indeed a higher flow rate of the leachate is needed with an increasing inoculum factor. At I=0.77 the maximum organic acids concentration amounted 7 kg COD/m^3, mainly acetic acid. The minimum leachate flow rate which is needed to prevent rate limitation amounts 1.4 (m^3/m^3.d). The actual flow rate was 1.0 (m^3/m^3.d), which is below the minimum level to prevent rate limitation by a suboptimal substrate supply to the methanogenic biomass. The higher retention time which is found at I=0.77 in comparison to the findings at I=0.55 suggest, that the suboptimal leachate flow rate is the main factor controlling the rate of the digestion process in the experiments described here. Although it was expected that at higher I values substrate inhibition of the methanogenic biomass should be of decreasing importance and should result in lower minimum SRT values, the minimum SRT did increase. The rate limitation is also a result of the fact that the fresh and digested (inoculum) solids are just roughly manually mixed before start-up. Another way of mixing, for instance in a mixing drum, possibly could reduce the minimum leachate flow rate necessary. The initial spatial separation of inoculum and substrate (organic acids) in the reactor is unlikely when the inoculum and raw organic waste solids are mixed more intensively. However, for other reasons it is questionable if an inoculum factor of 0.77 is attractive. The BIOCEL concept is based on the application of rather plain technology and a minimum reactor handling (filling and drawing).

Since application of inoculum factor of 0.77 implies a digestion time of only 7-10 days, this means that a reactor has to be loaded once a week, and consequently processing of 1 ton of solid waste needs the handling intensity for 5.6 m^3 reactor. An inoculum factor of 0.5 needs handling for 2.57 m^3 reactor. Since an inoculum factor of 0.77-0.9 does not result in a lower solids retention time an inoculum factor of 0.5-0.6 is more attractive for practice.

The effect of the leachate flow rate was also observed in experiments conducted with VFY waste reduced in particle size with a shredder before the digestion. Particle size reduction was thought to be essential for a higher degradation rate of the volatile VFY-solids.

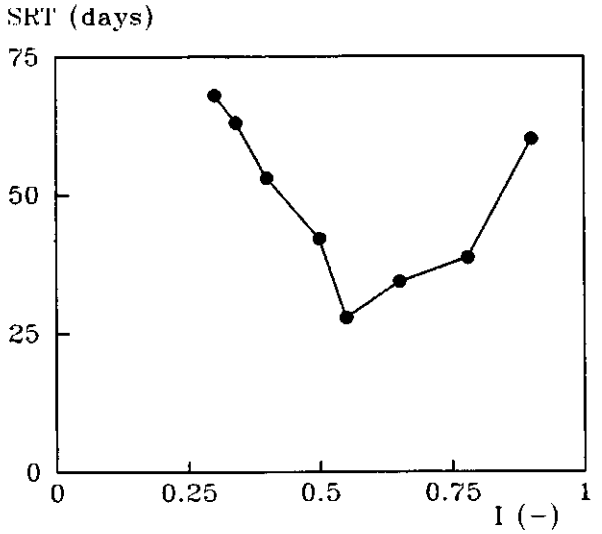

Fig. 6 The effect of the inoculum factor on the solids retention time during dry anaerobic digestion in a BIOCEL reactor on pilot plant scale.

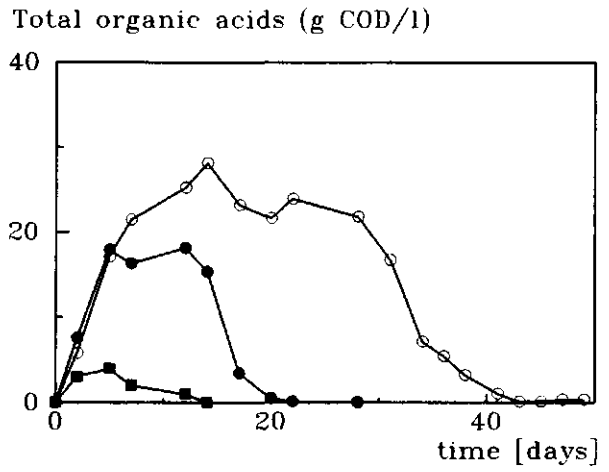

Fig. 7 Relation of the organic acids concentrations and the inoculum factor I during dry anaerobic digestion in a BIOCEL reactor on pilot plant scale; (○) I=0.3;(●) I= 0.50;(■) I=0.77.

Due to the reduced porosity of the solid waste, the maximum possible leachate flow rate was 0.5 (m^3/m^3.d) with an organic acid concentration of 15 g/l during day 0-day 5. A solids retention time of 55 days was found at an inoculum factor of 0.5. The initial acid formation rate and the maximum methane yield of shredded VFY waste did not offer any significant differences with non-shredded VFY waste. Because of the negative effect on SRT the shredding of the VFY waste before the digestion was omitted.

Another factor effecting the maximum applicable leachate flow rate is the height of the reactor. In practice it is convenient to build compact reactors as high as possible to minimize the cost for ground area.

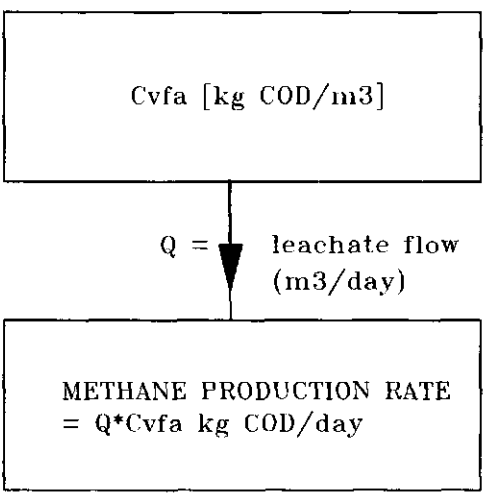

Fig. 8 Two compartment model for the initial phase during the dry anaerobic digestion in a BIOCEL reactor.

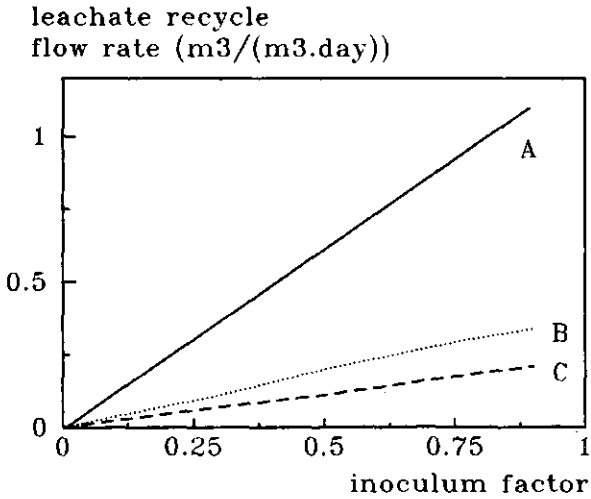

Fig. 9 Threshold levels of the leachate recycle flow rate as a function of the inoculum factor at several organic acids concentration;(A) 5 g COD/l;(B) 15 g COD/l;(C) 25 g COD/l; *the area above the individual lines indicate the values of the flow rate that are sufficient to prevent rate limitation by suboptimal substrate flow to the methanogenic biomass.*

As the porosity of the inoculum/raw solid waste mixture in the lower part of the reactor is reduced at increasing height of the digesting mass, the leachate flow rate might also be reduced below the optimum value. As the reactors of the present study were 2.3 m in height, the process has to be tested in a reactor with an height of c. 5 m.
For the practical application of the BIOCEL process this aspect of upscaling plays an important role since ground costs will be limited at these reactor heights. In one of the next paragraphs results of the final up-scaling are presented.

Influence of temperature

In previous investigations we found that the optimum temperature for the dry anaerobic digestion process in the BIOCEL process in the mesophilic temperature range is 35-40°C (Chapter 3). At temperatures beneath 30 °C the imbalance of the process by a higher acid formation than methane formation is inevitable. However, to maintain the reactor

temperature above 30 °C right from start-up might be hardly feasible, as the heating of solid waste mixture can be more difficult than heating a slurry because of the lower heat conductivity of the solid waste mixture in comparison to the slurry. In particular situations the temperature of the reactor input can be higher due to microbial activity by aerobic micro organisms during storage before the waste is collected, especially in summer time. In winter time the raw waste generally is 20 °C or lower. Heating of the digesting mass after start-up might be problematic, due to limited input of heat to reactor with the leachate. In order to assess different temperature regimes, three start-up experiments with an inoculum factor at 0.5 were carried out. One reactor was maintained at 35 °C (± 2), another reactor started at 43 °C, i.e. the temperature of the waste after a 2 day storage period before reactor loading and the temperature was allowed to decrease to 30 °C. The third start-up of a reactor was carried out at a gradually increasing temperature, viz. from 20 °C to 35 °C at 1.5 °C increments daily.

TABLE 1 provides the assessed minimum SRT's for the three temperature regimes. The start-up experiment at 43-30 °C gave similar results as the start-up experiment at 35 °C. In this experiment the DT amounted to 15 days. The temperature slowly decreased but remained higher than 30 °C during the digestion period. The reactor which was started at 20 °C required a significant much longer retention time, due to the relatively much higher acid formation rate compared to the methane formation rate.

TABLE 1 Influence of different temperature levels on the solids retention time during dry anaerobic digestion of solid organic waste on pilot plant scale

process temperature (°C)	SRT (days)
35	30
43..30	30
20..35	61

This resulted in a longer period with high organic acids concentrations and low pH values, which again negatively affected the required solids retention time. These results imply that directly after of start-up the temperature of the digesting mass should be in the optimum range of 35-43 °C, which can be roughly considered as the optimum temperature range. In this way a prolonged digestion time which is caused by a period of imbalance of the digestion process can be prevented.

Results of 450 m³ digester

Considering the results of the 5 m³ digesters, two important questions should be answered during the final phase of the pilot scale investigations. The first question is, whether the digestion process is able to proceed at larger digester heights, since the height of the 5 m³ digester was only 2.3 m. The height of the reactor should be as high as possible to limit the demand for ground area. The maximum height of the digester is likely to be determined by the actual porosity of the solid waste bed, since the rate of the leachate recycle will depend on the initial porosity of the bed. The necessity for a minimum leachate recycle rate is discussed earlier in this chapter. The second question that should be answered is whether it is possible to produce a valuable compost from the digested residue. The production of such a compost is essential for the applicability of anaerobic digestion of VFY waste for practice in the Netherlands. Therefore the digested VFY residue of the 450 m³ digester is used for investigating several post treatment methods. Also the heavy metal content of the compost will be determined and discussed.

Digester performance

The digester of 450 m³ was started up at I= 0.5. The digester was similar to the digesters of 5 m³, accept that the system was not heated with a hot water boiler and a coil place inside the digester, but by heating the leachate with a heat exchanger. The digester was started up for three subsequential digestion runs. The results of the third run, are presented in Fig. 10, 11 and 12. From Fig. 10 can be concluded that the digestion process proceeds well. Within 20 days the biogas yield amounts to 90 m³/ton organic waste, with a mean methane yield of 55 vol. %. In the experiments with the 5 m³ digesters 15 days is found for DT at I=0.5.

From Fig. 11 it appears, that the optimum digester of 35-40 °C temperature is established only after 5 days. As was discussed earlier, a period with a suboptimal digester temperature, can increase the digestion time due to high fatty acids concentrations. In Fig. 12 it apppears that the maximum VFA concentrations is as high as 18 g VFA-COD/l and decreases after 5 days. The digestion time amounts to 20 days under these conditions. Regarding the time needed for heating the digester up to 35 °C, it can be concluded that the digestion time can be shortened by accelerating the heating, so that the digester has its optimum temperature of 35-40 °C within 1 day. As in the experiment the leachate was already recycled at maximum rate, this cannot be carried out by increasing this rate. It can therefore be recommended to heat the waste before it is brought into the reactor, e.g. by heating the moisture that is added to decrease the total solids content down to 30 %.

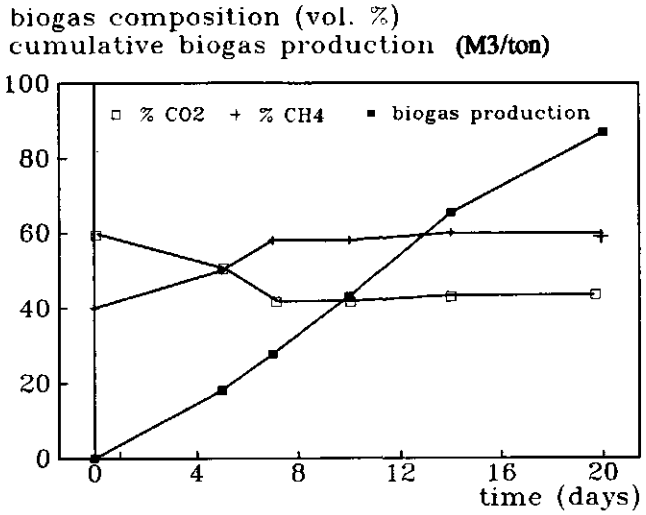

Fig. 10 Cumulative biogas production and biogas composition during anaerobic digestion of solid waste in the 450 m³ digester.

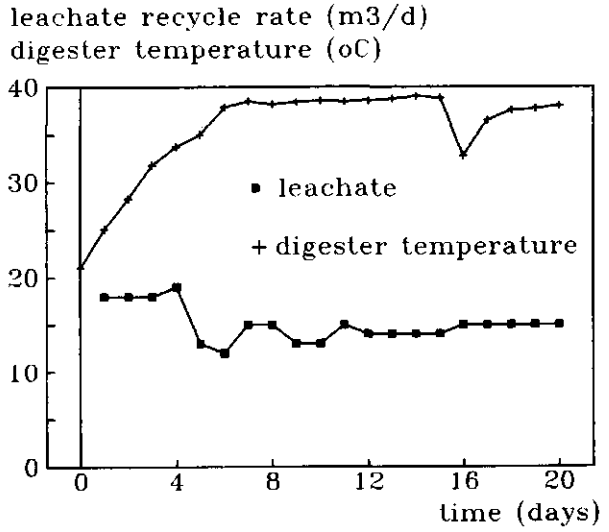

Fig. 11 Digester temperature and maximum applicable leachate recycle rate in the 450 m³ digester.

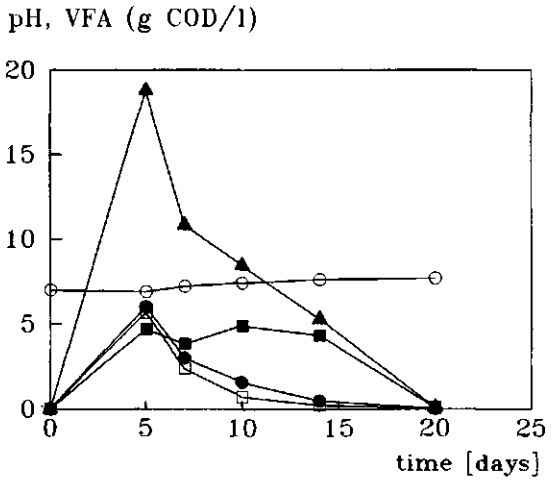

Fig. 12 VFA concentrations and pH during anaerobic digestion of solid waste in the 450 m^3 digester. (○) pH; (▲) total VFA 's; (●) acetic acid;(■) propionic acid; (○) butyric acid.

Post treatment of the digested residue

The digested residues have a mean total solids concentration of 40 %. Although the stability is presumably high enough, a secondary treatment step is necessary to yield a useful end product or compost. This treatment must result in an increase of the total solids content up to that of aerobically produced compost, c. 65 % TS. Therefore an industrial scale fluid bed manure dryer was used for drying experiments. An additional effect of this thermal treatment is the disinfection by the relatively high temperature (70-80 °C) that is reached in the drying mass. 10 tons of digested VFY waste was dried in this way up to 80 % TS. Due to problems with clogging of the fluid bed floor plate the waste had to be sieved. This was possible only when the digested waste was mixed 1:1 with dried compost. In TABLE 2 the composition of the residue before and after drying is given. During the drying also condensate water is produced, which is 0.2 m^3 per ton of 'fresh' waste.

TABLE 2 Composition of wet and dried digested VFY waste

	% TS	% VS[2]	C[1]	N[1]	P[1]
before drying	40	35	150	6	5
after drying	86	35	150	6	5

[1]: g/kg total solids;

A main disadvantage of a thermal treatment is the high energy demand. In the anaerobic digestion process biogas is produced, that can be applied as fuel for the thermal dryer. However, since thermal treatment consumes approximately 30 % (28 Nm^3) of the biogas, there is less energy output from the process. An alternative method for thermal treatment is a secondary treatment by aerobic composting. During aeration of the residue heat is produced by aerobic micro organisms; by the aeration water vaporizes from the residue and a dry stable end product is produced. Since the easy degradable part of the waste is converted to biogas, the rate of the aerobic degradation will be rather low. To enhance the heat production during the aeration, a support material should be added. In our experiments two materials were tested: wood chips and saw dust. The results are shown in TABLE 3. The best results were obtained with saw dust. From the mean temperature during the composting can be concluded that the digested residue is stable when stored in a static pile. The most important effect of the support material on the rate of the secondary composting is therefore the stimulation of heat production due to degradation of the organic matter in the support material. This effect results in dry residue that can easily be sieved to produce a valuable compost.

TABLE 3 Effect of secondary aerobic treatment on the total solids content of BIOCEL residue (total solids in % w/w)

type of residue	day 0	day 30	mean pile temperature (°C)
no additions	40	41	36
+ wood chips	57	59	45
+ saw dust	58	68	53

Heavy metal content of the digested residue

The useful products of dry anaerobic digestion according to the BIOCEL-concept are biogas and a compost-like residue. The utilization of the residue of the digestion depends strongly on the heavy metal content. Since compost is mostly used as a soil conditioner in agriculture, the use is restricted to compost with a very limited concentration of chemical contaminations like heavy metals. Only composts (produced aerobically and anaerobically as well) that are produced from source separated organic fraction of MSW will meet the 1995-standards for 'compost' in the Netherlands.

The heavy metal content of residues from four digestions was determined. In TABLE 4 the results are given, as well as the future standards in the Netherlands. The heavy metal content of the digested VFY-waste appears to be below the Dutch future standards for compost.

TABLE 4 Heavy metal contents (mg/kg dry solids) of the compost-like end-product produced after dry anaerobic digestion in the BIOCEL process

	Cr	Cu	Ni	Pb	Cd	Zn
BIOCEL residue	39	29	12	17	0.8	150
Standards[1]	100	50	50	150	1.0	250

[1]:1995-1999 Standards according to BOOM (Besluit Overige Organische Meststoffen, 1992).

CONCLUSIONS

Dry anaerobic digestion of Vegetable Fruit and Yard waste wastes in a BIOCEL reactor on pilot plant scale (5 m^3, 450 m^3) proceeds at similar rates as was found in lab scale reactors. The effect of leachate recycle on the rate of the digestion process is more obvious than in lab scale reactors. The absence of leachate recycle (0.3 $m^3/(m^3.day)$ resulted in a digestion time of 180 days. Dependent on the grade of mixing of fresh substrate and the inoculum, leachate recycle is essential to achieve a high rate digestion. Particle size reduction of the VFY waste resulted in a prolonged digestion time due to a strongly decreased maximum leachate recycle flow rate. The optimum flow rate of the

leachate recycle depended on the inoculum factor and was in the range of 0.8 - 2.5 $m^3/(m^3.day)$. The optimum inoculum factor (I), i.e. the ratio of digested solids and total initial solids (inoculum solids plus VFY waste solids), is in the range 0.5-0.6. A solids retention time of 28-30 days is found, which is identical to results from lab scale experiments. The maximum volatile solids loading rate amounts to 7-10 kg $VS/(m^3.d)$. At an inoculum factor of 0.4 or lower longer retention times and lower loading rates can be applied. At these values for I the period during which suboptimal conditions (high organic acids, low pH values) are observed is too long to prevent strong inhibition of the methane formation. The suboptimal conditions are due to the higher grade of imbalance of acid formation and methane formation at low values of the inoculum factor.

The temperature at start-up should be above 30 °C. Start-up at 20 °C and gradually increasing to 35 °C resulted in a retention time of a factor two higher than start-up at 35 °C. If the organic solid waste had a temperature of 43 °C, which was observed in the summer period due activity of aerobic micro organisms during storage, further heating during the digestion was not necessary, and a similar solids retention time was found as with reactor start-up at 35°C in the winter period. Thermal drying and aerobic post-treatment (after-composting) as well are applicable to produce compost in the BIOCEL process. Aerobic post composting results within 30 days in a dry residue (65 % TS). The addition of a support material, such as wood chips or saw dust, to the residue to increase the porosity is essential. Thermal drying with an industrial drier is also possible and results in a pasteurized, and therefore plant pathogen-free compost. However, the drying process consumes 30 % of the biogas produced during the process, and can be energetically less favourable than post composting, provided the aerobic after-composting does not need any energy supply for aeration.

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CHAPTER 8

SUMMARY AND CONCLUSIONS

Potentials of anaerobic digestion of the organic fraction of Municipal Solid Waste

This thesis describes the technological potentials of dry anaerobic digestion of the organic fraction of Municipal Solid Waste using batch systems.

In Chapter 1 it is argued that the potentials for anaerobic digestion of the organic fraction of MSW are great. Since 50 % of the Dutch MSW produced consists of an organic fraction (the Vegetable Fruit and Yard waste) which can be collected through source separation, 180,000,000 m^3 natural gas equivalents and 1,200,000 tons of compost can be produced from VFY waste. As the biogas can replace fossil fuels, anaerobic digestion can contribute, to some extend, to the limitation of CO2 emissions from fossil fuels.

The potentials of anaerobic digestion for MSW management have not yet been sufficiently explored on full scale. This is mainly due to the lack of appropiate digester concepts, which are technologically and economically successful.

The existing systems for anaerobic digestion of organic solid waste, particularly the organic fraction of MSW, were reviewed in a literature study. So far the only way anaerobic digestion of MSW is taken advantage of at significant scale, is the recovery of biogas from landfills. In most of these landfills anaerobic digestion takes place spontaneously, however the process is for the most part mot controlled here.

The most promising digestion concepts for anaerobic digestion of MSW are the so-called 'two-phase' systems, and the 'single-stage dry digestion systems' at high solids concentrations (higher than 20 % TS), based on batchwise or continuously fed digesters. Full-scale application of the two-phase systems were not described in the literature at the start of the research programme. The only full-scale application of a continuous dry digestion system is the VALORGA process. Single-stage batch dry digestion systems may offer important benefits over continuously fed digesters or two-stage systems. Batch digestion systems are characterized by technological simplicity, both in construction and operation and can therefore be operated at low cost. Since operation costs are obviously an important factor in solid waste management, dry anaerobic digestion of MSW in batch systems are presumably more economically favourable than systems based on continuous digestion.

With this in mind, a research programme was started in 1985 to develop the BIOCEL system based on batchwise anaerobic digestion yielding biogas and compost. The research programme was financially supported by the Dutch National Programme for reuse of

Waste (NOH), which is coordinated by NOVEM, the Dutch Organization for Energy and the Environment, and RIVM, the Dutch Institute for Public Health and the Environment. The research was carried out on laboratory scale as well as on pilot-plant scale. Chapters 2 to 7 present the experimental work.

Start up methods

Chapters 2 and discuss the difficulties and main features of suitable start-up procedures for the batchwise dry anaerobic digestion of organic fractions of Municipal Solid Waste. For start-up of the dry digestion of the organic fraction of MSW the addition of a methanogenic inoculum appears to be essential.

There are essentially two possible situations at start-up of batch digesters:

a) the first start-up when already digested waste is not available,

b) regular start-up when part of the digester output can be recycled for inoculation.

The first start-up of a batch reactor fed with mechanically separated organic fraction proceeds unbalanced at a seed/substrate solids ratio of 0.04 - 0.08. This inbalance results in pH values below 6, organic acid concentrations up to 40-60 g COD.l^{-1} and ethanol concentrations up to 15 g.l^{-1}. Under these conditions production of methane is negligible. To enhance the start-up, several start-up procedures were investigated, such as the addition of buffer chemicals, the application of aerobic precomposting, and mixing with aerobically stabilized organic material. The best results were obtained with $NaHCO_3$ at a buffer/substrate solids ratio of 0.06 (kg.kg^{-1}). To enhance the first start-up of the dry batch digestion , an aerobic precomposting step was applied. Such an aerobic treatment could be useful in removing the easily degradable compounds, leaving the conversion of the ligno-cellulose part of the organic fraction to anaerobic digestion. At least 19.5 % of the Volatile Solids should be converted in the aerobic composting period to bring the acid formation in balance with the methane formation. This amount of aerobically degraded VS results in a 40 % loss of the potential methane production, which obviously represents a major drawback for using partial composting as a method to enhance the start-up of the digestion under 'dry' conditions.

When digesting the organic fraction in presence of compost at a ratio of 40/100 w/w based on the initial amount of solids, and when applying leachate recycling, the stabilization rate increases significantly. When using the digested residue of a completed digestion for regular start-up as the methanogenic inoculum, at a ratio of 40/100 w/w

based on the initial total solids, the required digestion time becomes even shorter. The results allow to conclude that dilution with compost or digested organic fraction psitively affects the start-up of the dry anaerobic digestion. The required digestion time under these conditions is 36 days.

Start-up of dry anaerobic digestion of Vegetable Fruit and Yard (VFY) waste, the source-separated organic fraction of Municipal Solid Waste, was also investigated (Chapter 6). In this case the first start-up should be carried out with dewatered digested pig manure. This type of methanogenic inoculum is already adapted to the high ammonium-nitrogen concentrations (3.2 g/l) and high concentrations of organic acids (up to 25 g COD/l) which may also be detected during start-up of the digestion of VFY waste. Anaerobic granular sludge is not suitable since it is not adapted to the environmental stress conditions during the first stage of batch digestion. During regular start-up with digested VFY as the inoculum a higher minimum inoculum factor (ratio of inoculum solids and total initial solids at start-up) has to be applied to achieve a balanced digestion. The total solids retention time (SRT) at an inoculum factor of 0.50 is 28 days, the mean methane production rate is 0.8 l STP/l-r.day. These values are in the same order as those found for other systems based on continuous dry anaerobic mesophilic digestion.

Influence of temperature and total solids concentration

In Chapter 3 the influence of temperature and of the total solids concentration of the rate of the anaerobic digestion process was investigated. The effect temperature was determined by calculating the first-order rate constant k_{CH4} (day-1) for the degradation of the volatile solids to CH_4 at a specific temperature, and subsequently plotting the values of k_{CH4} against the temperature according the Arrhenius law. The highest value for k_{CH4} was found at 40 °C. At 55 °C a much lower value was found. At 14 ° and 20°C the rate of digestion proceeded slowly and incompletely due to an initial higher acid formation rate then the methane formation rate of the inoculum. The initial acid formation rate shows much less of a response towards an increasing temperature than the methane formation rate. The effect of the total solids concentration on the rate of digestion highly depends on the (first) start-up conditions. The ratio of compost solids and total amount of solids at start-up is an important parameter in this respect. The decreasing rate of the digestion at increasing total solids concentration and at an inoculum factor of 0.50 could be due to high organic acid concentrations (up to 30 g/l) and low pH values (5.5-6.0) which were present in the digesters after 7 days. When a ratio of compost solids to total initial solids of 0.8 was applied, up to a total solids concentration of 50 % inhibition of the digestion could not be observed .

Transport problems of leachate in solid waste beds

Chapter 4 describes the effects of suboptimal transport in the solid waste bed of solid waste digesters. It was found that dry anaerobic batch digestion of solid organic wastes can proceed at pH values as low as 5.2 and organic acid concentrations of 40-50 g COD/l in the digester environment. Anaerobic digestion at low total solids concentrations under similar conditions is not possible. The existence of methanogenic zones with optimal conditions (higher pH, lower concentrations of organic acids) is very likely and may explain this discrepancy. During the initial stage of the digestion process environmental gradients are observed, but methanogenic zones, if present, are too small to be detected. After 60 days the methanogenic zones could be demonstrated by pH profiles. The mean pH was 5.7, while the pH in the reactor environment varied between 5.4 and 6.8. The organic acids concentration was as high as 60 g COD/l. After leachate recycle started the methane production rate increased immediately, which was indirect proof of the presence of methanogenic zones. The formation of methanogenic zones during an imbalance of the dry digestion is due to heterogeneous mixing characteristics of the reactor contents.

Microbial aspects

Chapter 5 describes the phenomenon of methanogenesis in dry anaerobic digestion of solid wastes under extreme conditions, such as high salt concentrations, and pH values below 6. This was studied in relation to the methanogenic biomass present in these environments. The maximum specific methanogenic activity of the enrichment culture dropped considerably at pH values below 7.0. Methanogenesis is possible at an initial acetate concentration as high as 583 mM and at pH = 7.0. Microscopic observations of enriched cultures showed that the predominant organisms resemble the genus *Methanosarcina sp.*

Pilot-scaleexperiments

Chapter 7 describes pilot-scale experiments with the BIOCEL system. Scaling up of the process proceeded successfully. The digester volumes tested were 5 m^3 and 450 m^3 respectively. The maximum feasible loading rate is 7 kg VS/(m^3.day) which is similar to the loading rate reported for experiments on laboratory scale. Per ton organic waste 90 m^3 (STP) biogas can be recovered. A reactor temperature of 20 °C at start-up gradually increased to 35 °C, resulted in a prolonged digestion time, while a temperature of 43 °C at start-up with a gradual decrease to 30 °C gave a similar digestion time as start-up at 35 °C. Particle size reduction of the VFY resulted in a longer solids retention time which was related to the reduced leachate recycle flow that could be applied. The optimum value for the inoculum factor I, i.e. the ratio of inoculum solids and the initial total solids at start-up, is 0.5 - 0.6. The solids retention time is 30 days under these conditions. At

higher values of I, longer retention times are observed due to a suboptimal leachate recycle flow rate. At lower values of the inoculum factor (0.5 or lower) the solids retention time exceeds 50 days, due to the relatively long period of suboptimal conditions (pH below 6, organic acid concentrations up to 40 g COD/l). Thermal drying and aerobic posttreatment (after composting) as well, can be applied for producing compost with the BIOCEL process.

Design for full-scaleplants

In this thesis the potentials of anaerobic digestion of the organic fraction of MSW are assessed on laboratory scale as well as on pilot-scale. On basis of the results of the experiments on several scales it can be concluded that the process is ready for full-scale application.

A flow sheet of a full-scale plant for anaerobic digestion of organic solid waste is presented in Fig. 1. To minimize the effects on the environment, (such as odour emissions), the complete installion is located in a hall. This 'indoor composting' will, in fact, be a standard for composting plants and anaerobic digestion plants for VFY waste in The Netherlands. The air from the process hall is treated by air washing and biofiltration.

Since no water is evaporated during the process, the production of a net amount of polluted residual effluent inevitable. This process water can be treated in a small-scale biological post treatment step, which removes at least 80 % of the residual COD and ammonia. The effluent can be discharged to the local sewers.

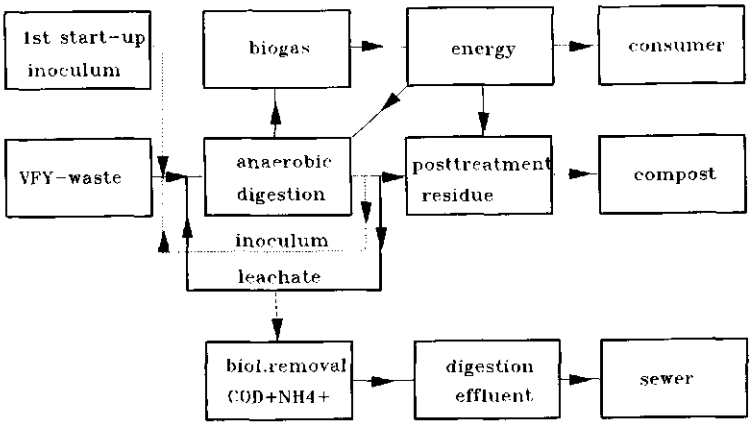

Fig. 1 Flow sheet of a full-scale BIOCEL plant for dry anaerobic digestion of solid organic waste.

In the case of VFY waste the mass balance for the anaerobic digestion of 1 ton of VFY-waste in a full-scale plant is presented in Fig. 2. During digestion 90 m^3 STP biogas per ton of VFY waste is produced. Part of this biogas is available as energy supply for the installation. By converting the biogas to electrical energy the installation runs on its own energy. The type of posttreatment applied to the residue will determine the amount of excess energy produced, which can be sold to the public electric network. It can therefore be concluded that anaerobic digestion of VFY-waste results in net energy production. In this respect it is very attractive. In addition to environmental and energy aspects, economical aspects also have to be taken into consideration. From several studies it appears that the batch system for mesophilic digestion, as applied in the BIOCEL system, shows the lowest operation costs (ref. 1,2). This is mainly the result of the higher investment costs required for systems based on two-stage digestion of continuous dry digestion.

Considering the investment costs of aerobic composting systems the BIOCEL system also can compete with several systems.

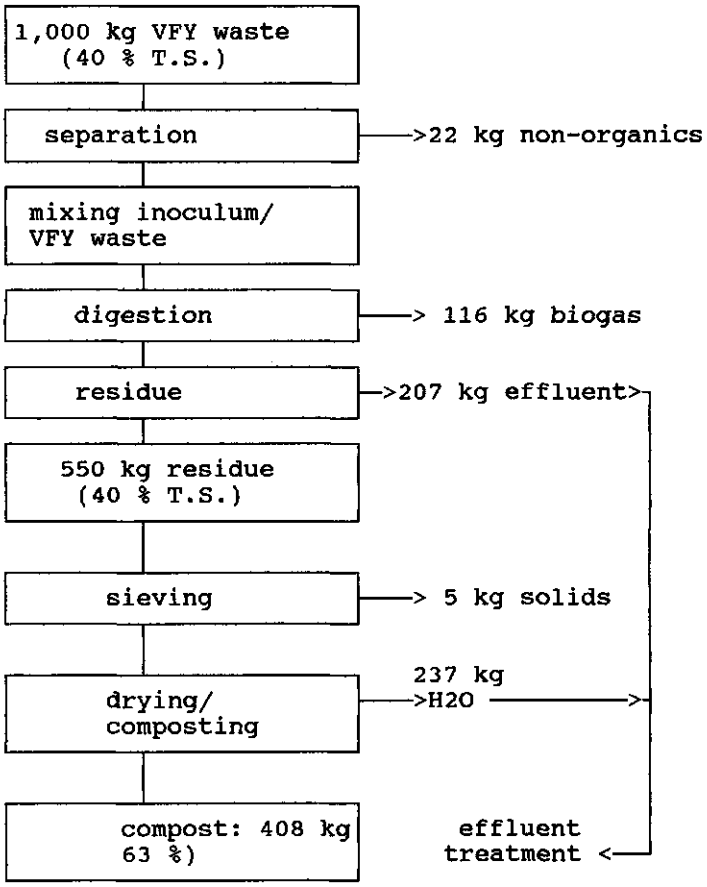

Fig. 2 Mass balance for dry anaerobic digestion of VFY waste

Topics for further research

As can be concluded from the results presented in this thesis, there is sufficient understanding of anaerobic digestion at high solids concentrations in a batch system for full-scale application without major problems. However, in additon to the determination of the type of methanogenic bacterium that predominates in the methanogenic biomass, other microbiological aspects were not investigated in this thesis. As mentioned in Chapter 1, after a short literature review of the kinetics of anaerobic digestion of particulate organic matter, the microbiological processes concerning hydrolysis of particulate matter, in fact, still forms a black box system. This aspect requires far more research, especially because of the importance fo optimizing the rate of hydrolysis to increase the biogas yield. It is obvious that, due to the extreme conditions (high fatty acid concentrations, high ammonium concentrations), inhibition affects the rate of the hydrolytic processes. In relation to this aspect, the exact composition of the waste, the degradation of the individual components, and the kinetics of the degradation of these compounds are interesting topics for further study.

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HOOFDSTUK 9

SAMENVATTING EN CONCLUSIES

Mogelijkheden voor anaërobe gisting van de organische fractie van huishoudelijk afval

In dit proefschrift wordt de technologische mogelijkheden beschreven van anaërobe vergisting als verwerkingsmethode voor de organische fractie van huishoudelijk afval. Hierbij wordt uitgegaan van ladingsgewijs (batch) bedreven vergisters.

In hoofdstuk 1 wordt aangetoond, dat de mogelijkheden voor de anaërobe vergisting van de organische fractie van huishoudelijk afval aanzienlijk zijn. In Nederland wordt er per jaar ca. zes miljoen ton huishoudelijk afval geproduceerd, waarvan 50 % bestaat uit wordt door de organische fractie, het zogenaamde Groente-, Fruit- en Tuinafval. Anaërobe vergisting van deze fractie zou 180.000.000 m^3 aardgas-equivalenten en 1.200.000 ton organische meststof, de compost, kunnen leveren. Biogas kan dienen als vervanger voor fossiele brandstoffen, waardoor de netto uitstoot van CO2, het belangrijkste broeikasgas, kan worden beperkt.

De mogelijkheden van anaërobe gisting voor de verwerking van huishoudelijk afval worden nog onvoldoende benut, gezien het geringe aantal praktijktoepassingen. Dit wordt hoofdzakelijk veroorzaakt door het ontbreken van vergistingsconcepten, die technologisch en economisch succesvol zijn.

In een literatuuronderzoek zijn de bestaande systemen voor de vergisting van vast organisch afval, in het bijzonder de organische fractie van huishoudelijk afval, beoordeeld op hun technologische mogelijkheden en beperkingen. De enige toepassing, waarbij anaërobe vergisting op relevante schaal benut wordt, is biogaswinning uit gecontroleerde vuilstorten. In een groot aantal van deze vuilstorten vindt anaërobe gisting spontaan plaats, maar de gistingsprocessen kunnen onvoldoende wordt beheerst. Slechts een gedeelte van het biogas kan worden gewonnen, een aanzienlijk deel komt in de atmosfeer terecht.

De tot nu toe op proefschaal ontwikkelde en meest belovende vergistingsconcepten zijn 'tweetrapssystemen', en 'ééntrapssystemen' bedreven bij hoge droge stof-concentraties (hoger dan 20 % droge stof). De ééntrapssystemen kunnen uitgaan van zowel batchvergisters (batch=ladingsgewijs) als continu gevoede vergisters. Bij de aanvang van het onderzoek was van de tweetrapssystemen geen installatie op praktijkschaal gerealiseerd, van de continue één trapssystemen was in de literatuur één praktijk-installatie beschreven. Gezien de technologische eenvoud en de daarmee gepaard gaande relatief lage

investeringen, is geconcludeerd dat batch-systemen economische voordelen bieden boven continu gevoede systemen.

Op basis van deze conclusie is in 1985 een onderzoekprogramma gestart naar de anaërobe vergisting van de organische fractie van huishoudelijk afval volgens het zogenaamde BIOCEL procédé, een ééntraps batch-systeem, resulterend in de produktie van biogas en compost. Het onderzoekprogramma is gefinancierd in het kader van het Nationaal Onderzoekprogramma Hergebruik Afvalstoffen (NOH), dat wordt gecoördineerd door NOVEM, de Nederlands Organisatie voor Energie en Milieu en het Rijks Instituut voor Volksgezondheid en Milieuhygiëne. Mede financiers waren de Landbouwuniversiteit Wageningen (vakgroep Milieutechnologie) en Heidemij Realisatie. Het onderzoek is uitgevoerd zowel op laboratoriumschaal als op pilot plant (=proef-fabriek) schaal. In de hoofdstukken twee tot en met zeven wordt het experimentele werk gepresenteerd, dat in het kader van het onderzoekprogramma is uitgevoerd.

Opstart-procedures

In hoofdstuk 2 en 6 worden een aantal zaken onderzocht, die een rol spelen bij de opstart van droge anaërobe batchvergisting van de organische fractie van huishoudelijk afval (HHA), verkregen door mechanische scheiding (hoofdstuk 2) en van aan de bron gescheiden organische fractie (GFT-afval, hoofdstuk 6)).

In hoofdstuk 2 wordt geconcludeerd, dat voor een snelle start van de vergisting het enten met methaanvormend entmateriaal essentieel is. Twee situaties kunnen worden onderscheiden bij de opstart:

a) de eerste opstart bij afwezigheid van reeds vergist afval

b) reguliere opstart wanneer vergist afval als entmateriaal kan worden gebruikt

De eerste opstart van batchreactoren, gevoed met mechanisch gescheiden organische fractie van HHA, verloopt onevenwichtig bij een ent/afval droge stofverhouding van 0,04 - 0,08, hetgeen resulteert in pH waarden beneden 6, organische zuurconcentraties variërend 40 tot 60 g CZV/l en onder bepaalde omstandigheden tot ethanol concentraties tot 15 g/l. Onder deze condities is de methaanproduktie te verwaarlozen. Ter versnelling van de opstart zijn verschillende procedures onderzocht, zoals toevoeging van buffers, aërobe voorbehandeling en mengen met aeroob gestabiliseerd afval. Van de onderzochte buffers blijkt $NaHCO_3$ het best te voldoen, bij een buffer/afval droge stofverhouding van 0,06 kg/kg. Eveneens is getracht om de opstart de versnellen door het toepassen van een aërobe voorcompostering. Een dergelijke voorcompostering heeft tot doel, om de snel

verzurende verbindingen gedeeltelijk aëroob af te breken. Bij deze methode moet minimaal 19,5 % van de organische stof worden afgebroken, voordat de zuur- en waterstofvormingsnelheid in evenwicht is met de zuur waterstofconsumptiesnelheid van het entmateriaal. Deze afbraak van organische stof, resulteert in een 40 % lagere biogasopbrengst per kg organische fractie. Dit laatste is een belangrijk nadeel van aërobe voorcompostering.

Als de organische fractie van HAA wordt vergist na mengen met aëroob gestabiliseerd materiaal in de verhouding 0,40 kg compost droge stof/kg droge stof, en onder toepassing van recirculatie van vrijkomend lekwater (bij 30 % TS), wordt de snelheid van de vergisting aanzienlijk verhoogd. Als vergist residu van een vergister als entmateriaal wordt toegepast, bij een ent/afval droge stofverhouding van 0,40 kg/kg, wordt de actuele gistingstijd nog aanzienlijk korter. De gistingstijd die onder deze condities (30 % TS, 35 °C) wordt gemeten is 36 dagen.

Opstart van de droge anaërobe vergisting van de GFT-afval, verkregen door scheiding aan de bron is eveneens onderzocht. De eerste opstart van de vergisting van dit afval moet worden uitgevoerd met vergiste ontwaterde varkensmest. Dit type entmateriaal is reeds geadapteerd aan hoge ammonium-stikstof concentraties (3,2 g/l) en hoge zuurconcentraties (25 g CZV/l), die bij de opstart van de vergisting van GFT-afval worden gemeten. Anaëroob korrelslib is geen goed entmateriaal, aangezien het niet is geadapteerd aan deze extreme omstandigheden. Bij reguliere opstart met vergist GFT-afval als ent neemt de snelheid van de vergisting toe met de zogenaamde entfactor, de verhouding van ent-droge stof en de totale hoeveelheid droge stof bij de opstart. Bij een entfactor van 0,50 bedraagt de gistingstijd 28 dagen. De gemiddelde biogasproduktiesnelheid bedraagt dan 0,8 liter/liter-reactor/dag. Deze waarden liggen in dezelfde orde van grootte als voor systemen gebaseerd op een continu gevoede vergisting.

Invloed van de temperatuur en de droge stof-concentratie.

In hoofdstuk 3 wordt de invloed van de temperatuur en de droge stof-concentratie op de snelheid van de droge vergisting beschreven. De invloed van de temperatuur is bepaald door berekening van de eerste orde reactie snelheid constanten k_{CH4} (dag^{-1}) uit de conversie van de organische stof in methaan bij een bepaalde temperatuur en vervolgens de waarden van k_{CH4} uit te zetten tegen de temperatuur volgens de vergelijking van Arrhenius. De hoogste waarde voor K_{CH4} wordt gevonden bij 40 °C. Bij 55 °C wordt een veel lagere waarde gevonden. Bij 14 °C and 20 °C verloopt de vergisting traag en onvolledig door een initieel hogere zuur-en waterstofvormingssnelheid dan de methaanvormende capaciteit van het entmateriaal. De aanvangssnelheid van de zuur- en waterstofvorming laat een veel geringere respons zien bij een toename van de temperatuur dan de

methaanvormingssnelheid.

De invloed van het droge stof-gehalte op de snelheid van de vergisting hangt sterk af van de (eerste) opstart procedure. In dit verband speelt de verhouding compost droge stof/totale hoeveelheid droge stof een rol. De afname van de snelheid bij toenemend droge stof-gehalte is waarschijnlijk het gevolg van de hoge zuurconcentraties (max. 30 g CZV/l) en lage pH waarden (5,5-6,0) die tijdens entfactoren van 0,50 worden gemeten. Bij entfactoren van 0,80 is geen invloed op de snelheid van de vergisting te verwachten tot 50 % TS.

Transport problemen van de vloeistoffasein vast afval-bedden

In hoofdstuk 4 wordt ingegaan op het transport van de vloeistoffase in het vaste bed van batchvergisters bedreven bij droge stof-gehaltes van 30 % of hoger. Gevonden werd, dat droge anaërobe vergisting kan plaats vinden bij pH waarden van 5,2 en vetzuurconcentraties van 40-50 g/l in de vergister. Anaërobe vergisting onder deze condities is gewoonlijk onmogelijk in vergisters bedreven bij laag droge stof-gehalte (lager dan 10 % TS). Het bestaan van methaanvormende gebiedjes, die tijdens droge anaërobe vergisting kunnen voorkomen, zou dit verschil kunnen verklaren. In een serie proeven is geprobeerd deze zones aan te tonen door het bepalen van pH profielen in een vergister met een bed-hoogte van 3 meter. In de eerste fase van de vergisting (dag 0-10) zijn de zones te klein om te kunnen meten. Na 60 dagen konden deze zones aan de hand van de pH variatie in de vergister worden vastgesteld. De gemiddelde pH was 5,7, de laagste pH bedroeg 5,38 de hoogste pH 6,80. De organische zuur-concentratie was 60 g CZV/l. Na 100 dagen is het bestaan van de methanogene zones indirect aangetoond door het toepassen van recirculatie van uitgelekt vocht. De methaanproduktie steeg hierna onmiddellijk. De vorming van methaanvormende plaatsen tijdens een onevenwichtig verloop van de vergisting wordt veroorzaakt door de grote verschillen in samenstelling in de vergister.

Microbiologischeaspecten van de methaanvorming

In hoofdstuk 5 is het verschijnsel van methaanvorming onder extreme condities, zoals zoals hoge zoutconcentraties, lage pH (lager dan 6) en hoge acetaat-concentraties (tot 40 g/l), bestudeerd. Experimenten zijn uitgevoerd met vergist methaanvormend afval. De maximale specifieke methanogene activiteit, bepaald met acetaat als substraat, daalde sterk bij pH waarden lager dan 7. Methaanvorming blijkt mogelijk bij een aanvangsconcentratie aan acetaat van 583 mM en bij pH=7,0. Microscopisch onderzoek liet zien, dat de biomassa werd gedomineerd door methanogenen van het geslacht *Methanosarcina*, een methaanvormend bakterie-geslacht, dat vaak voorkomt in extreme anaërobe milieus.

Droge anaërobe batch vergisting van GFT-afval op pilot plant schaal

Hoofdstuk 7 beschrijft de resultaten van het (succesvol) opschalen van het BIOCEL-proces van laboratoriumschaal naar pilot plant schaal. De vergistervolumes bedroegen respectievelijk 5 m^3 en 450 m^3. De maximale omzettingscapaciteit van de vergisters op pilot schaal bedraagt 7 kg VS/m^3.dag, vrijwel gelijk aan de capaciteit verkregen op laboratoriumschaal. Per ton GFT-afval wordt 90 m^3 (STP) geproduceerd. Een vergister-temperatuur van 20 °C bij de opstart, die binnen 10 dagen stapsgewijs wordt verhoogd tot 35 °C, geeft een langere gistingstijd in vergelijking met een opstart-temperatuur van 35 °C, en een opstart temperatuur van 43 °C, die stapsgewijs daalt tot 30 °C binnen 20 dagen.

Verkleining van het GFT-afval resulteert in een lange gistingstijd, veroorzaakt door de lagere percolaat-recirculatiesnelheid. De optimale waarde voor de entfactor I, bedraagt 0,5-0,6. De berekende vaste stof verblijftijd (SRT) bedraagt 30 dagen onder deze omstandigheden. Bij lagere entfactoren (0,60 of hoger) worden langere SRT's gemeten door de suboptimale percolatiesnelheid. De lagere percolatiesnelheden bij hogere entfactoren worden voornamelijk veroorzaakt door een geringere doorlatendheid van het afvalbed. Dit is bevestigd met een model-berekening. Bij lagere entfactoren (0,4 of lager) is de vaste stofverbijftijd langer dan 50 dagen, hetgeen wordt veroorzaakt door de relatief lange periode, waarin slechte condities voor de vergisting heersen (pH lager dan 6, zuurconcentraties tot 40 g COD/l).

Verschillende opwerkingsmethoden van het vergiste residu tot compost zijn getest. Zowel thermische droging (droging met hete lucht) als nacompostering zijn toepasbare methoden voor het BIOCEL procédé.

Ontwerp voor vergistingsinstallaties op praktijkschaal

In dit proefschrift zijn de potenties van droge anaërobe batchvergisting van de organische fractie van huishoudelijk afval aangetoond op zowel laboratoriumschaal als op preof-fabriek-schaal. Op basis van de behaalde resultaten kan worden geconcludeerd dat het proces gereed is voor praktijktoepassing.

Een schema van een praktijkinstallatie voor anaërobe vergisting van vast organisch afval is weergegeven in Fig. 1. Om de effecten van emissies van geur en van restafval en afvalwater te beperken, wordt de installatie overdekt bedreven. Gezien de eisen die gesteld worden aan maximale geuremissies van vergistingsinstallaties is verwerking in gesloten hallen dè standaard voor te bouwen GFT-verwerkingsinstallaties in Nederland. De lucht van de proceshal kan worden behandeld met gaswassers en biofilters. De produktie van verontreinigd water (percolaat) is onvermijdelijk, omdat tijdens de vergisting geen water wordt afgevoerd door verdamping. Het effluent kan worden gezuiverd in een eenvoudige waterzuiveringsinstallatie, waar ca. 80 % van de CZV en

stikstof kan worden verwijderd. Het voorgezuiverde effluent kan daarna op het riool worden geloosd. De massabalans voor de vergisting van 1 ton GFT-afval is weergegeven in Fig. 2

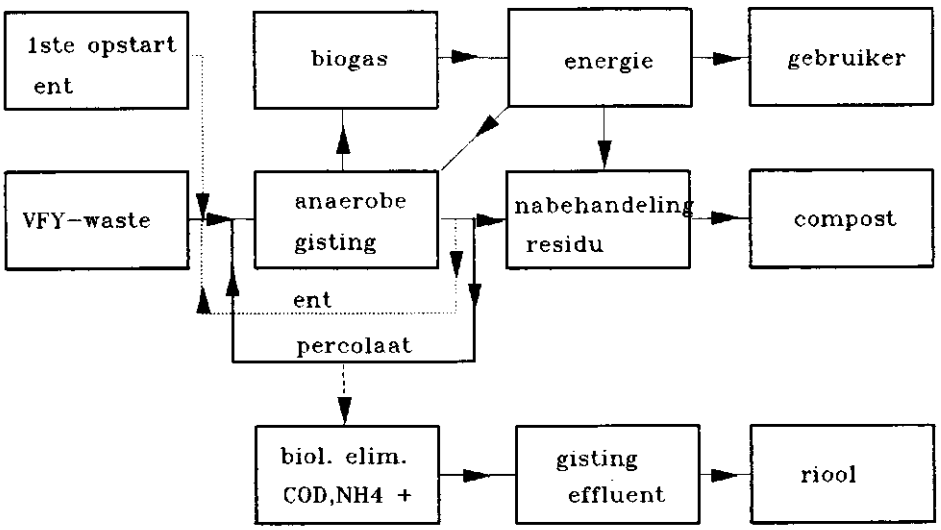

Fig. 1 Schema van een BIOCEL-praktijkinstallatie voor de anaërobe vergisting van vast organisch afval

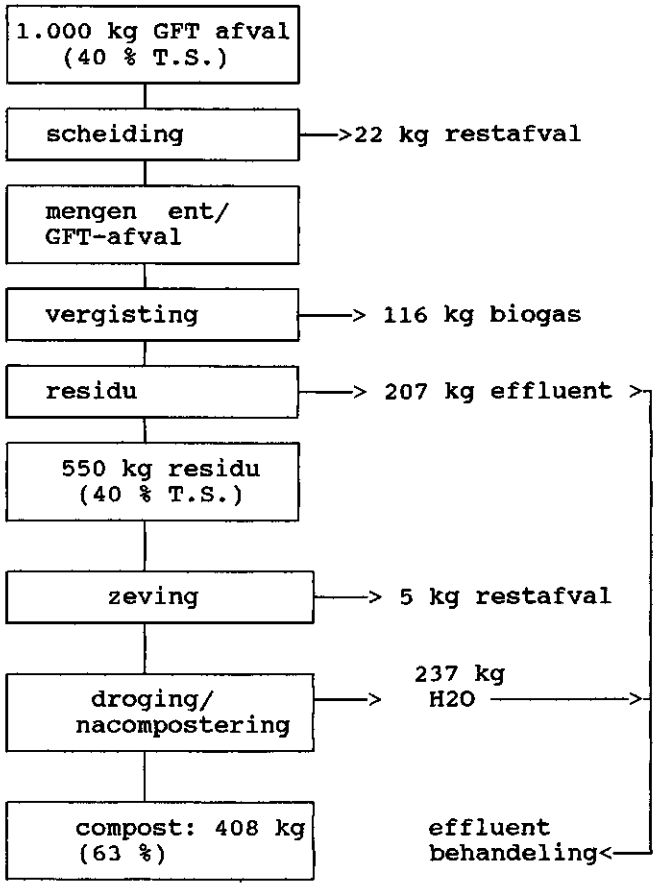

Fig. 2 Massa balans voor anaërobe vergisting van GFT-afval

Tijdens de vergisting wordt gemiddeld 90 m^3 biogas per ton afval geproduceerd. Een gedeelte van het biogas (ca. 60 %) wordt benut voor energievoorziening van de installatie. Het resterende biogas wordt omgezet in elektrische energie en kan worden afgezet, b.v. aan het openbare elektriciteitsnet. Vergisting van GFT-afval resulteert in netto energieproduktie en is daarom een aantrekkelijk alternatief voor aërobe compostering. Behalve milieu-aspecten en energie-aspecten moeten ook de economische aspecten van anaërobe vergisting in beschouwing worden genomen. Uit diverse recentelijk uitgevoerde vergelijkende studies blijkt, dat ééntrapsvergisting, zoals deze wordt toegepast in het BIOCEL procédé, leidt tot relatief lage exploitatiekosten in vergelijking met continue vergistingssystemen en tweetrapssystemen (1,2). Deze laatste vergen aanzienlijke hogere investeringen, hetgeen de exploitatie kosten sterk verhoogd.

In vergelijking met een aantal aërobe composteringsystemen wordt voor het BIOCEL -

systeem een lagere exploitatieprijs berekend (1,2).

Mogelijkheden voor verder onderzoek

Op basis van de resultaten die in dit proefschrift zijn gepresenteerd, kan worden geconcludeerd, dat voldoende kennis bestaat van de anaërobe gisting bij hoge droge stofgehalten in ladingsgewijs bedreven systemen om het proces op praktijkschaal toe te passen. Er kan echter worden opgemerkt, dat van de microbiologische aspecten alleen aandacht is besteed aan de methanogene biomassa. In hoofdstuk 1 is geconcludeerd, dat onvoldoende kennis bestaat over de microbiologie en de kinetiek van de hydrolyse (vervloeiing) van organische stof tijdens anaërobe gistingsprocessen. In feite vormt deze fase van de vergisting nog een 'black box'-systeem. Dit onderwerp zal verder onderzocht moeten worden, ten einde de biogasopbrengst uit vaste organische afvalstoffen te kunnen optimaliseren. Het is vrij aannemelijk, dat de condities, die tijdens de vergisting optreden, ook de hydrolyse-snelheid kunnen verlagen. In dit verband zijn een aantal interessante gebieden aan te wijzen voor verder onderzoek, zoals het onderzoek naar de exacte samenstelling van het te vergisten afval, afbraak van de afzonderlijke componenten van het afval en de afbraakkinetiek van deze componenten.

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Curriculum vitae

De auteur van dit proefschrift is geboren op 2 april 1959 te Pijnacker, (Z-H.). In 1977 behaalde hij het VWO-diploma aan het Christelijk Lyceum voor Delft en Rijswijk. In datzelfde jaar werd begonnen met studie aan de toenmalige Landbouwhogeschool te Wageningen, de huidige Landbouwuniversiteit. In 1984 werd het doktoraalexamen afgelegd in de studierichting Milieuhygiëne, met als hoofdvakken (anaërobe) waterzuivering en microbiologie, en als bijvakken hydrobiologie en proceskunde. Van 1985 tot 1989 werkte hij als wetenschappelijk projektmedewerker bij de vakgroep Milieutechnologie (toen nog Waterzuivering geheten) van de Landbouwuniversiteit, alwaar het onderzoek is verricht naar droge anaërobe vergisting van vast organisch afval. Vanaf 1989 is hij werkzaam bij Heidemij Realisatie BV te Waalwijk als medewerker Onderzoek en Ontwikkeling en is verantwoordelijk voor de verdere ontwikkeling van het BIOCEL-procédé, alsook voor de ontwikkeling van nieuwe composteringmethoden en biotechnologische bodemreinigingstechnieken.