

## Anaerobic digestion of the organic fraction of municipal solid waste with recirculation of process water

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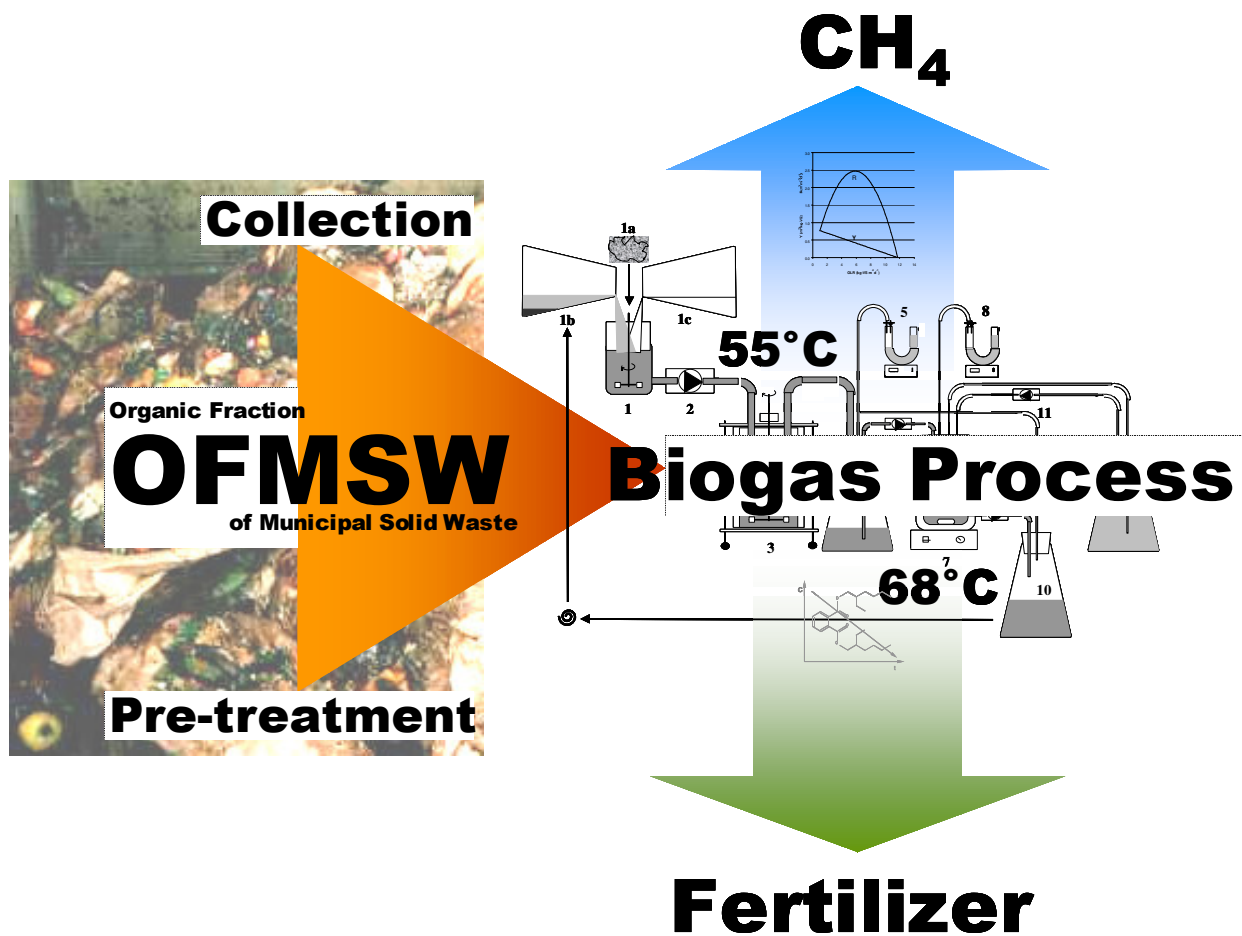
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# Anaerobic digestion of the organic fraction of municipal solid waste with recirculation of process water

Hinrich Hartmann



Ph.D. Thesis



Environmental Microbiology & Biotechnology  
Research Group  
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Technical University of Denmark



## Preface

The work presented in this Ph.D. thesis was conducted at BioCentrum-DTU at the Technical University of Denmark from September 1999 to October 2002 under supervision of Professor Birgitte K. Ahring.

Other results of this Ph.D. work such as inspiring thoughts, numerous excel files, deeper insights into the whole biogas process, but also headaches from technical problems with GC-MS analysis or pumping equipment are not displayed here, but everybody, who has conducted experimental work, knows, that their description would fill just as many pages.

As a matter of fact, scientific work cannot be distracted from the environment it is conducted in. In this context, all my colleagues of the Environmental Microbiology & Biotechnology Research Group deserve my great gratitude for creating a pleasant and inspiring working atmosphere, looking at anaerobic processes from so many different views.

A special gratitude to Birgitte Ahring for a well-balanced supervision between inspiring ideas, freedom of my own choice and support whenever necessary.

A very special thanks to Thomas Andersen who took so much care of the reactors and who never complained about my modification ideas.

Many thanks to Frank Haagensen, Henrik B. Nielsen, Mads Torry-Smith, Marianne Lange, and Zuzana Mladenovska for proofreading of the manuscripts, Melissa Gerrard for getting my English smoother and Henrik B. Nielsen for the Danish corrections. It is their credit that this thesis does not only consist of long twisted sentences.

Thanks also to Bjarne Bro from the municipality of Grindsted and its inhabitants for supplying the substrate for my project. Their waste was of great value. In the hope that other municipalities will soon follow their example of high quality waste collection.

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Lyngby, October 2002

Hinrich Hartmann

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Sooner or later everybody will see  
that there is no other power than  
Renewable Energy

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## Introduction to the thesis

The purpose of this Ph.D. project was to promote the treatment of the organic fraction of municipal solid waste (OFMSW) by anaerobic digestion (AD). In contrast to landfilling, incineration and composting, anaerobic digestion is the only waste treatment method that fulfills the demands of sustainability by recovery of the waste's energy content in the form of methane and of its nutrient content by using the effluent as fertilizer on agricultural land.

Although the breakthrough of AD of OFMSW was predicted some years ago and AD is nowadays regarded as a proven technology, its implementation is still far behind other waste treatment processes.

In Denmark, the governmental plan "Waste 21", which set targets for the national waste management in the period 1998-2004, assigned to implement AD as the dominating waste treatment method for OFMSW by the year 2004. With respect to this aim, the starting point for the present research was to identify problems and to innovate solutions for anaerobic digestion of OFMSW in centralized biogas plants in Denmark, where OFMSW is co-digested together with manure.

This project focused on the following:

- Which demands are to be fulfilled in order to provide OFMSW as a substrate for the biogas plant?
- How does the use of higher quantities of OFMSW affect the biogas process?
- What kind of modifications in the reactor installation and process operation have to be made if high loads of OFMSW are added to the co-digestion process or when OFMSW is used as the sole substrate?
- What is the effect on the quality of the processed effluent as fertilizer by the addition of OFMSW?

The Ph.D. study aimed to address these questions on three different levels:

- Identification of the specific problems of AD of OFMSW in Denmark.
- Exploration of how the conventional AD process of OFMSW can be implemented.
- Investigation of a new configuration for the AD of OFMSW in order to improve the process.

The results of this study are collected in six papers.

**PAPER 1** and **PAPER 2** are an introduction to the AD process of OFMSW by reviewing previous studies within this research field. **PAPER 1** deals with the application of AD on the treatment of solely OFMSW while **PAPER 2** gives an overview of co-digestion processes for the treatment of OFMSW.

**PAPER 3** describes the different processes of AD of OFMSW applied in Danish biogas plants, including experiences with collection and pre-treatment methods used.

**PAPER 4** presents the experimental results for the co-digestion of OFMSW together with manure and the treatment of 100% OFMSW with recirculation of process water under thermophilic conditions (55°C).

**PAPER 5** displays the experimental results for the implementation of a hyper-thermophilic (68°C) post-treatment designed to enhance the hydrolysis and sanitation, and for ammonia stripping.

**PAPER 6** presents the experimental results for levels of xenobiotics found in the influent and effluent of biogas plants treating OFMSW. Since the phthalic acid ester DEHP (Di-(2-ethylhexyl)phthalate) was identified as the main contaminant in OFMSW, the focus was on the degradation of this compound in the investigated thermophilic and hyper-thermophilic reactor set-up.

An overview of the results found is given in the following summary.

## Summary

### 1 OFMSW as substrate for the AD process

The quality of OFMSW, in terms of composition of different organic waste fractions and content of contaminants, is very important for the biogas process of OFMSW. This is expressed in all research on AD of OFMSW that is displayed in **PAPER 1**. Experiences with waste quality in correlation to collection and pre-treatment methods used in Denmark are found in **PAPER 3**.

The organic fraction of municipal solid waste is a simple definition of the organic matter found in household waste, consisting of kitchen waste, i.e. fruit and vegetable waste and food residues, but also garden waste and possibly waste paper. The actual characteristics of OFMSW when brought to the biogas plant, are, however, highly influenced by the collection and pre-treatment methods used. Waste management of the organic waste stream by AD is, therefore, always a combination of three factors: collection, pretreatment and biogas process (figure 1).

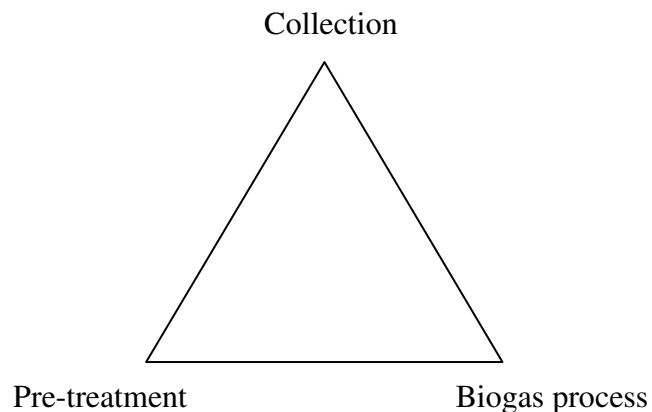


Figure 1: The interdependency of collection, pre-treatment and biogas process of OFMSW

Tremendous efforts have been made throughout the recent years in several municipalities in Denmark, just like in many other European countries, to build up a collection system for source-sorted household waste "clean" enough to be treated in a biogas plant. The interdependency of the three factors of the whole waste treatment concept for AD of OFMSW is mainly pronounced in the start-up period. Treatment in the biogas plant can only be established if the collection system guarantees a good quality collected waste, in terms of low contamination from plastics and inert material. Consumers, on the other hand, consider waste separation, especially in the beginning, purely as a time-consuming burden due to odor problems. They will only make an effort to collect waste properly as long as they know that the whole treatment concept is well functioning and that it is more reasonable to separate the waste than to treat the whole fraction in an incineration plant. Appealing to the consumer's environmental conscience is, therefore, often the first means of convincing the consumer of waste separation. In this phase, information to the consumer about the advantages of waste separation is crucial. In some municipalities in Europe the environmental conscience of consumers is no longer relied upon and stricter collection rules have been developed. One



example is, that collection of the organic waste is refused if the waste bin contains contamination like plastics.

In the context of the present Ph.D. study it should be sufficient to state that for the research on the technical process of anaerobic digestion of OFMSW it has to be kept in mind that the successful application of AD of OFMSW will always rely on the collection method and the quality of the waste delivered to the reactor. The treatment of OFMSW by anaerobic digestion is, therefore, characterized by a strong interaction between technology and society.

Recent news in Denmark that several municipalities are on the edge of stopping AD of OFMSW often give the impression that this is due to technical problems of the biogas process. This is only true in the sense that low waste quality with a high content of contaminants leads to technical problems at the biogas plants. These problems can, however, be avoided by establishing a collection and pretreatment system, which ensures low contamination of the waste. It has been proven, for example in the municipality of Grindsted, that source-sorted OFMSW collected in paper bags is successfully treated in co-digestion with sewage sludge.

From the review of previous international work and from the experiences in several Danish municipalities it can be concluded that source sorting and free-of-plastic collection is beneficial for the collection efficiency, the mechanical handling of the waste and the quality of the effluent of the biogas plant when it is used as fertilizer on agricultural land. In fact, the benefit from biogas production exceeds the treatment costs only if the waste is not collected in plastic bags. Paper bags used for waste collection contribute to the biogas production during anaerobic digestion. If OFMSW is used as the sole substrate and no buffer capacity and nutrients are added by co-digestion with, for example, manure or sewage sludge, attention should be drawn to the C:N ratio of the collected waste. This can be balanced by the ratio of different waste fractions like food waste (C:N low), garden waste (C:N medium) or waste paper (C:N high).

## **2 The biogas process of OFMSW**

An overview of processes used for AD of OFMSW as the sole substrate in lab-scale, pilot-scale and full-scale plants is given in **PAPER 1**. Aspects of co-digestion of OFMSW are found in **PAPER 2**.

Low performance of the biogas process, when using exclusively OFMSW as substrate, can be caused by high solids content, possible nutrient deficiency and low pH of the waste. Generally, the co-digestion of OFMSW offers several advantages concerning a balance of nutrients and adjusting the buffer capacity by the addition of, for example, manure. OFMSW, on the other hand, has a biogas potential, which per m<sup>3</sup> of waste is up to 10 times higher than that of manure. This makes OFMSW an attractive substrate for improving the biogas plant's economy.

Comparing the different process strategies for AD of OFMSW, the highest biogas yields were achieved by a low-solids digestion process with diluted OFMSW at thermophilic temperatures. Moreover, a cost-benefit analysis, regarding both biogas production and VS reduction, shows, that the operation of the biogas process at a lower organic loading rate (OLR) and a higher hydraulic retention time (HRT) than those used for maximum biogas production, is the most cost-efficient.

In the present investigation, three process configurations were studied:

- Co-digestion of OFMSW and manure under thermophilic conditions (55°C) in a ratio of 50% of VS (volatile solids) from both substrates.
- Treatment of 100% OFMSW with recirculation of process water.
- Treatment of 100% OFMSW with recirculation of process water and hyper-thermophilic (68°C) post-treatment.

Results for the first two configurations can be found in detail in **PAPER 4**, and for the latter configuration in **PAPER 5**. The process performance was investigated in 4.5 l lab-scale continuously stirred tank reactors (CSTR) with an active volume of 2.6 - 3.5 l for the thermophilic treatment and a 1.2 l hyper-thermophilic CSTR with an active volume of 0.2 - 1 l. OLR of the reactors was 2.3 – 4.0 g-VS·l<sup>-1</sup>·d<sup>-1</sup>. The designed HRT was 15-20 days for the thermophilic and 1-5 days for the hyper-thermophilic reactor.

## 2.1 Co-digestion of OFMSW

The biogas process was adapted during 6 weeks from just manure to its co-digestion with OFMSW, in a ratio of 50% (VS/VS). In the long run, process performance was stable despite fluctuations in the feed volume. VFA concentrations were low and a biogas yield of 540-590 ml/g-VS was obtained. Without the addition of water the co-digestion ratio of 50% (VS/VS) would result in a TS concentration of 16.6% TS. This means, that co-digestion of OFMSW and manure in a ratio of 50% (VS/VS) would be at the limit for mechanical handling by conventional pumping technology. For higher co-digestion ratios of OFMSW, recirculation of process water would be necessary to achieve a higher dilution of the waste. This configuration was studied in the second part of the research.

## 2.2 Treatment of OFMSW with recirculation of process water

Adaptation from the 50% (VS/VS) co-digestion treatment to the treatment of 100% OFMSW was achieved during a period of 8 weeks. The process was stable, indicated by low VFA (volatile fatty acids) concentrations, but the pH in the reactor dropped significantly from 8.2 to 7.7 when the added OFMSW was diluted by water. Addition of the liquid effluent fraction for dilution of influent OFMSW showed a significant benefit. The pH stabilized at the level of co-digestion due to the accumulation of ammonia in the recirculation stream. Applying a recirculation of the effluent in a ratio of 59%, an ammonia level of 1.5 g-N/l was reached, which was in the same range as in the 50% (VS/VS) co-digestion ratio with manure. A respective free ammonia concentration of 0.42 g-N/l showed no adverse effects on reactor performance. Both in the co-digestion configuration and the treatment of 100% OFMSW with recirculation of process water, a methane yield of 380-420 ml/g-VS from OFMSW was achieved, which corresponds to a biogas yield 181 – 217 m<sup>3</sup> biogas per ton OFMSW.

Recirculation of process water could be implemented by centrifugation of the effluent from the biogas process in a decanter centrifuge. The solid fraction would be discharged as a fertilizer product and the liquid fraction would be used for dilution of the OFMSW feed. Under the investigated conditions (thermophilic process, 15 d HRT, 6% TS concentration in influent) 72-87% of the influent mass was recovered as process water. This would mean that the amount of process water would be sufficient for dilution of OFMSW in a ratio of 1:5. With recirculation of 100% of process water, the ammonia would reach a level of 3.7 g-N/l, equivalent to 1.0 g-N/l free ammonia (55°C, pH 8.0). This free ammonia concentration could be suspected to inhibit the process in the thermophilic reactor and would make removal of ammonia necessary. An ammonia removal of 10% would be sufficient to establish a level of 2.4 g-N/l and 0.67 g-N/l free ammonia, respectively.

### **2.3 Hyper-thermophilic post-treatment**

A hyper-thermophilic post-treatment was investigated with respect to enhanced hydrolysis, improved sanitation efficiency and ammonia stripping. The post-treatment was implemented for treatment of the effluent from the thermophilic reactor. The hyperthermophilic reactor was operated at HRT of 1 – 5 days. VS reduction and biogas yield of the combined system was 78-89% and 640 -790 ml/g-VS, respectively. VS reduction in the combined system was up to 7% higher than in the single-stage treatment, but no increase in methane yield was observed. At HRT of 3 days and lower, the methanogenic activity in the hyper-thermophilic system dropped to a minimum. Optimal HRT for the hyper-thermophilic reactor was identified as 1-2 days since hydrolytic activity in the reactor was highest for this configuration. Volatile fatty acids produced were recirculated with the process water into the thermophilic reactor.

The pathogen reducing effect (PRE) of the thermophilic and the hyper-thermophilic treatment was determined by cultivation of fecal enterococcus in the influent and the effluents of the process. Fecal enterococcus was used as an indicator organism for pathogenic contamination. The results indicated an additional PRE by the hyper-thermophilic treatment at 1 day HRT and showed almost complete removal of the indicator organism.

The efficiency of the hyper-thermophilic reactor for ammonia stripping was studied by pumping the headspace gas through a sulfuric acid solution. 10% of the ammonia load was removed in the hyper-thermophilic reactor with a low gas flow.

Implementation of the hyper-thermophilic post-treatment would be only a minor modification at the biogas plants, which often have already a separate hygienisation tank operated at a temperature of 70°C. This thermal treatment could be substituted by the biologically active post-treatment.

### **3 Effluent quality - degradation of xenobiotic contaminants**

The concept of AD of OFMSW does fulfill its real value if the effluent of the biogas process is used as fertilizer on agricultural land and nutrients are recycled back into the natural cycle. If AD of OFMSW is applied as co-digestion together with manure, it is crucial that the addition of OFMSW to the process does not influence the quality of the effluent in such a way that it cannot be used as fertilizer and also the effluent deriving from the manure treatment has to be discharged like other waste. In such a case, the addition of OFMSW would have a negative impact on the whole concept of waste treatment in the biogas process.

There are three criteria for the effluent of the biogas process to be accepted as fertilizer on agricultural land:

- Sanitation of OFMSW
- No plastic contamination visible
- Contamination with xenobiotics below threshold values

From the abovementioned investigations it can be concluded that visible plastic contamination can be avoided by waste collection without plastic bags and an effective source-sorting system. Sanitation is improved by the described hyper-thermophilic treatment. Contamination of OFMSW with xenobiotic compounds and their status throughout the biogas process was studied in the final part of this Ph.D. project. The results are found in detail in **PAPER 6**.

Analyses of samples from different biogas and composting plants treating OFMSW identified the phthalic acid ester DEHP (di-(2-ethylhexyl)phthalate) as the main contaminant in OFMSW. DEHP is produced in large amounts as plasticizer and as an additive for paints and glues. It is considered a ubiquitous pollutant in many aquatic and terrestrial environments and is suspected to have carcinogenic, mutagenic and likely xeno-estrogenic effects. It may, therefore, not exceed a concentration threshold of 50 mg/kg dry matter in waste material when applied as fertilizer on agricultural land in Denmark. In the OFMSW delivered to the plants DEHP was found in concentrations more than half of the threshold value. Due to a dry matter reduction of more than 50% during the anaerobic digestion process, the concentration per kg of dry matter would exceed the threshold limit if degradation of DEHP does not occur.

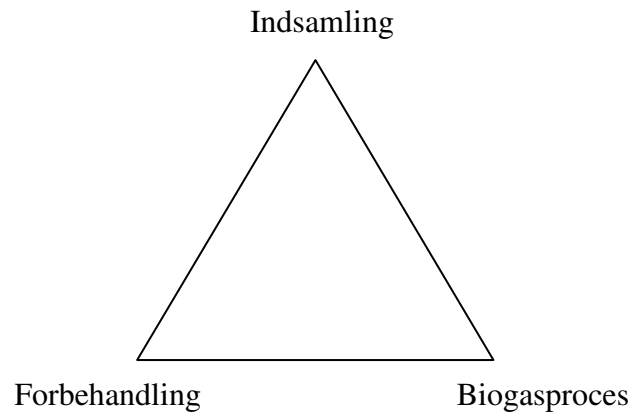
DEHP has been described as recalcitrant towards biological degradation both under aerobic and anaerobic conditions. This is suspected mainly to be due to its low water solubility. The present investigation showed, however, that the combination of the thermophilic and the hyper-thermophilic treatment meant, that 34 – 53% of DEHP was removed. The removal rates were one magnitude higher than in previous aerobic experiments. This could be suspected to be due to the higher temperature and the high TS removal in the present investigation, which increased the bioavailability of the compound. Contamination of DEHP in the effluent bound to the residual organic matter, was around the same concentration per kg of dry matter as in the influent. Contamination of the collected OFMSW with DEHP should, therefore, not exceed the threshold. This again indicated the necessity of establishing source sorted waste collection with low plastics contamination.

## Resumé

### 1 Organisk dagrenovation som substrat i biogasprocessen

Kvaliteten af organisk dagrenovation (ODA), med hensyn til sammensætning af forskellige organiske affaldsfraktioner samt indhold af urenheder, har en stor betydning ved behandling i biogasprocessen. Det er fremhævet i alle undersøgelser om anaerob nedbrydning af ODA, som findes i **artikel 1**. Erfaringerne med affaldskvaliteten i forhold til indsamling og forbehandlingsmetoder anvendt i Danmark findes i **artikel 3**.

Organisk dagrenovationen er en simpel definition af den organiske del af husholdningsaffaldet bestående af køkkenaffald, dvs. frugt- og grøntsageaffald samt madrester, men derudover også haveaffald og papiraffald. Den virkelige karakteristik af ODA, når den udbringes til biogasanlæg, er dog i højt grad afhængig af den anvendte indsamlingsorden og forbehandlingsmetode. Affaldsbehandling af ODA, vha. biogasprocessen, er derfor altid en kombination af tre faktorer: indsamling, forbehandling og biogasproces (figur 1).



Figur 1: Afhængighed af indsamling, forbehandling og biogasproces ved behandling af organisk dagrenovation

Flere kommuner i Danmark, ligesom mange andre i andre europæiske lande, har gjort en stor indsats for at opbygge et indsamlingssystem af kildesorteret husholdningsaffald, der er "rent" nok til at blive behandlet på biogasanlæg. Afhængigheden af de tre faktorer, som udgør hele behandlingskonceptet af ODA i biogasprocessen, er mest udpræget i opstartsperioden. Behandling i biogasanlæg kun kan gennemføres med succes hvis indsamlingssystemet garanterer en høj kvalitet af det indsamlede materiale mht. lav kontaminering med plastik og andre fremmedlegemer.

Forbrugerne på den anden side opfatter affaldsseparatoring især i begyndelsen som en tidskrævende belastning forbundet med lugtgener. De vil kun gøre en indsats for at indsamle affaldet ordentligt så længe de ved at hele behandlingskonceptet virker, og at det er mere hensigtsmæssigt at separere affaldet end at behandle det hele på forbrændingsanlæg.

At appellere til forbrugerens miljøbevidsthed er derfor ofte den første måde at overbevise folk til affaldsseparatoring. I denne fase er information om fordele af affaldsseparatoration og affaldsbehandling i biogasanlæg afgørende. I nogle europæiske kommuner appelleres ikke

længere kun til forbrugerens miljøbevidsthed, men der er også blevet indført skarpere indsamlingsordninger. Det betyder for eksempel, at indsamling af organisk dagrenovation afvises hvis affaldsbeholderen indeholder urenheder i form af plastik.

I sammenhæng med det foreliggende Ph.D.-arbejde bør det være tilstrækkelig at fastslå, at det for en undersøgelse omkring den tekniske del af biogasprocessen skal huskes, at en succesrige anvendelse af ODA i biogasprocessen altid vil være afhængig af indsamlingsmetoden og af kvaliteten af affaldet, som leveres til biogasanlægget. Behandling af organisk dagrenovation i biogasprocessen er derfor præget af en stærk vekselvirkning mellem teknologi og samfund.

Seneste nyheder om at forskellige kommuner opgiver eller overvejer at opgive en separat indsamling af den organiske dagrenovation, til behandling i biogasanlæg, giver ofte det indtryk at det skyldes tekniske problemer med biogasprocessen. Det er kun sandt i den grad, at en dårlig affaldskvalitet med et højt indhold af urenheder fører til tekniske problemer på biogasanlægget. Disse problemer kan dog undgås ved etablering af et indsamlings- og forbehandlingskoncept som sikrer en lav forurening af affaldet. Det har for eksempel vist sig i Grindsted kommune, at kildesorteret husholdningsaffald, som indsamles udelukkende i papirposer, behandles med stor fordel i samudrødning med spildevandsslam.

Ud fra tidligere international arbejde og fra erfaringerne i forskellige danske kommuner kan der konkluderes, at kildesortering og en "fri for plastik" indsamling er til fordel for både indsamlingseffektiviteten, den mekaniske affaldshåndtering og kvaliteten af effluenter fra biogasprocessen mht. anvendelse som gødningsmiddel. Gevinsten fra biogasproduktionen overstiger faktisk kun behandlingsomkostninger når affaldet ikke indsamles i plastikposer. Papirposer som anvendes til indsamling af affaldet omdannes til biogas gennem den anaerobe nedbrydning. Hvis organisk dagrenovation anvendes udelukkende som substrat i biogasprocessen, og ingen bufferkapacitet eller næringsstoffer er tilført i form af for eksempel gylle eller spildevandsslam i samudrødningsprocessen, så skal der lægges mærke til C:N forholdet af det indsamlede affald. Dette kan indstilles vha. af en blanding af forskellige affaldsfraktioner som for eksempel madaffald (C:N lav), haveaffald (C:N middel) eller papiraffald (C:N høj).

## 2 Biogasprocessen af organisk dagrenovation

Et overblik over processerne anvendt til bioforgasning af organisk dagrenovation som eneste substrat i laboratorie-skala, pilotskala og fuld-skala anlæg findes i **artikel 1**. Aspekter ved samudrødning af ODA er beskrevet i **artikel 2**.

Et højt tørstofindhold, en mulig mangel på næringsstoffer og en lavt pH værdi kan forårsage forstyrrelser af biogasprocessen når ODA udelukkende anvendes som substrat. Generelt tilbyder samudrødning af organisk dagrenovation en række fordele, for eksempel afbalancering af næringsstoffer og bufferkapaciteten ved blanding med eksempelvis gylle. ODA har på den anden side et biogaspotentiale som per kubikmeter affald er op til ti gange så stort som gylles. Det gør ODA til et fordelsagtig substrat mht. forbedring af anlægsøkonomien.

Ved sammenligning af de forskellige processtrategier til bioforgasning af ODA ses det, at det største biogasudbytte blev opnået ved termofil nedbrydning og procesføring med lavt tørstofindhold ved fortynding af ODA. En rentabilitetsberegning, med henblik på både biogasproduktionen og VS reduktion, viser derudover, at den højeste gevinst opnås ved en procesføring med lavere belastning (OLR) og højere opholdstid (HRT), end ved de procesværdier som fører til den højeste biogasproduktion.

I det foreliggende arbejde blev tre proceskonfigurationer undersøgt:

- Samudrådning af ODA og gylle under termofile forhold (55°C) i blandingsforholdet af 50% organisk materiale (VS) fra begge substrater.
- Behandling af 100% ODA med recirkulering af procesvandet.
- Behandling af 100% ODA med recirkulering af procesvandet og en hypertermofil (68°C) efterbehandling.

Resultater for de to første konfigurationer vises i **artikel 4**, og den sidste konfiguration i **artikel 5**. Processen blev undersøgt i 4.5 l laboratorie-skala kontinuerlig omrørt tank reaktorer (CSTR) med et aktivt volumen på 2.6 – 3.5 l til den termofile behandling og en 1.2 l hypertermofil CSTR reaktor med et aktivt volumen på 0.2-1 l. Den organisk belastning af reaktorerne var 2.3 – 4.0 g-VS·l<sup>-1</sup>·d<sup>-1</sup>. Opholdstiden i den termofile reaktor og den hypertermofile reaktor blev indstillet til hhv. 15-20 dage og 1-5 dage.

## 2.1 Samudrådning af ODA

Biogasprocessen blev adapteret i løbet af 6 uger fra behandling af gylle til samudrådning af ODA og gylle i et blandingsforhold af 50% (VS/VS). På lang sigt var processen stabil trods svingninger i fødevolumen. Koncentrationen af flygtige fedtsyrer (VFA) var lav og et biogasudbytte på 540-590 ml/g-VS blev opnået. Uden tilsætning af vand vil dette blandingsforhold føre til en tørstofkoncentration på 16.6% TS. Dette vil betyde, at et blandingsforhold af 50% (VS/VS) vil være på kanten af en affaldshåndtering med almindelig pumptechnologi. For højere blandingsforhold til samudrådning af ODA vil en recirkulering af procesvandet være nødvendig for at fortynde affaldet. Denne konfiguration blev undersøgt i den anden del af projektet.

## 2.2 Behandling af ODA med recirkulering af procesvandet

Processen blev adapteret fra samudrådning i blandingsforhold på 50% (VS/VS) til en behandling af 100% ODA i løbet af 8 uger. Processen var stabil med lave VFA koncentrationer, men pH i reaktoren faldt signifikant fra 8.2 til 7.7 når ODA, fortyndet med vand, blev tilført til en reaktor. Tilsætning af væskefraktionen, fra processens effluent, for at fortynde ODA, viste en signifikant gevinst. pH stabiliserede på samme niveau som i samudrådning pga. akkumulering af ammonium i recirkuleringsvandet. Ved en recirkuleringsrate på 59% blev der opnået en ammoniumkoncentration på 1.5 g-N/l, som var på samme niveau som i samudrådning i blandingsforholdet på 50% (VS/VS) med gylle. En tilsvarende ammoniakkoncentration af 0.42 g-N/l viste ingen hæmning på nedbrydningsprocessen. Både i samudrådning og i behandling af 100% ODA med tilbageførelse af procesvandet var metanudbyttet fra ODA 380-420 ml/g-VS, hvilket svarer til 181 – 217 m<sup>3</sup> biogas per ton ODA.

Tilbageførelse af procesvandet kunne iværksættes vha. centrifugering af effluenten fra biogasprocessen i en decantercentrifuge. Den faste fraktion kunne udledes som gødningmiddel, mens væskefraktionen kunne anvendes til fortynding af den tilførte ODA. Ved de betragtede procesforhold (termofil proces, 15 dage opholdstid, 6% tørstof i influent) kunne 72-87% af den tilførte masse genvindes som procesvand. Dvs., at mængden af procesvandet vil være tilstrækkelig til fortynding af ODA i blandingsforholdet af 1:5. Ved en tilbageførelse af 100% af procesvandet ville ammoniumkoncentrationen opnå et niveau på 3.7 g-N/l, svarende til en ammoniakkoncentration på 1.0 g-N/l. Denne ammoniakkoncentration vil med stor sandsynlighed giver anledning til proceshæmning i den termofile reaktor og derfor vil det være nødvendigt at fjerne ammoniakken. 10% fjernelse af

ammonium vil være tilstrækkelig for at opnå et niveau på 2.4 g-N/l, tilsvarende til 0.67 g-N/l ammoniak.

### **2.3 Hypertermofil efterbehandling**

En hypertermofil efterbehandling blev undersøgt mht. øget hydrolyse, forbedret hygiejnisering og ammoniak stribning. Efterbehandlingen blev udført til behandling af effluenter af den termofile reaktor. Opholdstiden i den hypertermofile reaktor var mellem 1 og 5 dage. En VS reduktionen og et biogasudbytte på hhv. 78-89% og 640-790 ml/g-VS blev opnået. VS reduktionen var op til 7% højere end i den enfasede termofile behandling, men ingen forøgelse af biogasudbyttet blev observeret. Ved en opholdstid af 3 dage og mindre faldt den metanogene aktivitet til et minimum. Den optimale opholdstid i den hypertermofile reaktor var 1-2 dage, eftersom den hydrolytiske aktivitet var højest for denne konfiguration. De producerede flygtige fedtsyrer blev tilbageført med procesvandet til den første termofil reaktor.

Den patogen forringende effekt af den termofil og den hypertermofil behandling blev målt gennem kultivering af fækal enterococcus i processens influent og de tilsvarende effluenter. Fækal enterococcus blev brugt som indikatororganisme for patogen forurening. Resultaterne viste at den hypertermofile behandling ved 1 dag opholdstid havde en forøgede hygiejniseringseffekt og at indikatororganismen blev næsten fuldstændig fjernet som følge af behandlingen.

Effektiviteten af den hypertermofil reaktor til ammoniakstribning blev undersøgt vha. af pumpning af gasset fra reaktorens headspace gennem en svovlsyre opløsning. 10% af ammoniakken kunne fjernes i den hypertermofil reaktor ved et gasflow svarende til fire gange flowet af biogassen, som blev produceret i den termofile reaktor.

Iværksættelse af den hypertermofile efterbehandling ville kun betyde en lille ændring på biogasanlæggene som ofte har en hygiejniseringstank med en driftstemperatur på 70°C i forvejen. Denne termiske behandling kan erstattes med den biologisk aktive efterbehandling.

## **3 Effluent kvalitet – nedbrydning af miljøfremmede forbindelser**

Konceptet ved nedbrydning af ODA i biogasprocessen opfylder kun sit sande mål, når effluenter af processen anvendes som gødningsmiddel på markerne og næringsstofferne bliver tilbageført til det naturlige kredsløb. Når behandling af ODA iværksættes som samudrødning med gylle, der er bestemt til gødning, er det altafgørende, at tilsætningen af ODA til biogasprocessen ikke fører til en forværring af effluentens kvalitet i den grad, at effluenter ikke længere kan bruges som gødningsmiddel, og at denne skal behandles som affald i stedet. I dette tilfælde ville tilsætning af ODA til biogasprocessen have en meget negativ virkning på hele konceptet af affaldsbehandling i biogasprocessen.

Der findes tre kriterier for at acceptere effluenter fra biogasprocessen som gødningsmiddel:

- Hygiejnisering af ODA
- Ingen synlig plastikforurening
- Forurening med miljøfremmede stoffer under afskæringsværdier

Fra de ovennævnte undersøgelser kan drages konklusionen, at synlig plastik i effluenter kan undgås ved affaldsindsamling uden plastikposer og en effektiv kildesortering. Den krævede hygiejnisering kan opnås ved den omtalte hypertermofil behandling. Forurening af



ODA med miljøfremmede stoffer og deres skæbne gennem biogasprocessen blev undersøgt i den endelige fase af det foreliggende Ph.D. projekt. Resultaterne findes i detaljere i **artikel 6**.

Analyserne af prøver fra forskellige biogas- og komposteringsanlæg, som behandler ODA, viste at phthalatesteren DEHP (di-(2-ethylhexyl)phthalate) var det mest betænkelige forurenende stof i affaldet. DEHP produceres i store mængder til brug som blødgører af PVC og som tilsætningsstof i farver og lim. Det anses som en allestedsnærværende forurenende stof i mange vand- og jordmiljøer og er mistænkt for at have en kræftfremkaldende, en mutagen og en hormonlignende effekt. Derfor blev der i Danmark fastsat et afskæringsværdi på 50 mg/kg-TS i organisk affald, når dette skal bruges til gødning på marker. I den organiske dagrenovation, som blev behandlet på de forskellige anlæg, var DEHP koncentrationen mere end halvdelen af afskæringsværdien. Pga. reduktionen af tørstoffet med mere end 50% gennem biogasprocessen ville koncentrationen per kg tørstof overstige denne værdi hvis DEHP ikke nedbrydes.

DEHP er kendt som en svært biologisk nedbrydelige forbindelse under både aerobe og anaerobe betingelser. Det skyldes hovedsageligt pga. dens lave vandopløselighed. Den foreliggende undersøgelser viste dog, at i kombinationen med den termofile og den hypertermofile behandling blev 34 – 53% af DEHP fjernet. Fjernelsesrater var mere end en faktor 10 større end i tidligere aerobe eksperimenter. Der kan antages, at denne større nedbrydningseffektivitet skyldtes den høje temperatur og den høje TS reduktion, som havde en forøgelse af biotilgængeligheden af DEHP til følge. Forurening med DEHP i effluenten, som var bundet til den tilbageværende organisk materiale, var i ca. samme koncentration per kg tørstof som i influenten. Forurening af den indsamlede ODA med DEHP skulle derfor ikke overskride afskæringsværdien. Dette viser endnu en gang at det er nødvendigt at indrette en kildesortering af ODA med lav plastikforurening.

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# **PAPER 1**

## **Strategies for the anaerobic digestion of the organic fraction of municipal solid waste – An overview**

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# Strategies for the anaerobic digestion of the organic fraction of municipal solid waste – An overview

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**Abstract** Treatment of the organic fraction of municipal solid waste (OFMSW) by anaerobic digestion (AD) is at present the only real waste treatment technology that meets the demands of sustainable waste management. Different strategies have been investigated in the recent 15 years to optimize the AD process both in lab-scale, pilot-scale and full-scale. These process strategies are reviewed weighing high-solids versus low-solids, mesophilic versus thermophilic and single-stage versus multi-stage processes. The influence of different waste characteristics such as composition of biodegradable fractions, C:N ratio and particle size is described. Generally, source sorting of OFMSW and a high content of food waste leads to higher biogas yields than the use of mechanically sorted OFMSW. Thermophilic processes are more efficient than mesophilic processes in terms of higher biogas yields at different organic loading rates (OLR). Highest biogas yields are achieved by means of wet thermophilic processes at OLR's lower than  $6 \text{ kg-VS}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ . High-solids processes appear to be relatively more efficient when OLR's higher than  $6 \text{ kg-VS}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$  are applied. Multi-stage systems show in some investigations a higher reduction of recalcitrant organic matter compared to single stage systems, but they are seldom applied in full-scale. In addition to the reviewed processes an extended cost-benefit calculation is presented, regarding not only the biogas production, but also the treatment costs for the waste. Process operation shows the highest overall benefit at an OLR that is lower and a hydraulic retention time (HRT) that is longer than those values of OLR and HRT, at which the highest biogas production is achieved.

**Keywords** Anaerobic digestion; cost-benefit; high-solids; low-solids; mesophilic; multi-stage; organic fraction of municipal solid waste; organic loading; single-stage; thermophilic

## Introduction

Waste management has become one of the largest environmental concerns in the recent decades. The scarcity of land and uncontrolled contamination with gas and leachate emissions made landfilling, which was formerly the main waste management method, no longer an option in many European countries. Moving towards a sustainable waste management regime, the hierarchy of waste treatment methods has switched to minimization, recovery, incineration and landfill (Sakai et al., 1996). Biological treatment of OFMSW offers a waste management strategy that combines stabilization of the waste, i.e. the reduction of organic matter (volatile solids, VS), with recovery of nutrients, if the end product is used as fertilizer. AD does, furthermore, utilize the energy content of the waste and, to a large extent, convert it into a valuable energy source in the form of methane.

## Anaerobic digestion and incineration

Compared to incineration, the recovery of nutrients makes AD highly superior in the context of a sustainable waste treatment concept. Moreover, AD has the potential to treat the “wet” fraction of municipal solid waste (MSW) that is less amenable to incineration. Last, but not least, the bottom ash of incineration treatment has to be deposited as hazardous waste. The content of chlorinated compounds in OFMSW is disadvantageous for incineration since it contributes to the formation of hydrogen chloride (HCl) and products of incomplete combustion (PICs) such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs) are formed (Kanters and Louw, 1994). Incineration plants would, therefore, benefit from not treating OFMSW. Consequently, biological treatment and

incineration are not competing treatment processes, but should be seen as technologies for two separate waste streams, i.e. the biodegradable and the non-biodegradable waste (Alexiou and Osada, 2000). Incineration should be used only for the treatment of the non-biodegradable fraction of MSW. Source sorting of household waste into a biodegradable and a non-biodegradable fraction, which is a prerequisite for AD, would also improve the incineration process and thereby the entire management of MSW.

### **Anaerobic digestion and aerobic composting**

The main advantage of AD compared to composting is its positive energy balance. While composting represents an energy consuming process (around 30-35 kWh is consumed per ton of waste input), anaerobic digestion is a net energy producing process (100 – 150 kWh per ton of input waste). Furthermore, area requirements are lower and odor problems are minimized since the whole treatment process is performed in reactors (Braber, 1995). Furthermore, composting has a negative environmental impact due to considerable CH<sub>4</sub> emissions into the atmosphere, since also anaerobic degradation processes occur inside open composting piles (Edelmann et al., 2000).

The treatment capacities for AD in Europe are, however, still 20 times less than for aerobic composting, probably because AD was not considered to be a fully proven technology until around 1995. It was also more expensive, so many municipalities chose less risk and less investment (De Baere, 2000). With an increasing internalization of external costs, however, the positive environmental effects are considered within economical constraints. Economical feasibility can alter radically with energy prices, levies on waste disposal and land prices (Braber, 1995). In a life cycle assessment, Edelmann et al. (2000) showed that AD was advantageous compared to composting, incineration or to a combination of digestion and composting, mainly because of a better energy balance.

Several researchers have investigated a combined treatment of anaerobic and aerobic degradation. Comparing aerobic - anaerobic with anaerobic - aerobic process sequences at mesophilic temperatures (36°C), Krzystek et al. (2001) found that the VS reduction was similar in both cases, but the amount of produced biogas was four times higher when the first stage was anaerobic.

Mata-Alvarez et al. (1993) investigated process performance under anaerobic thermophilic conditions with pre-composted OFMSW compared to fresh OFMSW. Auto-heating of OFMSW taking place in less than one week after the sorting procedure was considered as pre-composting. The pre-composted material generally showed a loss of biogas yield and gas production rate. A higher biogas yield for the pre-composted OFMSW compared to fresh OFMSW reported for a HRT of 12 days was suspected to be due to the pre-composting, making complex organic matter more easily available for the anaerobic hydrolytic bacteria. This, however, cannot be clearly concluded from the presented data since the OLR used in the experiment of pre-composted OFMSW was significantly lower than in the experiment with fresh OFMSW at 12 days HRT. Thus, the pre-composting step showed no benefit for achieving higher biogas yields in the anaerobic digestion process.

In a two-stage process investigated by Kayhanian and Tchobanoglous (1993) the aerobic post treatment with a HRT of 3 days was mainly used for a further volume reduction by water evaporation, while the degradation of volatile solids was not significant after OFMSW was treated anaerobically for 30 days.

Pera et al. (1991) co-composted the effluent from anaerobic digestion of OFMSW together with fresh OFMSW for further biostabilization of the waste. The advantage of this method was that after mixing with fresh OFMSW the material could be arranged in a stable windrow. However, the energy content of the part of OFMSW used only as bulking material was lost.

Generally, these investigations do not show a significant improvement of combining AD of OFMSW with aerobic composting. However, aerobic composting could be beneficial as additional treatment for an accelerated degradation of possible xenobiotics contamination as phthalates, for example, since aerobic degradation rates for these compounds are often higher than under anaerobic conditions (Madsen et al., 1999).

It can be concluded that if an aerobic treatment of the waste is necessary due to contamination with xenobiotic compounds the composting process should always be applied as post-treatment in order to maximize the energy benefits of anaerobic digestion and minimize the amount of waste to be treated by the energy consuming composting treatment.

### **Waste characteristics**

The organic fraction of municipal solid waste is rather a heterogeneous substrate and the biogas yield in the AD treatment of OFMSW is dependent not only on the process configuration, but also on the waste characteristics. The content of lignocellulose, for instance, determines the biogas potential. The C:N ratio is an important parameter in estimating nutrient deficiency and ammonia inhibition and the particle size may influence the degradation rate of the waste.

The waste characteristics are highly dependent on the collection system. Source sorting of MSW generally provides OFMSW of higher quality, in terms of smaller quantities of non-biodegradable contaminants like plastics. Mechanically separated OFMSW is more contaminated, which leads to persistent handling problems and lower acceptability of the effluent product of the treatment process used as fertilizer on agricultural land (Braber, 1995).

### **Biodegradability**

The biodegradability and hence the biogas potential of the waste substrate depends on the content of carbohydrates, lipids and proteins, as well as the composition of cellulose, hemicellulose and lignin fractions. Due to the different percentage of these fractions in collected OFMSW (food waste, yard waste, paper), the biodegradability differs significantly. The ultimate biodegradability of OFMSW can be determined by long-term batch digestion studies, measurement of lignin content and chemostat studies (Kayhanian, 1995). Chandler et al. (1980) found that the biodegradable fraction can be directly related to the lignin content. The lignin content can be determined by sequential fiber analysis, according to Goehring and van Soest (1970), and is expressed as percent of dry weight of the VS.

Using this method, Kayhanian et al. (1991, 1992) estimated the biodegradable fraction of VS of food waste and yard waste to be 82% and 72% and of office paper, mixed paper and newsprint to be 82%, 67% and 22%, respectively (Kayhanian et al., 1991, Kayhanian and Tchobanoglous, 1992). Baeten and Verstraete (1988) reported a biodegradability of 60% for waste paper (journals, periodicals, packing paper) while paper sludge from a pulp-making factory with a lignin content of 15% showed only 25% bioconversion.

In general, food waste gives the highest biogas yield, which will decrease with increasing amounts of yard waste and low quality paper in the collected OFMSW. However, the addition of paper in a dry anaerobic digestion process of biowaste showed two positive effects: the biogas production rate increased from 3.6 to 7.1 l/l·d and the ammonia concentration dropped from 3.5 to 1.7 gNH<sub>4</sub><sup>+</sup>-N/l (Vermeulen et al., 1993).

### **C:N ratio**

The C:N ratio of the collected waste is determined by its composition. If the C:N ratio of OFMSW is too high, the waste used as single substrate will be deficient in nitrogen, which is needed for build-up of bacterial mass. If the C:N ratio is too low, the degradation of the substrate leads to increases in ammonia formation and this is toxic to the bacteria. The C:N

ratio, based on biodegradable organic carbon, for food and yard waste is below 20, and for mixed paper, it is more than 100 (Kayhanian and Tchobanoglous, 1992). For the degradation of OFMSW in high-solids anaerobic digesters, the optimum C:N ratio for methane production was found to be in the range of 25 to 30, based on biodegradable carbon (Kayhanian and Tchobanoglous, 1992, Kayhanian and Hardy, 1994, Kayhanian and Rich, 1995). OFMSW processed from MSW is nutrient deficient due to the removal of the nutrient rich food and yard waste fractions (Rivard et al., 1989). The nitrogen levels found in different types of OFMSW are listed in table 1. Since the different waste fractions are characterized by different C:N ratios, the desirable C:N ratio can be achieved by adjusting the ratio of the different fractions. When using processed MSW with a high content of paper, wood and cardboard, the addition of nutrients from digested sewage sludge can be beneficial for the digestion of OFMSW (Rivard et al., 1990). Co-digestion with nutrient rich organic wastes like manure would be another option to overcome nutrient deficiency (Hartmann et al., 2002).

**Table 1** Nitrogen levels found in OFMSW

Substrate	N (g-N/l)	Reference
Mechanically sorted OFMSW	3.75	Cecchi et al. (1991a)
Source-sorted OFMSW	6.4	Cecchi et al. (1991a)
Kitchen biowaste	3.5	Vermeulen et al. (1993)
Kitchen biowaste +paper (15%)	1.7	Vermeulen et al. (1993)
Simulated OFMSW: Mixture of newsprint, mixed office paper, yard waste, and food waste	3.0 – 3.7	Kayhanian and Tchobanoglous (1993)

### Particle size

Generally, the particle size of solids has a significant influence on the biodegradation rate, since the surface area to which enzymatic attack is possible, increases with a smaller particle size. Accordingly, Kayhanian and Hardy (1994) identified particle size as an important parameter in the performance of the high-solids anaerobic digestion process for OFMSW. Their results indicated that the rate of methane gas production was inversely proportional to the average feedstock particle size. Furthermore, it was concluded that reducing the particle size might also reduce material handling difficulties. However, there are several inconsistencies in the literature, as to whether particle size reduction is beneficial. Depending on the moisture content, shredding of the waste can lead to compaction of the waste and a lower optimal moisture content (Hamzawi et al., 1999).

### AD processes for the treatment of OFMSW

While waste characteristics determine the ultimate biodegradability and biogas potential of the waste, process design can influence significantly the practical biogas yield. In order to select the optimal strategy for AD of OFMSW, the different processes that have been applied throughout the last 15 years both in lab-scale, pilot-scale and full scale are summarized in table 2.

The AD processes can be divided into mesophilic and thermophilic, high-solids and low-solids concentration, and single stage and multi stage processes. For a better comparison of the biogas yields achieved by the treatment of OFMSW, only concepts where OFMSW was the predominant substrate are included. Co-digestion of OFMSW has been reviewed recently (Hartmann et al., 2002).

### **Wet versus dry fermentation**

Depending on the moisture content and hence the total solids (TS) concentration of the feed for the AD process, the process is termed low-solids = "wet" process with TS < 20%, high-solids = "dry" process with TS > 20%, and "semidry" process with TS of around 20%. Since OFMSW is a substrate with a high solids content of about 30% TS, the simplest treatment process of OFMSW alone is the high-solids treatment process. Throughout the 1990's a number of high-solids digestion plants were constructed and have shown operational reliability (Six and De Baere, 1992, ten Brummeler, 2000, de Laclos et al., 1997, Hamzawi et al., 1999). The capacity of dry fermentation processes in Europe was estimated to be 54% of the total AD processes for OFMSW in the year 2000 (De Baere, 2000). The advantage of high-solids fermentation is that organic loading rates of  $10 \text{ kg-VS} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$  and higher can be applied. However, complete mixing of the waste is not possible, and, therefore, full contact of biomass and substrate is not guaranteed. Consequently, individual processes run in different compartments of the reactor, which limits an optimal co-operation of the microbial groups involved in the AD process. Recirculation of the leachate can improve the homogeneity of the process (de Laclos et al., 1997, Hamzawi et al., 1999). Furthermore, in dry fermentation processes, handling problems often exist since conventional pumping is not possible for high-solids waste.

The wet digestion of OFMSW can be performed in conventional reactor systems where process homogeneity is obtained by continuous stirring. In order to lower the TS concentration, addition of liquid is necessary, either by recirculation of the liquid effluent fraction, or by co-digestion with a more liquid waste. The latter is an attractive method to combine several waste streams like sewage sludge or manure and OFMSW (Hartmann et al., 2002).

### **Thermophilic versus mesophilic conditions**

Traditionally, AD was mostly applied in the mesophilic temperature range of ambient temperature and up to 37°C. It was believed that thermophilic processes were less stable and led more rapidly to process failure. Throughout the recent 15 years, however, more and more thermophilic biogas plants have been established and nowadays most of the centralized biogas plants in Denmark are operated under thermophilic conditions, proving that stable thermophilic digestion is no longer a problem (Ahring, 1994). Thermophilic operation offers the advantage of a higher reaction rate, causing a more profitable process with a lower retention time.

Comparing mesophilic and thermophilic degradation of OFMSW, Cecchi et al. (1991, 1992) found for high-solids digestion of OFMSW and for the co-digestion of OFMSW and sewage sludge that the biogas production at thermophilic conditions, with a HRT of 12 days, was around double the biogas production at mesophilic conditions and with a HRT of 15 days. This surplus in gas production was enough to compensate for the additional energy consumption for heating the digester (Cecchi et al., 1991b, Cecchi et al., 1992b). The change from mesophilic to thermophilic conditions was achieved throughout 2 months without particular evidence of digester instability (Cecchi et al., 1993). Pavan et al. (1994) investigated the process stability after changes of operative parameters like OLR (increase of 15-40% over 2 days), TS feed (increase of 40% over 10 days), HRT (decrease of 20% over 2 days) and temperature (increase of 10°C in 6 days). In general, the thermophilic semi-dry anaerobic digestion process showed to be very robust and was able to buffer these variations, reaching new stationary conditions within a week.

Thermophilic operation leads to a better hygienisation of the waste material than mesophilic treatment. Typical pathogens found in manure and slurry are eliminated within some hours of thermophilic treatment at the biogas plant, while they may survive for longer



periods in digester tanks which operate at mesophilic temperatures. The 90% decimation time for a number of pathogenic bacteria was less than 1.2 hours at 53°C, while it was between 0.9 and 7.1 days at 35°C (Bendixen, 1994). Fecal coliforms could not be detected in the effluent of the thermophilic DRANCO process whereas the original waste contained  $3 \cdot 10^3$  CFU/gTS (CFU: colony forming units) and conventional aerobic compost produced in windrows from the same original material still counted  $2 \cdot 10^2$  CFU/gTS (Six and De Baere, 1992). Kübler (1994) reported that after addition of pathogen seeds of *Salmonella typhimurium*, *Escherichia coli* and *Candida albicans* none of these were detected after 11 h of thermophilic treatment at 55°C while up to  $10^7$ - $10^9$  CFU/ml was detected in a reference batch of the pathogen-infected waste after storage at room temperature. The thermophilic process was also shown to be useful for weed seed elimination (Kübler, 1994, Engeli et al., 1993). Additional treatment at higher temperatures can be beneficial for further sanitation. In Denmark, a treatment of household waste at temperatures more than 70°C for 1 hour is required if the waste is used as fertilizer for consumable crops (Bendixen, 1994).

The drawback of a higher concentration of free ammonia at higher temperatures can be overcome by, for example, co-digestion of waste streams with high ammonia content with other kinds of waste with a lower content (Kayhanian 1999). For the anaerobic digestion of OFMSW, this can be achieved by the mixing of, for example, food waste and paper, due to their low and high C:N ratio.

AD processes at temperatures higher than the moderate thermophilic temperature range have so far only been scarcely investigated. Rintala and Ahring (1994) studied the combination of a 70°C hydrolysis continuously stirred tank reactor (CSTR) with a thermophilic (55°C) upflow anaerobic sludge blanket (UASB) reactor. The overall biogas production was, however, low in this configuration, presumably due to the waste quality or the HRT applied that was too short for effective hydrolysis in the pre-treatment step. Scherer et al. (2000) studied single stage and multi-stage reactor configurations operated under thermophilic and hyperthermophilic conditions. Compared to a conventional thermophilic reactor (55°C) the VS reduction was highest in the combination of a hyperthermophilic (60 - 70°C) first stage and a thermophilic second-stage reactor.

### **Two-phase versus single-phase treatment**

Single-phase treatment is, generally, the more predominant AD treatment applied in full-scale for OFMSW, and two-phase digestion has, so far, not been able to prove its benefit in the market place (De Baere, 2000). However, ongoing investigations have been conducted to optimize the process by separation of hydrolysis and methanization in different reactors. The main idea is to optimize the conditions for the hydrolytic bacteria in one reactor and for the methanogens in the other reactor in order to improve the overall degradation rate. Hamzawi et al. (1999) concluded in an overview of high-solids digestion systems used for the treatment of OFMSW, that a two-phase treatment could be operated at significantly shorter HRT and higher OLR than in a conventional single-stage high-rate digester.

Chynoweth et al. (1992) introduced a Sequential Batch Anaerobic Composting (SEBAC) process consisting of three  $0.7 \text{ m}^3$  reactors for the treatment of high-solids waste. All three reactors were operated under thermophilic conditions (55°C), with each operating at the same retention time (7 or 14d). After an initial stage where VFA concentration increased up to 3000 mg/l in the first reactor, a balanced methane fermentation process developed. However, most of the total methane was developed in stage 1, so this system did not show proper separation of the microbial groups and thus the benefit of dividing the system into three reactors was dubious.

Mtz.-Viturria et al. (1995) compared a two-phase and a single-step wet anaerobic digestion system for fruit and vegetable wastes at mesophilic temperature. The two-phase

system consisted of a hydrolyzing reactor packed with Raschig rings and a methanization reactor, which was divided into an UASB reactor in the lower section and an anaerobic filter at the top. Especially at higher loading rates, the overall performance was worse than in a single-stage system. It was concluded that under these conditions the hydrolyzing reactor was overloaded, the VFA became too high and the methanogenic activity in this reactor decreased.

Kübler and Schertler (1994) investigated a three-phase process for the anaerobic digestion of organic waste with separate acidification, hydrolysis and methanization, called the BTA (Biotechnische Abfallverwertung GmbH) process. The whole reactor system was operated under mesophilic conditions and showed highest overall VS reduction of 84% with a HRT of 82 h and a pH of 7.3 in the hydrolysis reactor. In a second pilot-scale investigation the system was reduced to two stages, and consisted of a buffer tank operated at ambient temperature and a thermophilic methanization reactor. (Kübler, 1994). The investigations were, however, performed without a single-stage control reactor, so the benefit of several stages could not be evaluated. From the change to a more simple two-stage system it can be assumed that the multi-stage system was not beneficial.

Hofenk et al. (1984) designed a two-phase process in a pilot study where solid matter was hydrolyzed in the first reactor and the resulting solution, with a high VFA content, was treated in a UASB methanization reactor. The effluent from the UASB was used for percolation of the waste in the hydrolysis reactor. The system was operated batch wise with a solid retention time in the whole system of 3–6 weeks. Both reactors were operated at the same temperature. In one experimental phase mesophilic, in the other thermophilic. Recirculation of the process water showed to be beneficial for the bacterial distribution in the whole reactor system. When operating the system on OFMSW, VS reduction of 58-69% was achieved after 4 and 6 weeks, retention time, respectively. However, the experiments were characterized by percolation problems and the capacity of the UASB reactor decreased after several runs due to deterioration in the structure of the granular sludge.

Recent research has shown that a post-treatment at 68°C is beneficial for hydrolysis of recalcitrant organic matter, which was not degraded by way of a conventional thermophilic treatment. An optimal retention time of 1-2 days was identified and the released VFA's were recirculated with the liquid fraction of the effluent for dilution of the OFMSW load to the first thermophilic reactor. The high temperature post-treatment improved the sanitation of the waste and could combine ammonia stripping to avoid inhibition effects from recirculation of the process water (Hartmann and Ahring, 2005). Furthermore, the hyperthermophilic second stage was beneficial for reduction of phthalic acid esters found in OFMSW (Hartmann and Ahring, 2003).

It can be concluded that two-stage processes can be beneficial for enhancing the overall degradation efficiency, but the process design should be kept simple in order to avoid operational problems in the long run. A separate hydrolysis reactor can be advantageous for treatment of waste containing larger fractions of recalcitrant organic matter, while the separation into two stages can lead to overload problems when using substrates with a high content of easily degradable organic matter. Generally, the separation into two reactors is most optimal if the two processes, hydrolysis and methanization, can be successfully separated. This means that a HRT in the hydrolysis reactor of 5 days and shorter should be applied in order to gain the highest overall VS reduction. For wet-digestion systems, the post-treatment configuration for hydrolysis shows to be more advantageous than pre-treatment. Presumably, high-solids systems benefit from liquefaction of the waste in the hydrolysis reactor, which enables a better contact of substrate and biomass in the second methanization reactor.

**Table 2** Process parameters and biogas yields in previous studies of AD of OFMSW

Waste composition	Temp	Process description		HRT	OLR	Biogas yield	CH <sub>4</sub> content in biogas	Biogas prod. rate	VS red.	Year	Reference	
		lab-scale (S) – pilot scale (P)										
		- large scale (L)										
		Size	TS									
	(°C)			d	kgVS m <sup>-3</sup> d <sup>-1</sup>	m <sup>3</sup> /kgVS	%	m <sup>3</sup> m <sup>-3</sup> d <sup>-1</sup>	%			
<b>Wet digestion processes:</b>												
Processed MSW (drum sieve – dry separation) – highly organic fraction (fibers), low in wood, plastic, inerts	35	S + P	4 l, 9 l, 1600 l	Co-digestion with (0-70%) raw sewage sludge (SS)	15	6.4	0.05 (20%SS)	50	0.29 <sup>a</sup>	46	1981	(1) Diaz et al. (1981)
					15	4.8	0.39 (20%SS)	65	1.87 <sup>a</sup>	78		
					15	3.2	0.29 (20%SS)	50	0.93 <sup>a</sup>	75		
					15	1.6	0.20 (60%SS)	57	0.32 <sup>a</sup>	53		
					15	1.6	0.27 (40%SS)	57	0.43 <sup>a</sup>	61		
					30	1.1	0.34 (0% SS)	52	0.38 <sup>a</sup>	77		
					30	1.1	0.51 (40% SS)	60	0.56 <sup>a</sup>	61		
Food market waste	35	P	3 m <sup>3</sup>	4%TS (plant design was 10.5%TS with dilution by recirculation of 75% of the effluent filtrate)	12	2.8	0.76 <sup>b</sup>	63	2.10 <sup>a</sup>	90-91	1992	(2) Mata-Alvarez et al. (1992a), Mata-Alvarez et al. (1992b)
					14	2.4	0.77 <sup>b</sup>		1.80 <sup>a</sup>			
					16	2.1	0.76 <sup>b</sup>		1.60 <sup>a</sup>			
					20	1.7	0.76 <sup>b</sup>		1.30 <sup>a</sup>			
Food market waste (fruits and vegetables)	35	S	Two-stage: 1.3 l hydrolyzing, 0.5 l methanization reactor	6% TS	5	12.6	0.20 <sup>c</sup>	49	2.52	27	1995	(3) Mtz.-Vituria et al. (1995)
					6	9.4	0.31 <sup>c</sup>	60	2.91	38		
					9	6.3	0.46 <sup>c</sup>	64	2.88	53		
					18	3.1	0.63 <sup>c</sup>	64	1.96	72		
Fresh OFMSW	36	S	6 l CSTR reactor in batch feed mode	10% TS, 6% VS by dilution with water	12	5.0	0.50	n.d.	2.50	50	2001	(4) Krzystek et al. (2001)

**Table 2 (cont.)** Process parameters and biogas yields in previous studies of AD of OFMSW

Waste composition	Temp	Process description		HRT	OLR	Biogas yield	CH <sub>4</sub> content in biogas	Biogas prod. rate	VS red.	Year	Reference	
			lab-scale (S) – pilot scale (P)									
			- large scale (L)									
	(°C)	Size	TS	d	kgVSm <sup>-3</sup> d <sup>-1</sup>	m <sup>3</sup> /kgVS	%	m <sup>3</sup> m <sup>-3</sup> d <sup>-1</sup>	%			
Processed MSW – low in food + yard waste, high in paper, wood, cardboard; pellets of 95% TS	37	S	3.5 l CSTR reactors	5% TS + nutrient solution	14	3.4 <sup>d</sup>	0.52 <sup>b</sup>	63	1.78	70	1990	(5) Rivard et al. (1990)
					20	2.4 <sup>d</sup>	0.52 <sup>b</sup>	62	1.24	75		
					30	1.6 <sup>d</sup>	0.50 <sup>b</sup>	n.d.	0.80	81		
Source-sorted OFMSW	50-56	P	3.4 m <sup>3</sup> BTA process	6-16% TS; dilution by recirculation of process water	6	12.8 <sup>e</sup>	0.28 <sup>c</sup>	69	3.50	38	1994	(6) Kübler (1994)
					9	8.6 <sup>e</sup>	0.36 <sup>c</sup>	64	3.10	52		
					12	6.4 <sup>e</sup>	0.39 <sup>c</sup>	68	2.50	45		
					21	3.7 <sup>e</sup>	0.41 <sup>c</sup>	67	1.50	55		
Grey waste, 30-45% VS and 60-75% VS	55	S	Single stage, 2-stage and 3 stage experiments with 2.5 l(hydrolysis) and 8.5 l (methanogenesis) reactor	6-18% TS, dilution by addition of water	7	7.6	0.22	60-65	1.67 <sup>a</sup>	27	2000	(7) Scherer et al. (2000)
					4	10.6	0.16		1.70 <sup>a</sup>	46		
					14	7.3	0.25		1.83 <sup>a</sup>	36		
					14	5.4	0.33		1.78 <sup>a</sup>	48		
					14	4.5	0.41		1.85 <sup>a</sup>	44		
					14	3.1	0.74		2.29 <sup>a</sup>	68		
					14	6.1	0.53		3.23 <sup>a</sup>	77		
					14	4.3	0.64		2.75 <sup>a</sup>	80		
	60+55				14	3.5	0.54		1.89 <sup>a</sup>	76		
	Source sorted OFMSW, food and vegetables, not yard waste, collected in paper bags	55+68	S	Two-stage: 3.5 l thermophilic reactor and 1 l hyperthermophilic reactor	6% TS, diluted with recirculated liquid fraction of effluent	22	2.3	0.82	59	1.89 <sup>a</sup>		
18						3	0.72	57	2.16 <sup>a</sup>	80		
18						3.4	0.70	63	2.38 <sup>a</sup>	82		

**Table 2 (cont.)** Process parameters and biogas yields in previous studies of AD of OFMSW

Waste composition	Temp	Process description		HRT	OLR	Biogas yield	CH <sub>4</sub> content in biogas	Biogas prod. rate	VS red.	Year	Reference
	(°C)		lab-scale (S) – pilot scale (P) - large scale (L) Size TS	d	kgVSm <sup>-3</sup> d <sup>-1</sup>	m <sup>3</sup> /kgVS	%	m <sup>3</sup> m <sup>-3</sup> d <sup>-1</sup>	%		
<b>Semi-dry digestion processes:</b>											
Source-sorted (SS) or mechanically sorted (MS) OFMSW	35	P	3 and 2.2 m <sup>3</sup>	20% TS(SS)	14	4.2	0.64	63	2.68 <sup>a</sup>	1990	(9a) Mata-Alvarez et al. (1990)
					18	3.2	0.62	62	2.00 <sup>a</sup>		
					25	2.1	0.63	63	1.33 <sup>a</sup>		
				21% TS(MS)	16	6.8	0.23	51	1.53 <sup>a</sup>		(9b)
				OFMSW as single substrate or in co-digestion with sewage sludge (16%TS)	16	4.1	0.23	63	0.93 <sup>a</sup>		
					32	3.4	0.28	57	0.97 <sup>a</sup>		
Mechanically sorted (MS) OFMSW	48-55	P	3 and 2.2 m <sup>3</sup>	9 – 19%TS	6	19.9	0.23	57	4.60	1992	(10) Cecchi et al. (1992a)
					6	18.5	0.24	61	4.40		
					8	13.5	0.30	53	4.10		
					9	14.4	0.29	63	3.5		
					12	6.9	0.40	62	2.80		
OFMSW, grass clippings, wood, waste from tomato plants, potato starch factory, sugar beet	R1+R2: 33-55	S	R1: 25-200l, R2: 20l (UASB)	Two-phase (hydrolysis in R1, methanization in R2)	R1: 12-60h	R2:	R1+R2:	R1:	R2:	1985	(11) Hofenk et al. (1984)
					R1+R2: 3-6 weeks						
					15	15	0.38	65	5.70		
					30	(COD)	0.46		6.90		
					15	8		3.00			
					30	(COD)		3.70			

**Table 2 (cont.)** Process parameters and biogas yields in previous studies of AD of OFMSW

Waste composition	Temp	Process description		HRT	OLR	Biogas yield	CH <sub>4</sub> content in biogas	Biogas prod. rate	VS red.	Year	Reference
	(°C)		lab-scale (S) – pilot scale (P) - large scale (L) Size TS	d	kgVS	m <sup>3</sup> d <sup>-1</sup>	m <sup>3</sup> /kgVS	%	m <sup>3</sup> m <sup>-3</sup> d <sup>-1</sup>	%	
<b><u>Dry digestion processes:</u></b>											
OFMSW	37	P	5 m <sup>3</sup> BIOCEL reactor	30	7	0.26 <sup>c</sup>	n.d.	1.83 <sup>f</sup>	n.d.	1992	(12) Hamzawi et al. (1999), ten Brummeler (2000)
		L	14 x 720 m <sup>3</sup> plant							1997	
Source-sorted food and garden waste, collected once a week; 52,000 t per year from 300,000 inhabitants	40	L	2 x 3,300 m <sup>3</sup> VALORGA process	20 55	10.5 <sup>e</sup> 3.8 <sup>e</sup>	0.35 <sup>f</sup> 0.48 <sup>f</sup>	n.d.	3.68 <sup>a</sup> 1.82 <sup>a</sup>	n.d.	1997	(13) de Laclos et al. (1997)
Organic household waste, no waste paper	55	L	56 m <sup>3</sup> DRANCO plant	15-21	10 – 16.5	0.45	55	5.0-8.0	55	1988	(14) Baeten and Verstraete (1988), Six and De Baere (1992)
Simulated OFMSW: Mixture of newsprint, mixed office paper, yard waste, and food waste	55	P	1.9 m <sup>3</sup> (aerobic second stage 0.77 m <sup>3</sup> )	15 20 30	17.9 13.2 8.9	0.35 0.45 0.55	49 50 50	3.50 4.50 5.50	64 <sup>h</sup> 65 <sup>h</sup> 67 <sup>h</sup>	1993	(15) Kayhanian and Tchobanoglous (1993)
Kitchen biowaste +15% paper	55	S	40 l reactor	20 <sup>k</sup> 42	12.4 <sup>k</sup> 5.2	0.57 <sup>k</sup> 0.69	55	7.10 <sup>k</sup> 3.60	n.d.	1993	(16) Vermeulen et al. (1993)

**Table 2 (cont.)** Process parameters and biogas yields in previous studies of AD of OFMSW

Waste composition	Temp	Process description		HRT	OLR	Biogas yield	CH <sub>4</sub> content in biogas	Biogas prod. rate	VS red.	Year	Reference	
		lab-scale (S) – pilot scale (P)										
		- large scale (L)										
		Size	TS									
	(°C)			d	kgVSm <sup>-3</sup> d <sup>-1</sup>	m <sup>3</sup> /kgVS	%	m <sup>3</sup> m <sup>-3</sup> d <sup>-1</sup>	%			
OFMSW (mainly paper, yard and food waste)	55	P	3 x 0.7 m <sup>3</sup> reactors (SEBAC)	Feed is moistened and inoculated by recycled leachate from stage 3	21 (3x7)	6.4	0.34 <sup>c</sup>	n.d.	2.18 <sup>1</sup>	n.d.	1992	(17) Chynoweth et al. (1992), Hamzawi et al. (1999)
					42 (3x14)	3.2	0.39 <sup>c</sup>					
Fruit, yard and vegetable waste	55	P	15 m <sup>3</sup>	18-40% TS in horizontal stirred tank reactor	13	11	0.34 <sup>c</sup>	60-65	3.70	n.d.	1993	(18) Hamzawi et al. (1999)
		L	KOMPOGAS reactor (200 m <sup>3</sup> plant)		40	7	0.39 <sup>c</sup>		2.70			

<sup>a</sup> calculated by  $R = Y \cdot OLR$

<sup>b</sup> calculated by  $Y_{biogas} = Y_{CH_4} / \%CH_4$

<sup>c</sup> calculated by  $Y = R / OLR$

<sup>d</sup> calculated by  $OLR = R / Y$

<sup>e</sup> calculated by  $OLR = C_{in} / HRT$ , assuming TS average is 11% and VS/TS = 0.7

<sup>f</sup> calculated by  $Y_{biogas} = Y_{CH_4} / \%CH_4$ , assuming 60% methane content in biogas; only value of methane yield is given

<sup>g</sup> calculated by  $OLR = C_{in} / HRT$ , assuming VS/TS = 0.7

<sup>h</sup> calculated from the ratio of biodegradable VS (BVS) to total VS with BVS/VS = 0.68

<sup>i</sup> with addition of waste paper

<sup>k</sup> assuming a CH<sub>4</sub> content of 55% in the biogas

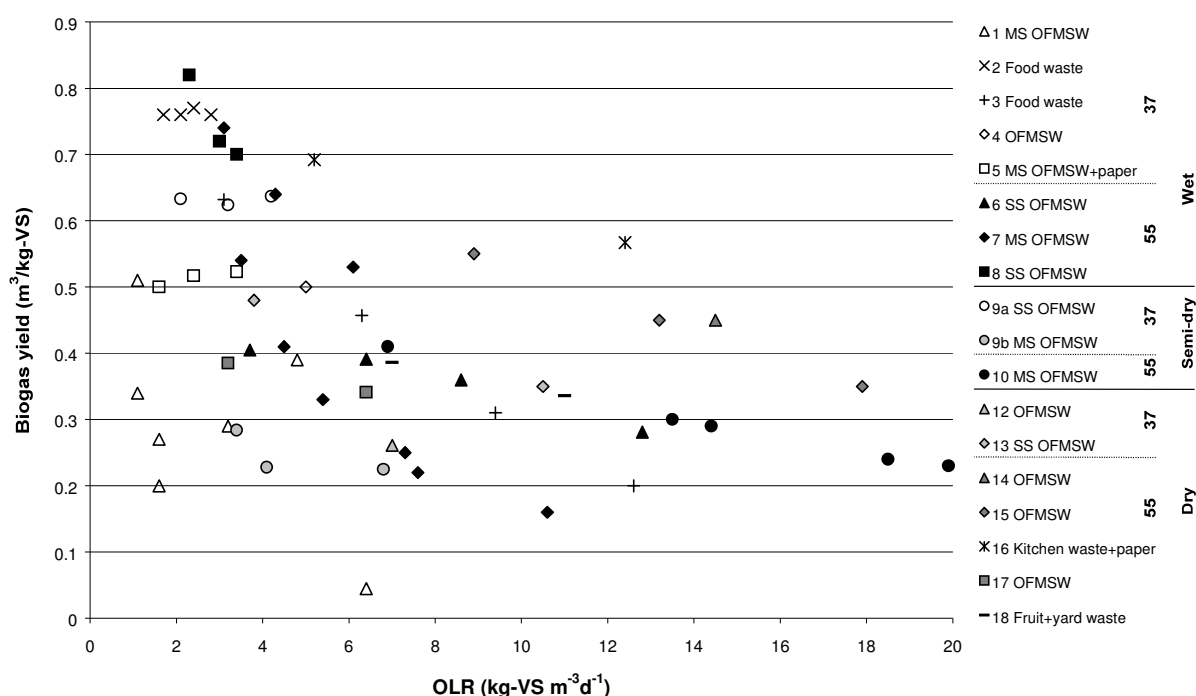
n.d.: no data

## Evaluation of the different strategies

Guided by the overview of the biogas yield achieved in the different investigations at various organic loading rates (figure 1), we will show the influence of operation temperature and solids concentration of the process and of the waste quality on the outcome of the process. The biogas yield of each process investigation is plotted against the OLR results and the results of each investigation are listed under the reference number in table 2 and divided into 6 process categories according to different temperatures (mesophilic, thermophilic) and solids concentration (wet, semidry and dry).

Comparing the biogas yield of each category with regard to the waste quality, it is obvious that highest yields are achieved if the waste consists of food, fruit and vegetables (2, 3, 16). Furthermore, it can be seen that the yields of source-sorted OFMSW (SS-OFMSW, 9a, 8, 6, 13) are often significantly higher than of processed mechanically sorted OFMSW (MS-OFMSW, 1, 9b, 7, 10). The addition of paper shows a beneficial effect on the increase of the biogas yield (5, 16).

Regarding the different AD processes for OFMSW, the highest biogas yields were obtained in thermophilic wet digestion processes (8, 7) at  $OLR < 6 \text{ kg-VS} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ . The achieved biogas yields were higher than  $0.6 \text{ m}^3/\text{kg-VS}$  (8, 7). In all process categories, wet, semidry, and dry, thermophilic processes, generally, yield more biogas than mesophilic process operation. Most investigations reveal a decline of the biogas yield with increasing OLR. The decrease is more pronounced for wet than for dry AD processes. If an OLR higher than around  $6 \text{ kg-VS} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$  is applied, the biogas yield for semidry and dry process operation is higher than for wet digestion processes.



**Figure 1** Biogas yield versus OLR in the reviewed AD processes (reference 11 is not included due to uncertainties in the reported COD data)



## Process efficiency related to OLR, HRT

Since the advantages of AD are both biogas production and waste stabilization, attention should be drawn to both issues under the optimization of the AD process and not only to the biogas production rate. In the following we will show that, when the VS reduction is also taken into account, the process is more optimal when it is operated at different OLR and HRT than if only the biogas production rate was regarded.

The total benefit  $B_{\text{tot}}$  of the biogas process is defined as the difference between the benefit from the biogas production  $B_{\text{gas}}$ , and the cost of both the waste treatment ( $C_{\text{waste}}$ ) and disposal or post-treatment ( $C_{\text{eff}}$ ) of the effluent. Calculation of the costs and benefits per kg of volatile solids (VS) and per  $\text{m}^3$  of gas produced, can be done in the following way:

$$B_{\text{tot}} = B_{\text{gas}} - C_{\text{waste}} - C_{\text{eff}} = b_{\text{gas}} \cdot g - c_{\text{VS}} \cdot w - c_{\text{VSeff}} \cdot e \quad (\text{€/d})$$

where  $b_{\text{gas}}$  is the price per  $\text{m}^3$  of methane ( $\text{€/m}^3_{\text{gas}}$ ),  $g$  is the biogas production per day ( $\text{m}^3_{\text{gas}}/\text{d}$ ),  $c_{\text{VS}}$  is the cost per kg-VS of the waste ( $\text{€/kg-VS}$ ),  $w$  is the VS load of the reactor per day ( $\text{kg-VS/d}$ ),  $c_{\text{VSeff}}$  is the cost per kg-VS in the effluent ( $\text{€/kg-VS}_{\text{eff}}$ ), and  $e$  is the amount of VS in the effluent per day ( $\text{kg-VS/d}$ ).

The amount of VS in the effluent is determined by the VS reduction  $r_{\text{VS}}$  (%):

$$e = w - r_{\text{VS}} \cdot w = w \cdot (1 - r_{\text{VS}})$$

and therefore:

$$B_{\text{tot}} = b_{\text{gas}} \cdot g - [c_{\text{VS}} + c_{\text{VSeff}} \cdot (1 - r_{\text{VS}})] \cdot w$$

For a fixed reactor volume the total benefit of the process will then be given by:

$$B_{\text{tot}} = b_{\text{gas}} \cdot R - [c_{\text{VS}} + c_{\text{VSeff}} \cdot (1 - r_{\text{VS}})] \cdot \text{OLR}$$

where  $R$  is the biogas production rate ( $\text{m}^3 \cdot \text{m}^{-3}_{\text{reactor}} \cdot \text{d}^{-1}$ ) and OLR the organic loading rate ( $\text{kg-VS} \cdot \text{m}^{-3}_{\text{reactor}} \cdot \text{d}^{-1}$ ).

If the composition of the waste in terms of carbohydrates, proteins, fat, cellulose and lignin is the same for different organic loading rates, we can say that the VS reduction is proportional to the biogas yield  $Y$  ( $\text{m}^3_{\text{biogas}}/\text{kg-VS}$ ) with  $r_{\text{VS}} = Y/Y_{\text{max}}$  where  $Y_{\text{max}}$  is the biogas yield after an infinite digestion time, also denoted as biogas potential:

$$B_{\text{tot}} = b_{\text{gas}} \cdot R - [c_{\text{VS}} + c_{\text{VSeff}} \cdot (1 - Y/Y_{\text{max}})] \cdot \text{OLR}$$

The biogas production rate  $R$  is the product of the organic loading rate and the biogas yield achieved at a specific OLR:

$$R = Y(\text{OLR}) \cdot \text{OLR}$$

The biogas yield  $Y$  will, generally, be lower at higher OLR since the contact of biomass to substrate will decrease at higher OLR and at a certain OLR the process will be overloaded leading to VFA increase and process inhibition by, for example, high ammonia concentration. In several investigations displayed in figure 1 a linear relationships between the biogas yield and the organic loading rate can be found (Cecchi et al., 1992a, Scherer et al., 2000). If we write the general dependency of the methane yield on the OLR as

$$Y = Y_{\text{max}} + dY/d\text{OLR} \cdot \text{OLR}$$

where  $Y_{\text{max}}$  is the biogas potential and  $dY/d\text{OLR} < 0$  is the drop in the biogas yield with increasing OLR, it follows for the biogas production rate  $R$  to be:

$$R = Y_{\text{max}} \cdot \text{OLR} + dY/d\text{OLR} \cdot \text{OLR}^2$$

This relationship between the biogas production rate  $R$  and the organic loading rate  $OLR$  is well reflected in, for example, the experimental data obtained by Kayhanian and Hardy (1994).

Since  $OLR$  is defined by

$$OLR = C / HRT$$

where  $C$  is the concentration of VS in the influent to the reactor ( $\text{kg-VS/m}^3$ ) and  $HRT$  is the hydraulic retention time (d), the biogas production rate  $R$  will be dependent on  $HRT$  according to:

$$R = Y_{\max} \cdot C \cdot (HRT)^{-1} + dY/dOLR \cdot C^2 \cdot (HRT)^{-2}$$

Applying these equations for  $R$  and  $OLR$  to the calculation of the total benefit, it follows:

$$B_{\text{tot}} = (b_{\text{gas}} \cdot Y_{\max} - c_{\text{VS}}) \cdot OLR + [b_{\text{gas}} + (1/Y_{\max}) \cdot c_{\text{VSeff}}] \cdot dY/dOLR \cdot OLR^2$$

and

$$B_{\text{tot}} = (b_{\text{gas}} \cdot Y_{\max} - c_{\text{VS}}) \cdot C \cdot (HRT)^{-1} + (b_{\text{gas}} + (1/Y_{\max}) \cdot c_{\text{VSeff}}) \cdot dY/dOLR \cdot C^2 \cdot (HRT)^{-2}$$

For the optimum of  $OLR$  and  $HRT$  we find:

$$OLR_{\text{opt}} = (b_{\text{gas}} \cdot Y_{\max} - c_{\text{VS}}) / [-2 \cdot dY/dOLR \cdot (b_{\text{gas}} + (1/Y_{\max}) \cdot c_{\text{VSeff}})]$$

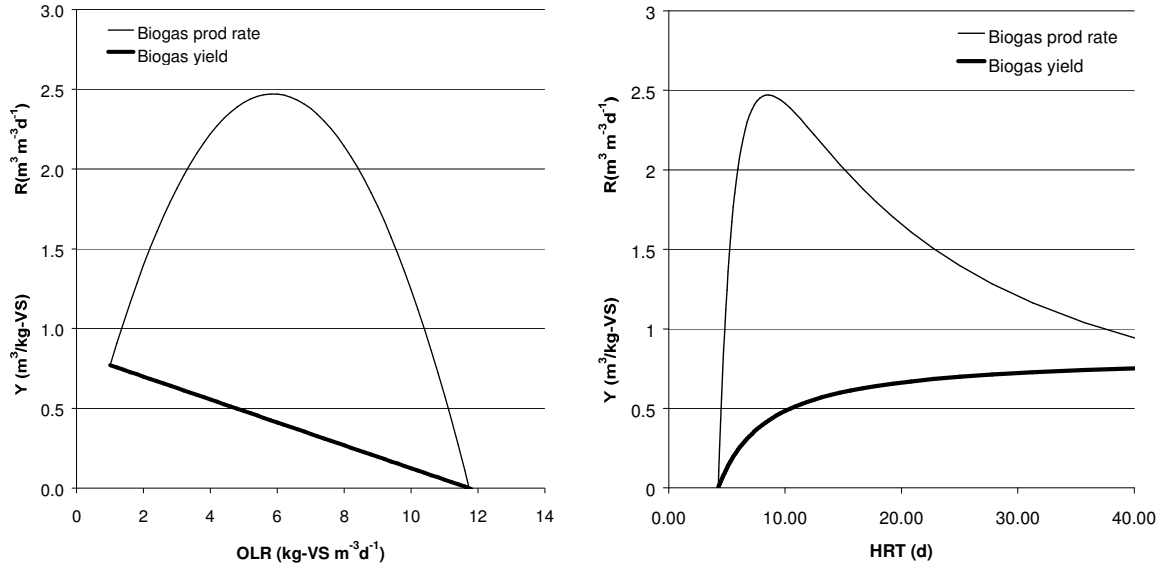
and

$$HRT_{\text{opt}} = \{-2 \cdot dY/dOLR \cdot C \cdot [b_{\text{gas}} + (1/Y_{\max}) \cdot c_{\text{VSeff}}]\} / (Y_{\max} \cdot b_{\text{gas}} - c_{\text{VS}})$$

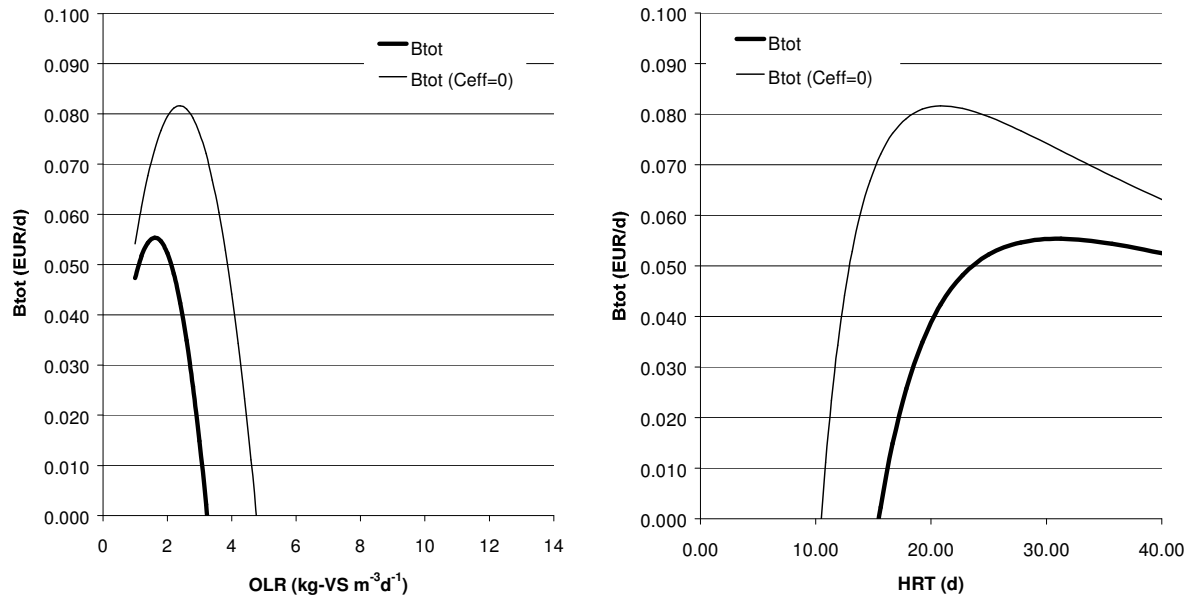
These equations show that if the treatment costs per kg VS of the waste  $c_{\text{VS}}$  and the costs for effluent VS  $c_{\text{VSeff}}$  are not considered ( $c_{\text{VS}} = 0$ ,  $c_{\text{VSeff}} = 0$ ), the total benefit is only described by the gas production rate  $R$  and the biogas price  $b_{\text{gas}}$ . The optimum  $OLR$  will then be where the biogas production rate is highest, although this is, in fact, not the true optimum. Considering waste as a valuable resource, calculations show that AD at lower  $OLR$  and longer  $HRT$  is a more beneficial overall process. How much lower  $OLR$  and how much longer  $HRT$  should be depends on the treatment and post-treatment costs in relation to the biogas benefit and on how much the biogas yield of the process decreases with increasing  $OLR$ .

The calculations above assume that  $c_{\text{VS}}$  is constant and independent of  $OLR$ . This is based on the cost-benefit analysis by Clarke (2000), where the operational costs decreased with higher waste stream size (1000 kgTS/d), but no such dependency could be identified for higher  $OLR$  since the waste stream size is regulated by the reactor volume, rather than by the  $OLR$ .

In figure 2 the dependency of the biogas production rate and the biogas yield on  $OLR$  and  $HRT$  is shown. Figure 3 shows the shift of the optimum for the total benefit  $B_{\text{tot}}$  to lower  $OLR$  and longer  $HRT$ , respectively, when the waste treatment costs are considered. In the given example, the highest biogas production rate would be achieved at an  $OLR$  of  $5.9 \text{ kg-VS} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$  and a  $HRT$  of 8.5 d, respectively. The total benefit of the process, taking into account both treatment costs and costs for the treatment of the effluent, however, would have its maximum for operating the process at an  $OLR$  of  $1.6 \text{ kg-VS} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$  and a  $HRT$  of 30.9 d, respectively.



**Figure 2** Biogas production rate and biogas yield versus OLR (left) and HRT (right), where the relation between OLR and biogas yield is  $Y = 0.84 - 0.072 \cdot \text{OLR}$  (according to the regression found for thermophilic wet digestion process in reference 7 in figure 1) and the VS concentration in the influent of 5% = 50 kg/m<sup>3</sup>.



**Figure 3** Total benefit  $B_{\text{tot}}$  for AD dependent on OLR (left) and HRT (right), including only the waste treatment costs  $c_{\text{VS}} = 0.1$  €/kg-VS ( $C_{\text{eff}}=0$ ), and both waste treatment costs  $c_{\text{VS}}$  and costs for treatment of the effluent  $c_{\text{VSeff}} = 0.08$  €/kg-VS. The biogas price  $b_{\text{gas}}$  is 0.2 €/m<sup>3</sup>.

## Conclusions

By comparing investigations of strategies for the anaerobic digestion of OFMSW throughout the recent 15 years, the following conclusions can be drawn: The highest biogas yields for OFMSW are achieved at thermophilic wet process operation. Thermophilic processes are, generally, more efficient than mesophilic treatment systems. High-solids processes appear to be more efficient for higher loaded processes ( $OLR > 6 \text{ kg-VS}\cdot\text{m}^{-3}\text{d}^{-1}$ ) while low-solids processes are more beneficial at OLR lower than  $6 \text{ kg-VS}\cdot\text{m}^{-3}\text{d}^{-1}$ . Although the benefit of multi-stage systems in terms of higher biogas yield is shown in several investigations, the full-scale applications are mostly single stage. Source sorting of OFMSW is significantly beneficial with regards to higher biogas yields.

By performing an extended cost-benefit calculation of the AD process of OFMSW, the highest benefit is found for lower OLR and longer HRT than when only the biogas production rate is regarded.

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## **PAPER 2**

# **Co-digestion of the organic fraction of municipal waste with other waste types**

**Hartmann, H., Angelidaki, I. and Ahring, B. K.**

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## Co-digestion of the organic fraction of municipal waste with other waste types

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***H. Hartmann<sup>1</sup>, I. Angelidaki<sup>2</sup> and B. K. Ahring<sup>1</sup>***

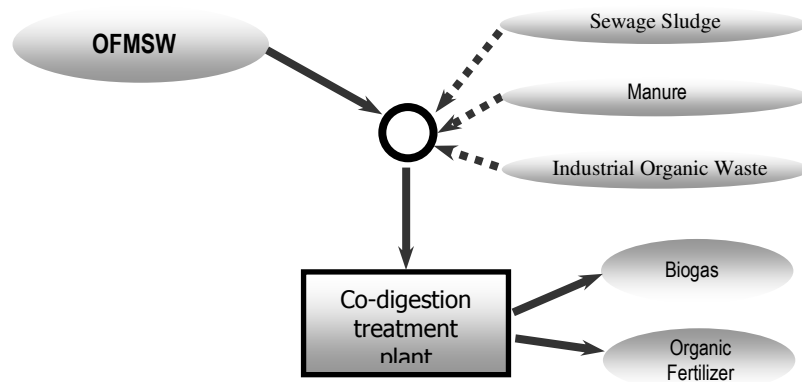
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### INTRODUCTION

Several characteristics make anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) difficult. By co-digestion of OFMSW with several other waste types it will be possible to optimize the anaerobic process by waste management. The co-digestion concept involves the treatment of several waste types in a single treatment facility. By combining many types of waste it will be possible to treat a wider range of organic waste types by the anaerobic digestion process (figure 1).

Furthermore, co-digestion enables the treatment of organic waste with a high biogas potential that makes the operation of biogas plants more economically feasible (Ahring *et al.*, 1992a). Thus, co-digestion gives a new attitude to the evaluation of waste: since anaerobic digestion of organic waste is both a waste stabilization method and an energy gaining process with production of a fertilizer, organic waste becomes a valuable resource.

Co-digestion treatment has been successfully applied to several agricultural and industrial organic waste types in recent years. In Denmark, for example, the co-digestion concept has been successfully used since the mid 1980's for the treatment of livestock waste and industrial organic waste in Joint Biogas Plants (Danish Energy Agency, 1995). However, at present only 7% of the overall OFMSW treated by anaerobic digestion in Europe was done so by means of co-digestion (De Baere, 2000). In this chapter we will show that co-digestion of OFMSW has several benefits which can be used for establishing a wider application of the anaerobic treatment of OFMSW.



**Figure 1:** Principle of co-digestion of OFMSW

## GENERAL ASPECTS OF CO-DIGESTION

Co-digestion is defined as anaerobic treatment of a mixture of at least two different waste types. The mixing of several waste types has positive effects both on the anaerobic digestion process itself and on the treatment economy.

The profit of co-digestion in the anaerobic degradation process is mainly within the following areas:

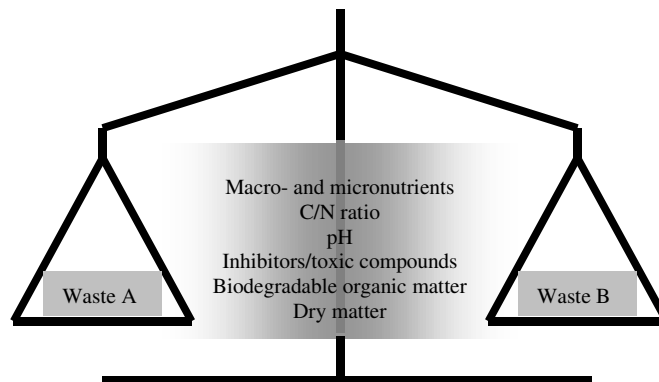
- Increasing the methane yield.
- Improving the process stability.
- Achieving a better handling of the waste.

Waste treatment by co-digestion is economically more favorable due to:

- Combination of different waste streams in one common treatment facility.
- Treatment of larger waste amounts in centralized large-scale facilities.

Co-digestion does further ensure a stable treatment of organic waste that varies significantly during the year, both in quantity and characteristics. (Angelidaki and Ahring, 1997; Ahring, 1995; Gavala *et al.*, 1999; Bozinis *et al.*, 1996; Hamzawi *et al.*, 1998).

Generally, the key for co-digestion lies in balancing several parameters in the co-substrate mixture (figure 2). Some qualities of each co-substrate can be advantageous for use in the biogas process while other qualities can hinder the degradation solely of this waste type.



**Figure 2:** The balance of co-digestion

The balance of nutrients, an appropriate C:N ratio and a stable pH are prerequisites for a stable process performance. High C:N ratio will lead to nitrogen deficiency whereas ammonia toxicity is the principal problem with low C:N ratio. Nutrient deficiency of a given waste can be adjusted by co-digestion together with a nutrient-rich waste type. The problem associated with ammonia toxicity can be corrected by dilution of the ammonia concentration in the liquid phase, or by adjusting the C:N ratio of the feedstock (Kayhanian and Tchobanoglous, 1992). The pH can be balanced by addition of waste with a high buffer capacity, which protects the process against failure due to pH drop when the VFA concentration increases. Referring to the effect on the degradation of toxic substances by co-digestion, it is not only the dilution by addition of other waste that serves as benefit (Hamzawi *et al.*, 1998). Furthermore, detoxification of toxic compounds can be achieved in the co-substrate mixture by, for example, co-metabolic mechanisms, where a compound is transformed along with the general metabolism of microbes using a primary substrate. For example, it has been shown that waste containing tetrachloroethene (PCE) in concentrations of up to 100 ppm can be degraded in co-digestion with manure (Ahring *et al.*, 1996).

In the treatment of organic waste with a high content of recalcitrant organic matter (i.e. lignocellulose), the co-digestion with waste rich in easily biodegradable organic matter will be advantageous for obtaining a higher biogas yield. Organic industrial waste is usually characterized by high concentrations of easily degradable substrates such as carbohydrates, lipids and proteins, having a high biogas potential (Ahring *et al.*, 1992a). Besides achieving a better economical feasibility of the treatment, the addition of easily degradable material has been shown to stabilize the anaerobic digestion process if added in a controlled fashion (Mathrani *et al.*, 1994). This effect could partly be due to a higher active biomass concentration in the reactor, which will be more resistant to inhibitory compounds. Furthermore, the inorganic parts of some organic waste types, such as clays and iron compounds, have been shown to counteract the inhibitory effect of ammonia and sulfide, respectively (Ahring *et al.*, 1992b). Finally, the dilution of waste with a high TS such as OFMSW by co-digestion with waste with a lower TS concentration such as manure resolves problems of pumping and mechanical treatment of solid waste (Angelidaki and Ahring, 1997).

## CO-DIGESTION OF OFMSW

Generally, the application of the anaerobic digestion process to OFMSW faces problems due to the following substrate characteristics (Kayhanian and Rich, 1996; Demirekler and Anderson, 1998; Kayhanian and Rich, 1995 Rintala and Järvinen, 1996; Mathrani *et al.*, 1994; Ahring and Johansen, 1992):

- High total solids (TS) content of typically 30 – 50%
- High C:N ratio
- Deficiency in macro- and micronutrients
- Content of toxic compounds (heavy metals, phthalates)

The benefit on the other hand of using OFMSW in an anaerobic co-digestion process is mainly the high content of easily biodegradable organic matter. This leads to a methane yield of up to 330 l/kgVS (Rintala and Järvinen, 1996; Diaz *et al.*, 1981; Six and De Baere, 1992; Rivard *et al.*, 1990).

Owing to the high total solids content of OFMSW both dry (TS content higher than 20%) and wet (TS below 20%) anaerobic processes have been developed (Cecchi *et al.*, 1988; Poggi-Varaldo *et al.*, 1997; Six and De Baere, 1992; Rintala and Järvinen, 1996). Co-digestion is used for both types of treatment, but mainly for the wet process. In high-solids systems the addition of co-substrates improves process performance due to a better nutrient balance. In wet digestion systems, co-digestion of OFMSW with more diluted waste streams enables a reduction of the TS concentration of OFMSW below 20%. The lower TS content of the wet treatment system offers an easier mechanical handling of the waste and allows for the use of a continuous stirred tank reactor for the anaerobic digestion.

The C:N ratio and the nutrient content of OFMSW vary significantly due to the composition of the single fractions of OFMSW. The different organic fractions (food waste, yard waste, paper, newspaper etc.) have different C:N ratios, which makes the treatment of OFMSW in itself a co-digestion process. C:N ratio based on biodegradable organic carbon is of food and yard waste below 20 and of mixed paper it is more than 100 (Kayhanian and Tchobanoglous, 1992). In high solids anaerobic digesters, the optimum C:N ratio for methane production with no adverse effect on the performance was found to be in the range of 25 to 30, based on biodegradable carbon. (Kayhanian and Tchobanoglous, 1992; Kayhanian and Hardy, 1994; Kayhanian and Rich, 1995). For mixtures with less than 50% OFMSW, an optimal C:N ratio between 25 and 80 has been reported (Hamzawi *et al.*, 1998; Kayhanian and Tchobanoglous, 1992). As can be seen from the different C:N ratios in food waste and yard waste compared to mixed paper, the optimum C:N ratio can thus be also adjusted by the right mixture of mixed paper to food and yard waste. It also shows that anaerobic digestion solely of food waste can lead to ammonia toxicity. Due to the different specific biodegradability of the single fraction the specific combination of the different fractions is one way to achieve optimal reactor operation (Hamzawi *et al.*, 1998). Most MSW processing technologies using modern separation techniques, however, result in the separation and removal of the food and yard waste fraction (Rivard *et al.*, 1990). This does not only lead to a higher TS content, but also reduces the nutrient value of the produced

OFMSW when used as a feedstock for anaerobic digestion, and results in a high cellulose content for the processed MSW caused by increasing the overall percentage of wood, paper and cardboard. Therefore, using this kind of processed MSW necessitates nutrient supplementation for effective biological conversion. OFMSW of such quality is recommended to be treated by co-digestion.

Recently, the level of toxic compounds found in OFMSW has been discussed. Investigations in Denmark have shown that cadmium contamination of OFMSW is derived from garden waste and not so much household waste, while the latter contributes to a higher degree with phthalates such as bis-(2-ethylhexyl)-phthalate (DEHP) contamination (Kjølholt *et al.*, 1998).

Impurities (plastics, metal, glass) found in OFMSW do often hinder the application of co-digestion if the effluent is intended to be used as fertilizer (De Baere, 2000). This is both because fertilizer should meet requirements for the content of toxic compounds (e.g. phthalates, heavy metals) and because farmers will not accept it if it has no clean appearance. The content of impurities and of toxic compounds found in OFMSW is much dependent on the collection system. In terms of the heavy metal content, for example, source-sorted household waste has generally a much better quality than OFMSW separated from municipal solid waste (MSW) by processing technology (Richard and Woodbury, 1992; Ahring and Johansen, 1992). The content of DEHP was reported to be influenced by the collecting material (plastic or paper bags), the acceptance of other material than the organic fraction in the collecting system, the collecting frequency, the temperature and the moisture of the waste (Kjølholt *et al.*, 1998). It is therefore a prerequisite to introduce an adequate collection system in order to supply the treatment plant with clean OFMSW that can be recycled to soil.

The potential of co-digestion, on the other hand, to improve the detoxification abilities in the anaerobic degradation process is an important quality to enable the processing of an environmentally safe fertilizer product from OFMSW in the anaerobic digestion process. Most investigations in the field of co-digestion of OFMSW have been made together with sewage sludge or livestock waste. Several large-scale plants are nowadays in operation using co-digestion of these substrates.

## **CO-DIGESTION OF OFMSW WITH SEWAGE SLUDGE**

With the large amount of sewage sludge (SS) produced in wastewater treatment plants and the large number of existing anaerobic digesters to stabilize it, the anaerobic co-digestion of OFMSW with sewage sludge is especially attractive (Hamzawi *et al.*, 1998). The co-digestion can be applied at existing treatment facilities without great investments and it combines the treatment of the two largest municipal waste streams. First attempts to dispose of garbage through a wastewater treatment plant took place in 1923. No or little attention was paid to this approach until the 1930s and 1940s, when the introduction of the home garbage grinder made the co-digestion of garbage and sewage more feasible (Diaz *et al.*, 1981).

Co-digestion of OFMSW together with sewage sludge is beneficial due to a number of substrate characteristics of both waste types that are complementary in their combination (figure 3).

The addition of high solids concentration of OFMSW to a sewage sludge digester operated with sludge having a low TS concentration will be possible even in rather high concentrations. The higher concentration of macro- and micronutrients in the sludge solids will compensate the lack of nutrients in OFMSW. The stabilizing effect of sludge on the digestion of OFMSW has been confirmed with sludge doses between 8 and 20% of feedstock volatile solids. (Kayhanian and Rich, 1996; Rivard *et al.*, 1990). While digested sludge has a mainly stabilizing effect on the digestion process, primary sludge increases furthermore the methane yield. Besides, it has been described that addition of primary sewage sludge significantly decreases imbalances observed during the start-up of the digesters (Demirekler and Anderson, 1998).

OFMSW		Sewage sludge
↓	Content of Macro- and Micronutrients	↑
↑	C:N ratio	↓
↑	Content of biodegradable organic matter	↓
↑	Dry matter content	↓

**Figure 3:** The different substrate characteristics of OFMSW and sewage sludge (symbols: ↑ high, ↓ low)

Most co-digestion studies conducted before 1990 were low-solids processes, typically at a total solids concentration of 4-8%. Recently, the high-solids anaerobic digestion process has also been utilized for the co-digestion of OFMSW and sewage sludge. In these high-solids digestion studies, the sludge was mainly used to provide sufficient nutrients for microbial growth and metabolism. The operational total solids concentration was maintained at 25-35%, the feedstock C:N ratio was held between 22 and 30, based on the biodegradable carbon and total nitrogen mass (Kayhanian and Tchobanoglous, 1992; Kayhanian and Rich, 1996).

The optimal mixture of OFMSW and sewage sludge is depending on the specific waste characteristics and the process concept used. For wet digestion systems, several researchers observed the best performance in terms of specific gas production and VS reduction with feedstock having an OFMSW:SS ratio in the range of 80:20 on a TS basis (Demirekler and Anderson, 1998; Diaz *et al.*, 1981), or a volume ratio of 25% OFMSW and 75% sewage sludge, respectively (Hamzawi *et al.*, 1998).

## CO-DIGESTION WITH LIVESTOCK WASTE

Livestock waste has been used for a long time as substrate in anaerobic digesters for the purpose of renewable energy production. This is because of its excellent characteristics for the use as basic substrate and because it is available in large amounts since it is the largest agricultural waste stream. In Denmark, positive experiences have been made with the large-scale co-digestion process of livestock waste and industrial organic waste types. The construction of 20 Joint Biogas Plants since the 1980s has given the possibility for combined anaerobic treatment and utilization of livestock waste and several types of organic waste from food processing industries. Nowadays, the organic fraction of municipal solid waste is co-digested together with livestock waste (and industrial organic waste) at five sites (Sinding, Studsgård, Vaarst-Fjellerad, Vegger, Århus).

Livestock waste is an excellent basic substrate for the co-digestion process because of the following reasons (figure 4). Livestock waste has a high buffering capacity originating mainly from the ammonia content and it has a high water content with total solids content typically 3-5% for livestock waste from pigs and 6-9% for livestock waste from cattle and dairy cows. Furthermore, it is rich in a wide variety of nutrients necessary for optimal bacterial growth and it has always been used for fertilizing and thus facilitates an easier application on agricultural soils. When treating livestock waste alone it has, on the other hand, typically a relatively low methane yield ranging from 10-20 m<sup>3</sup> CH<sub>4</sub>/ton. The reason for this is the low solids content and a high content of fibres consisting of lignocellulose. This fibre fraction is highly recalcitrant to anaerobic degradation and will often pass through the reactor mainly undigested.

OFMSW		Livestock waste
↓	Content of Macro- and Micronutrients	↑
↑	C:N ratio	↓
↓	Buffer capacity	↑
↑	Content of biodegradable organic matter	↓
↑	Dry matter content	↓

**Figure 4:** The different substrate characteristics of OFMSW and livestock waste (symbols: ↑ high, ↓ low)

Addition of industrial organic waste will therefore lead to a substrate with a higher biogas yield per m<sup>3</sup> feedstock than livestock waste alone. These industrial organic waste types are characterized by a high content of carbohydrates, proteins and lipids that are often bioavailable to a large extent, leading to a high biogas potential. The high biogas potential of OFMSW makes it like other organic industrial waste types a very attractive substrate for biogas plants (Mathrani *et al.*, 1994). By combining the two different waste types a methane yield higher than 25 m<sup>3</sup> CH<sub>4</sub>/ton feedstock can be achieved leading to an economically feasible digestion process (Ahring and Johansen, 1992).



The benefit of using livestock waste as basic medium in the co-digestion process has been shown together with several kinds of waste. The co-digestion process with livestock waste has been profitably applied to for example slaughterhouse waste, flotation sludge and fish-oil sludge (Ahring *et al.*, 1992a), fruit and vegetable waste, fish offal, pig manure, dissolved air flotation sludge and brewery sludge (Callaghan *et al.*, 1999). Another investigation showed that the fastest start-up of high-solids anaerobic digestion of a mixture of municipal solid waste, paper sludge and sewage sludge was obtained with reactors using a mixture of equivalent amounts of cow manure, soil and waste activated sludge as inoculum (Poggi-Varaldo *et al.*, 1997).

The co-digestion of OFMSW together with sewage sludge and manure was compared to co-digestion together with water, sewage sludge, or chemical nutrient solution, respectively. The co-digestion together with sewage sludge and manure showed best results both in terms of a stable digestion and markedly enhanced gas production rates (Kayhanian and Rich, 1995).

## **CO-DIGESTION WITH OTHER ORGANIC WASTE TYPES**

There have been conducted several studies where OFMSW was co-digested together with organic waste types other than sewage sludge or livestock waste. As other co-substrates olive mill effluents (OME), macroalgae, waste coming from kitchens, slaughterhouses and meat-processing industries were investigated (Angelidaki and Ahring, 1997; Cecchi *et al.*, 1993; Kübler *et al.*, 2000; Brinkman, 1999; Mata-Alvarez *et al.*, 2000).

The study of the co-digestion together with olive mill effluents (OME) is a good example of determining the right co-substrate for co-digestion of a given waste type (Angelidaki and Ahring, 1997). Olive mill effluents are characterized by high loads of soluble organic matter, low alkalinity, lack of ammonia and inhibitory effects of polyphenols. The main purpose was to find an appropriate co-substrate for the anaerobic digestion of olive mill effluents. Batch experiments were carried out with mixtures of OME together with livestock waste, sewage sludge and OFMSW, respectively, in different dilutions with water. It was shown that the co-digestion of OME together with OFMSW or sewage sludge could only be achieved with high dilution of the waste. OFMSW or sewage sludge had not sufficient buffer capacity to maintain an adequate pH range. The pH dropped severely and the digestion process was inhibited. In co-digestion with livestock waste, however, OME could be degraded without dilution. The positive effect of livestock waste was found to be mainly due to its high alkalinity. Reactor experiments showed that the co-digestion with OFMSW was possible, but more optimal with livestock waste.

## MODELLING THE CO-DIGESTION PROCESS

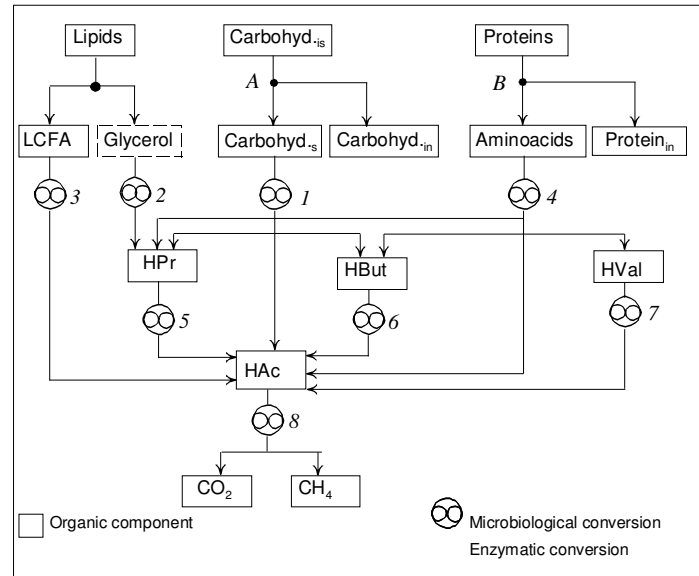
Organic waste management with co-digestion of the right substrates can be beneficial for the anaerobic digestion process. To exploit co-digestion in full, there is clearly the need to be able to predict the outcome of a certain waste combination strategy. The anaerobic treatment plants using co-digestion operate mainly on an empirical basis. However, successful combination of different types of waste requires careful management. The ability to predict the outcome of the process when mixing new waste is an important tool in optimizing the results. Consequently, the need for accurate modelling of the anaerobic degradation of mixtures of waste has arisen (Angelidaki *et al.*, 1997). There are two main approaches to study the co-digestion of different waste types:

On one hand there is the need to perform experiments and derive a mathematical model for the degradation of mixed wastewaters. As described in the example of co-digestion of olive mill effluents, this can be done by experiments of co-digesting one type of waste together with others in different ratios. On the other hand, from the derived models the biodegradation of given waste types can be modelled in different mixtures, with the objective to obtain a stable process with a high-energy yield to minimize capital and operational costs (Bozinis *et al.*, 1996).

Many models have been developed during the last 20 years. However, only few models include the digestion of complex substrates and only little attention has been directed to co-digestion utilizing different waste types in a mixture (Bozinis *et al.*, 1996; Angelidaki *et al.*, 1997; Gavala *et al.*, 1999; Mata-Alvarez *et al.*, 2000).

A model for the anaerobic degradation of different waste types in co-digestion has been developed which will be described in detail in the following (Angelidaki *et al.*, 1997). The model considers the hydrolysis of complex substrates and accounts the influence of the main characteristics of a substrate, i.e. lipid, protein and carbohydrates concentration. Several inhibition mechanisms are included (Angelidaki *et al.*, 1993; Angelidaki *et al.*, 1999). This model has been verified with several co-digestion experiments, one of them was the co-digestion of olive mill effluent (OME) together with manure. However, the model has not been applied for the co-digestion of OFMSW yet.

According to the anaerobic degradation pathway of complex substrates, the co-digestion model involves one enzymatic process (hydrolysis of undissolved organic matter) and eight bacterial groups (glucose fermenting acidogens, lipolytic bacteria, LCFA (long chain fatty acids) degrading acetogens, amino acid-degrading acidogens, propionate, butyrate and valerate degrading acetogens and aceticlastic methanogens, figure 5).



**Figure 5:** Main pathways of the organic component flow used in the model (Angelidaki *et al.*, 1999. Reprinted with kind permission from Wiley-Liss, Inc., a subsidiary of John Wiley & Sons, Inc.)

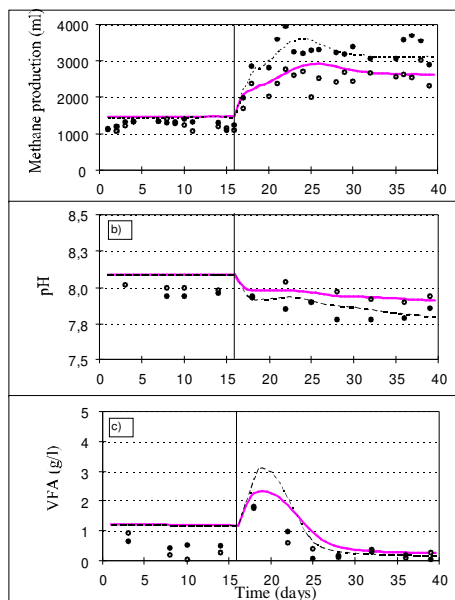
In the single degradation steps, stoichiometry as previously described (Hill, 1982), has been employed with some minor modifications (Angelidaki *et al.*, 1993). As parameters influencing the equilibrium of the reactions in the single stages the equilibrium relationship of ammonia, carbon dioxide and pH, the gas phase dynamics and temperature effects have been included. Four inhibition mechanisms are considered (free ammonia inhibition of the acetoclastic step, acetate inhibition of the acetogenic steps, volatile fatty acids (VFA) inhibition of the initial enzymatic hydrolytic step, inhibition caused by LCFA on all steps of the degradation process except hydrolysis).

For an accurate application of the model, a thorough analysis of the substrate characteristics is required. The biodegradable organic matter fraction is described by the volatile solids (VS) content together with specific content of insoluble and soluble organic matter. For encountering the inhibition effect, the content of ammonia and nitrogen released as ammonia during the degradation process, the LCFA content, VFA concentration and buffer capacity has to be defined as well. The buffer capacity is described by pH, alkalinity, phosphorus, cation- and CO<sub>2</sub> content.

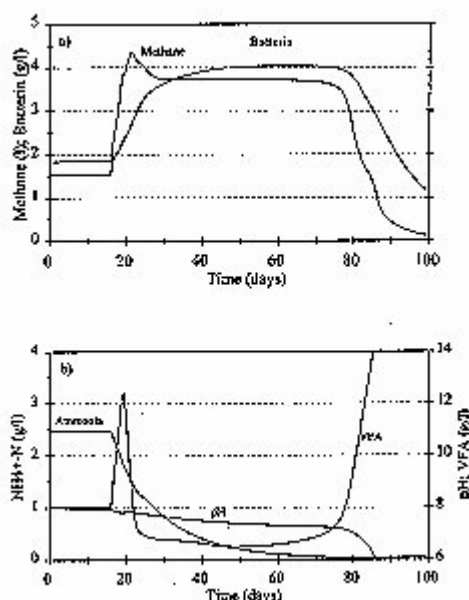
For modelling the co-digestion of OFMSW, further characteristics of OFMSW might be needed for an accurate process description. It has been shown, for example, that factors like the feed particle size play an important role in the digestibility of OFMSW (Hamzawi *et al.*, 1998; Kayhanian and Hardy, 1994).

The model describes well the dynamic response in methane production, pH and VFA concentration after introduction of the co-substrate (OME) to the basic substrate (manure). The simulation shows further the different types of behavior with different mixture ratios of both substrates (figure 6).

In a simulation a total shift from one substrate to the other (manure to OME) the model predicts a total collapse of the process, indicated by VFA rise, pH drop, drop in methane production and bacterial wash-out (figure 7).



**Figure 6:** Digestion of cattle manure alone and then change to co-digestion of OME and livestock waste at day 16; symbols:  $\circ$  experimental data for the 50:50 mixture of OME:manure;  $\bullet$  experimental data for the 75:25 mixture of OME:manure; — simulation data for the 50:50 mixture; - - simulation data for the 75:25 mixture (Angelidaki *et al.*, 1997)



**Figure 7:** Simulation of manure digestion and change of the influent to OME on day 16 (Angelidaki *et al.*, 1997)

## LARGE SCALE PLANTS EXPERIENCES WITH CO-DIGESTION

One of the first large-scale co-digestion plants for OFMSW and sewage sludge was operated in the United States by the Refcom (refuse conversion to methane) project in the 1980s. The Refcom system was based on a conventional low-solids digester design (Kayhanian and Rich, 1996; Cecchi *et al.*, 1988).

One of the first large-scale co-digestion plants for OFMSW in Europe was the Vaasa plant in Finland, which started its operation in 1989 (Rintala and Järvinen, 1996). The process has been tested on several waste types. The digester feed consists of mechanically or source-sorted OFMSW, thickened sewage sludge containing primary and waste activated sludge, slaughterhouse waste, fish waste and manure. The plant uses a wet digestion process with a TS content of approx. 10-15%. Both mesophilic and thermophilic treatment methods are in operation in two parallel reactors. One characteristic of the Vaasa Process is that a small part of the supernatant from the dewatering of the digested material is recirculated to be mixed with the fresh feed. Today, the Vaasa process is also in operation in Kil, Sweden and outside Tokyo, Japan.

The joint biogas plants in Denmark that admix OFMSW (Sinding, Studsgård, Vaarst-Fjellerad, Vegger, Århus) and Sweden's largest biogas plant in Kristianstad work with the same co-digestion concept: household waste is treated together with agricultural waste and industrial waste. The plant at Kristianstad has a capacity of 73,000 tons of biomass per year, of which 15% is OFMSW, 18% is industrial organic waste and 67% is manure. The biogas yield is around 40 m<sup>3</sup> biogas per ton feedstock. The energy production is 1.8 – 2 MW and the heat requirements of 600 to 800 households is covered. (Hedegaard and Jaensch, 1999). At Studsgård biogas plant in Denmark, 129,000 tons of biomass is treated per year, of which approximately 5% is OFMSW, 7% is industrial organic waste and 88% is manure. This plant achieves a biogas yield of approximately 35 m<sup>3</sup> biogas per m<sup>3</sup>. The power production can cover the electricity consumption of about 2700 families and the production of heat is large enough to supply about 700 single-family houses. At all of these plants, the admixing of OFMSW to the feedstock is performed by either direct transport into the digester (for example at Kristianstad, Vegger) or it is first mixed together with manure in a feedstock tank and then pumped into the digester (for example at Studsgård). The effluent quality for the use as fertilizer is very much dependent on the purity of the collected OFMSW. For example, although OFMSW at Studsgård is source-separated, it is necessary to separate out the solid fraction of the digested effluent and incinerate it because of high plastic impurities. The plastic impurities come from the plastic bags used to collect the OFMSW.

An example for the excellent performance of a large-scale co-digestion process of OFMSW and sewage sludge is the sewage treatment plant in Grindsted, Denmark (Skøtt, 1997; Hedegaard and Jaensch, 1999) (figure 8).

The OFMSW is co-digested together with sewage sludge and small amounts of industrial organic waste with the production of biogas for electricity generation and central heating supply. The municipality of Grindsted decided to build this new co-digestion plant in order to meet the formerly formulated requirements of recirculation of 50% of the municipal solid waste. About 1500 tons of the organic fraction of household waste coming from 6200 households is treated per year. The plant is situated outside inhabited areas of

the municipality, to avoid annoyance by waste delivery and to have short distances to nearby farms using the digested effluent as fertilizer.

In order to achieve an OFMSW supply with a high purity a new waste collection system was introduced into the Grindsted municipality. The OFMSW is source-sorted in paper bags and because of a good educational campaign the collecting system is accepted well in the community. Thus the problems in the treatment process arising from impurities of plastics clogging pumps and mixing equipment can be avoided. Furthermore, the dewatered effluent is accepted well by farms for use as fertilizer because of its high purity and its good fertilizing qualities.

The OFMSW used in the process is first shredded and metal impurities are removed before it is mixed with the sewage sludge in a pulper. The mixing ratio of OFMSW:sewage sludge is 1:9, leading to a dry matter content of 8-10%. Then, the mixture is macerated and glass and stones are separated before it is lead to a hygienization tank where it is heated at 70°C for one hour. Together with a minor amount of industrial organic waste (fatty sludge) the subsequent digestion takes place under mesophilic conditions (35°C). The biogas yield is approximately 25m<sup>3</sup> per m<sup>3</sup> of the influent. The biogas produced is loaded to a 247 kW CPH and/or a 706 kW boiler. The TS content is reduced to 3% in the effluent by the treatment. After dewatering, the solid fraction with a TS content of 21–25% can be easily stored for a whole year until it will be supplied to agricultural land in the spring during growth season.



**Figure 8:** The co-digestion plant for OFMSW and sewage sludge in Grindsted, Denmark (Shredding and conveyor equipment for OFMSW in the front, reactor in the background); (Photo: T. Skøtt)

## CONCLUSIONS

The anaerobic degradation of OFMSW by co-digestion with other organic substrates shows several advantages in terms of process stability and economical feasibility. The successful application of the co-digestion concept in large-scale has been demonstrated in a number of existing co-digestion plants. Since appropriate co-substrates (sewage sludge, livestock waste) will often be available, the anaerobic degradation of OFMSW can be realized by co-digestion at most sites. Co-digestion can optimize waste handling of several waste streams in a single treatment step. Modelling of the co-digestion process is a useful tool for determination of the appropriate co-digestion mixture; however, verification of a model that can simulate the co-digestion of the organic fraction of municipal solid waste with other waste is still missing. Furthermore, the benefit of co-digestion in the context of degradation of toxic compounds found in OFMSW needs to be studied in greater detail to ensure safe use of the effluent after anaerobic treatment.

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## **PAPER 3**

# **Efficiency of the anaerobic treatment of the organic fraction of municipal solid waste: Collection and pretreatment**

**Hartmann, H., Møller, H. B. and Ahring, B. K.**

*Waste Management & Research* (2004) **22** (1), 35-41



# Efficiency of the anaerobic treatment of the organic fraction of municipal solid waste: Collection and pretreatment

This report is based on several years of co-operation between our research groups with Danish biogas plants. Throughout the years, there has been a fruitful exchange of know-how and experiences in laboratory scale on the one hand and large-scale on the other, leading to a better understanding of the principles of the anaerobic digestion process and to an optimization of its large-scale implementation. In order to get an overview of the current situation concerning the treatment of the organic fraction of municipal solid waste (OFMSW) in Denmark, interviews were carried out with operators of the biogas plants where OFMSW is treated and the municipality staff responsible for waste management. With the aim of fulfilling the governmental goal to treat 150 000 tons of OFMSW by the year 2004 mainly by anaerobic digestion, the different municipalities are investigating different concepts of waste collection and treatment. The quality of the OFMSW treated is the key to smooth operation of the biogas process including a high biogas yield and production of an effluent that is feasible for use as fertilizer on agricultural land. Comparison of the different concepts leads to the conclusion that source-sorting of OFMSW in paper bags is preferable to collection in plastic bags and successive separation of plastics in a waste processing treatment plant.

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**Keywords:** Anaerobic digestion, collection, municipal solid waste, pretreatment

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## Introduction

The application of anaerobic digestion as a waste treatment method for the organic fraction of municipal solid waste (OFMSW) has evolved in Europe from a capacity of 122 000 ton per year in 1990 to 1 023 000 ton in the year 2000 (De Baere 2000). This represents, however, only 0.7% of the amount of OFMSW produced in Europe (Mata-Alvarez *et al.* 2000) and between 6% and 27% of the composting capacity in different European countries (De Baere 2000). De Baere (2000) predicted that the capacity for anaerobic digestion of OFMSW

would increase in the new millennium due to the general acceptance of anaerobic digestion as a reliable technology since 1995 and to the several advantages of this treatment process such as the recovery of energy and nutrients. However, the performance of the anaerobic digestion process depends to a great extent on the quality of the waste to be treated (Saint-Joly *et al.* 2000).

In this article we give an overview of the treatment of OFMSW in biogas plants in Denmark as a case

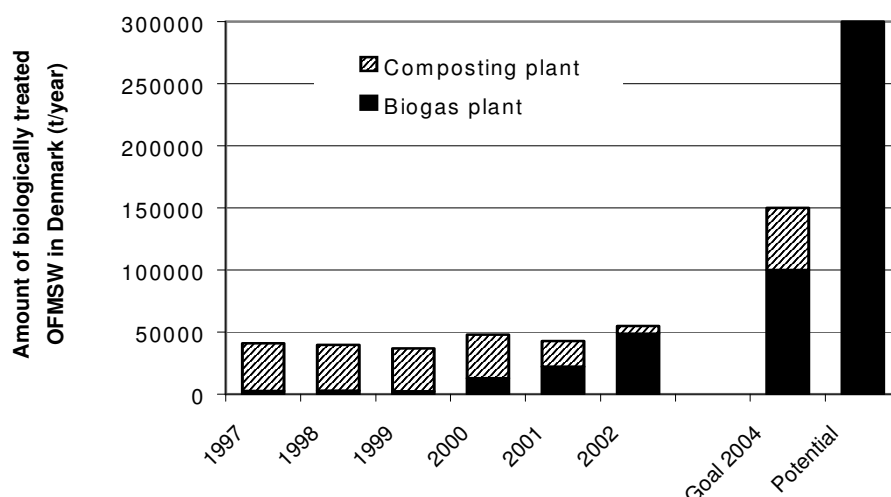


Fig. 1: Amount of biologically treated organic fraction of municipal solid waste (OFMSW) in relation to governmental goal and potential.

study for different approaches for the anaerobic digestion treatment of OFMSW in order to find the most efficient treatment technology. For the most optimal realization of the treatment method, the environmental and economical advantages have to be weighed against additional costs and energy requirements needed for the treatment. In particular, the extra costs for collection and pretreatment of OFMSW in order to produce a substrate that is free of contaminants have to be taken into account.

### Anaerobic digestion of OFMSW in Denmark

In Denmark, the anaerobic digestion treatment of OFMSW is with one exception generally applied as co-digestion with other types of organic waste such as manure, sewage sludge and industrial organic waste. This is due to the fact that a network of centralized biogas plants has been established since the beginning of the 1980's, based on the treatment of cattle and swine manure. Other organic substrates with a high biogas potential such as industrial organic waste are added at all of these biogas plants in order to achieve an economically feasible treatment process (Danish Energy Agency 1995). The addition of OFMSW is very attractive as OFMSW is a highly valuable substrate with a biogas potential per ton waste of up to 10 times that of agricultural waste such as manure (Braber 1995, Hartmann *et al.* 2001). On the other hand, as the effluent of the biogas plants is used as fertilizer, the added OFMSW has to be of high quality in terms of contamination. The amount of OFMSW added is restricted to a maximum of 20% of the treated volume by the fact that the biogas plant design is based on wet digestion treatment.

Biological treatment of OFMSW is competing with incineration as the only alternative treatment since landfilling is banned in Denmark. According to the

Danish governmental program "Waste 21", the aim is to treat an amount of 150 000 tons of OFMSW biologically by the year 2004, mainly by anaerobic digestion (Figure 1). At the end of 2002 only 45% of this amount was processed by biological treatment using anaerobic digestion and composting. The potentially treated amount of OFMSW in Denmark accounts for 40-42% of the total amount of municipal solid waste of 700 000 tons. This means that capacities for anaerobic treatment of OFMSW will be further extended and experiences of different collection, pretreatment and treatment processes should lead to optimal solutions in the future with concepts that are competitive to incineration.

Until the year 2000 anaerobic digestion had only a minor role in OFMSW treatment and composting was the dominant biological treatment. Since the year 2000 a shift from aerobic composting to anaerobic digestion has been observed (Figure 1).

OFMSW is treated in Denmark at eight out of 20 centralized biogas plants: Fangel, Grindsted, Hashøj, Nysted, Snertinge, Studsgård, Ålborg and Århus. The amount of OFMSW treated and the different collection and pretreatment methods used are listed in Table 1. In the year 2001, the ratio of OFMSW to other waste in the co-digestion plants was between 1.9%(w/w) (Snertinge) and 9.0%(w/w) (Studsgård).

In 2001, five of these eight biogas plants, Fangel, Hashøj, Nysted, Snertinge and Århus, started treating OFMSW that was previously treated by composting. The amounts treated in 2001 were in some cases (Ålborg, Århus) much below the expected amount for the following years, which is often due to technical problems during the establishment of procedures for collection and treatment of the waste. Different concepts such as the separation of a pumpable wet

Table 1: Amounts of organic fraction of municipal solid waste (OFMSW) treated in Danish biogas plants 2001 and collection and pretreatment methods used (according to information from the biogas plants)

	Grindsted	FA, HA, NY	Ålborg	Snertinge	Studsgård	Århus
Start	1997	2001	1990's	2001	1990's	2001
OFMSW (t/year)						
2001	2,000	6,000	300	900	11,000	2,000
Expected	4,000	12,000	3,000	1,800	11,000	17,000
Other types of waste (t/year)						
Manure	-	175,000	-	40,000	113,000	100,000
Sewage sludge	28,000	-	-	-	-	-
Industrial waste	4,000	n. d.	-	8,000	9,000	-
Collection system						
Indoor	Paper bags	Plastic bags	Plastic bags	Plastic bags	Plastic bags	Plastic bags
Outdoor	Paper bags or container	Paper bags or container	Paper bags or container	Paper bags or container	Paper bags or container	Plastic bags (green for OFMSW, black for grey waste)
Pretreatment						
Method	Crushing	Drum sieve + addition of straw	Dewaster	Dewaster	Roller sieve	Roller sieve
Ratio of reject	3%	25-30%	15 – 45%	20-40%	15 – 25%	15 – 45%

n.d.: no data; FA: Fangel, HA: Hashøj, NY: Nysted

fraction from OFMSW by a dewaster (for the waste treated at Snertinge and Ålborg) and the separation of the plastic fraction in a drum sieve after the addition of straw (for the waste treated at Fangel, Hashøj and Nysted) are still under investigation.

## Waste quality

The quality of OFMSW treated in biogas plants is crucial for balanced performance of the biogas process, the technical feasibility of the process and the use of the effluent as fertilizer on agricultural soil. Previous studies have shown that because of the complexity of OFMSW and the different possibilities for collection the results of anaerobic digestion of OFMSW can vary widely. The biogas yield will be dependent on the composition of the waste in terms of biodegradable fractions. Comparison of source- and mechanically selected OFMSW has shown that the biodegradation of the first is generally much higher (Mata-Alvarez *et al.* 1990). The C/N ratio and nutrient content will influence the stability of the process. Biodegradability, C/N ratio and the nutrient content of OFMSW vary significantly due to the composition of the single fractions (food waste, yard waste, paper, newspaper etc.) (Kayhanian and Tchobanoglous 1992, Kayhanian 1995, Plaza *et al.* 1996). Food waste, for example, will lead to high biogas yields due to the high content of biodegradable organic matter, but it can also lead to ammonia toxicity. Yard waste and newspaper, on the other hand, contain higher fractions of lignin and hemicellulose and will be characterized by lower biogas yields. The output of the treatment process will, therefore,

depend on the regulations regarding which waste fractions are included in the collection system.

In Denmark, all municipalities where OFMSW is treated in the biogas process are collecting organic household waste except baby napkins, while yard waste and newspapers are collected separately for composting and paper recycling. As most of the biogas plants are treating OFMSW in co-digestion with manure or sewage sludge, problems of nutrient deficiency, ammonia toxicity and low pH of OFMSW are of minor importance for the amount of OFMSW treated in 2002. The key to successful implementation of anaerobic treatment of OFMSW in large-scale processes is primarily the technical feasibility of the waste handling and the effluent quality. The influences of the waste quality on the anaerobic process during the treatment of larger amounts of OFMSW in the future and the development of new treatment concepts are currently under investigation (Hartmann *et al.* 2001).

OFMSW of low quality, particularly in terms of high plastic contamination, causes enormous technical problems at the biogas plant. Other impurities like metal are only of minor importance and can normally be easily removed. Plastics in the form of plastic bags etc. become wrapped around the stirring equipment in both the storage tanks and the reactor tanks, wear out pumps and form a top layer in the reactors. This leads to increased operation costs and process disturbances.

Furthermore, plastic contamination can ruin the concept of using the effluent as fertilizer. Farmers will not accept the effluent of the biogas process if there are plastic residues. As even small amounts of plastic are

visible this means that by adding OFMSW to the biogas process there is a risk that the co-digestion treatment at the biogas plant contaminates a large amount of manure that cannot then be used as fertilizer. Therefore, the biogas plants are intent on only adding OFMSW that is free of plastic contamination and they rather remove some parts of the organic matter during pretreatment in order that the treated fraction contains no plastics.

Last, but not least, there are restrictions on the content of heavy metals and xenobiotics in the effluent of the biogas plant when used as fertilizer and these compounds are often found in OFMSW, namely as phthalates from plastic impurities. Therefore, new concepts for the removal of the phthalate DEHP (bis-2-ethyl-hexyl phthalate) from OFMSW under anaerobic conditions are under investigation (Hartmann and Ahring 2003).

## Treatment concepts

The overall treatment of OFMSW in Denmark is often divided between two different groups of interest. There is the municipality that stands for waste collection and pretreatment on the one hand and the biogas plants where OFMSW is treated together with other kinds of waste on the other. Whereas the municipality is interested in having low costs for collection and treatment, the biogas plants are only able to treat OFMSW with low plastics contamination. The total efficiency of the waste treatment concept will, therefore, always depend on the co-operation of these two partners.

A high quality for the OFMSW that is supplied to the biogas plant can be achieved by two main concepts: either by establishing a source-sorting collection system that achieves a low content of contaminants and avoiding plastic bags in the collection (Grindsted) or by selective removal of plastic bags and other contamination from the collected OFMSW before it is supplied to the biogas plant (e.g. Ålborg, Århus), as shown in Figure 2. However, this separation has to be very efficient to ensure a high purity of the waste as earlier experiences have shown that compost derived from mechanical separation will not meet the required standards for useful application as soil conditioner (Braber 1995).

So far, only the municipality of Grindsted uses paper bags for collecting OFMSW. The waste is collected in paper bags both inside the house and outside for transportation. Source-sorting makes each individual household responsible for the waste quality and a good set of instructions must be provided concerning how to separate the waste and why this is necessary for successful implementation of the collection system. The example of the municipality of Grindsted has shown, that this is mainly necessary at the start-up of the system; later people will get used to it and tend to separate their waste automatically.

The efficiency of source separation in Grindsted can be seen by the fact that impurities in the waste only contribute 1% to the total waste amount, and 97% of the collected waste amount is supplied to the biogas process (Table 1). Consequently, the treatment concept is then quite simple, including only one pretreatment step for crushing and metal separation. The rest of the plastic contamination is withdrawn from the buffer tank where the OFMSW is mixed with sewage sludge (Figure 2).

In all other municipalities the organic waste is collected in plastic bags that have to be removed before the OFMSW is used at the biogas plant. Although the OFMSW is in most cases also source-separated with only up to 10% impurities, the separation of plastic bags causes a significantly higher loss of OFMSW that is not treated in the anaerobic digester. There are several different methods used for plastic separation.

In Ålborg and Snertinge a pumpable liquid fraction is pressed off the waste using a dewaster (Figure 2). The dewaster method is a simple treatment method that ensures a liquid fraction of OFMSW that is free of plastic contamination, but shows the highest reject mass of up to 45% of the collected material (Table 1).

In Studsgård and Århus the plastic is removed by use of roller sieves. In Århus the separation is rather costly as it includes several separation steps due to the fact that OFMSW and grey waste are collected together. After an optical separation of green plastic bags for OFMSW and black plastic bags for grey waste, the waste is crushed and metal and plastics are separated. Here too, a significant amount of 15-45% of organic matter of the original collected waste is lost, and disposed of by incineration. Furthermore, the plastic separation is still insufficient and a second separation is necessary after the OFMSW has been mixed with manure at the biogas plant (Figure 2).

The OFMSW delivered to Fangel, Hashøj and Nysted a drum sieve is used. Here, the addition of straw has been shown to improve the separation efficiency, but 25-30% of the collected OFMSW is still lost in the reject material (Table 1).

Regarding the overall concept from collection to treatment at the biogas plant, it can be seen that the less that the OFMSW is source-separated and the more contaminated it is, the higher are the reject masses and the more costly is the separation treatment. As the reject mass is not only plastic contamination, but contains a significant amount of organic material, the benefit from the treatment in the biogas plant, in terms of the biogas yield per ton of collected OFMSW, is reduced significantly.

Capital and operating costs for the different concepts are shown in Figure 3. For the plants that started in 2002 (Fangel, Hashøj, Nysted, Snertinge, Århus) the capital and operating costs are estimates for

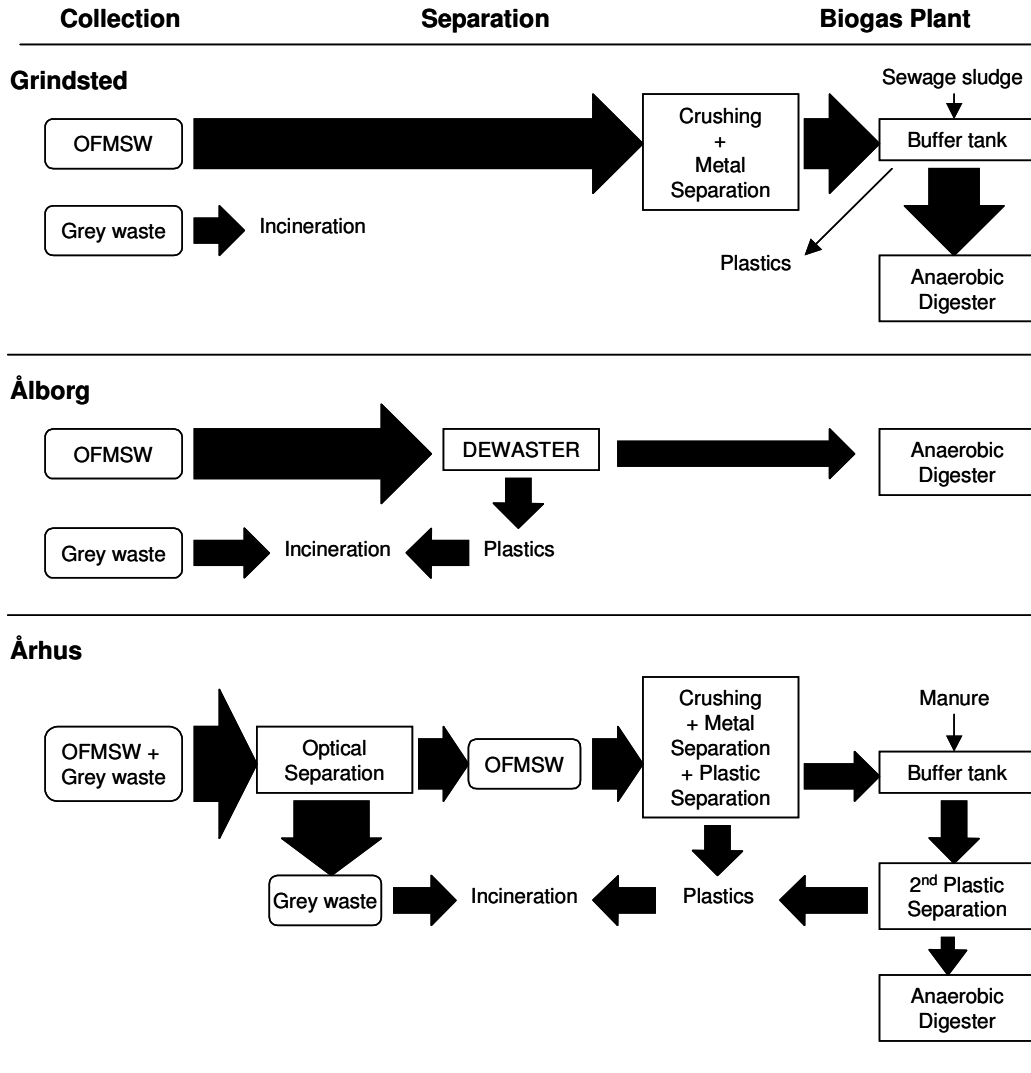


Fig. 2: Treatment concepts for organic fraction of municipal solid waste (OFMSW) at Grindsted, Ålborg and Århus

long-term operation made by the plant operators. Operating costs are costs for pretreatment and treatment of the collected waste, without collection costs and provision. The benefit from biogas production is calculated from the biogas yield, the price of biogas and the average of the rejected amount per ton collected waste by the pretreatment according to equation (1).

$$B = Y_{biogas} \cdot P_{biogas} \cdot (1 - r) \quad (1)$$

where  $B$  is the benefit (€/t),  $Y_{biogas}$  is the biogas yield ( $m^3_{biogas}/t$ );  $P_{biogas}$  is the price of biogas (0.202 €/m<sup>3</sup><sub>biogas</sub>); and  $r$  is the ratio of reject.

Detailed data of the biogas yield at the different plants was not available as the value is concealed in the yield of the co-digestion with manure or sewage sludge. Therefore, a biogas yield of 200 m<sup>3</sup>/t, which is derived from lab-scale reactor experiments with OFMSW from

Grindsted, is assumed for all plants (Hartmann *et al.* 2001).

Capital costs for the pretreatment are in the range of 1-2 million € for all sites where OFMSW is source-sorted whereas the capital costs are significantly higher for the optical separation plant for separation of OFMSW and grey waste. Operating costs for the pretreatment of OFMSW delivered to Hashøj, Fangel and Nysted are highest since transportation costs are significant because the biogas plants are situated up to 200 km away from the pretreatment site. The operating costs will be significantly lowered with establishment of a new biogas plant nearby, which is planned for future years.

Operating costs at the Grindsted plant are lowest for two reasons: first, the pretreatment process is simple and less work and energy consuming; and second, all other plants have a considerable amount of reject that has to be treated by incineration, for which a



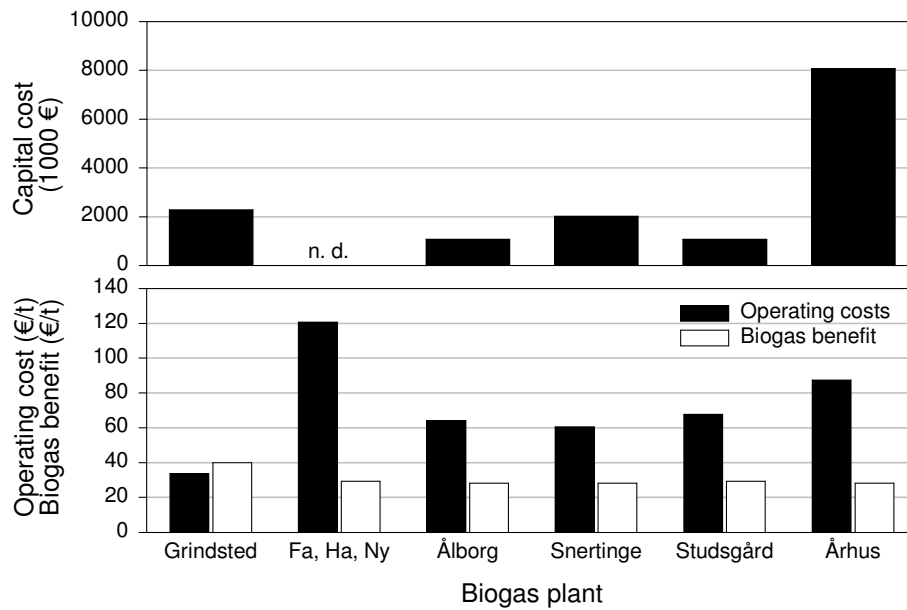


Fig. 3: Cost-benefit for different pretreatment methods; n.d.: no data; Fa: Fangel, Ha: Hashøj, Ny: Nysted

price of 80 €/t has to be paid. This clearly shows how the treatment costs increase significantly with each ton of rejected material. The biogas benefit, on the other hand, is highest for the treatment at Grindsted as the recovery of organic material is 97% whereas up to 45% is lost at the other plants during pretreatment.

Furthermore, the degradation of the paper bags in which the waste is collected in Grindsted probably contributes positively to the biogas potential of the waste.

In general, the treatment concept at Grindsted is the only one in which the benefit from biogas production is higher than the treatment costs. The investment costs for the optical separation unit in Århus are about four times higher than the average investment costs for the pretreatment at the other plants. These investment costs are, however, not reclaimed as the recovery of organic material is poor and the treatment costs are high.

It can be speculated that one reason why the Grindsted concept shows the best overall cost-benefit is that both the collection and the biogas treatment of OFMSW are in the hands of the municipality. The collection is, therefore, better adapted to the needs of the biogas process and the profit from the higher collection efficiency is paid directly back to the municipality.

## Conclusions

Anaerobic digestion is becoming the predominant treatment of OFMSW in Denmark. In order to establish anaerobic digestion as a low cost waste treatment of OFMSW, the whole treatment costs from collection, pretreatment and treatment at the biogas plant should be considered. Costs for pretreatment and treatment at the biogas plant can be reduced and biogas production can be enhanced with a collection system that ensures low plastics contamination.

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## **PAPER 4**

# **Anaerobic digestion of the organic fraction of municipal solid waste: Influence of co-digestion with manure**

**Hartmann, H. and Ahring, B. K.**

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# Anaerobic digestion of the organic fraction of municipal solid waste: influence of co-digestion with manure

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## Abstract

Anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) was investigated in two thermophilic (55°C) wet digestion treatment systems R1 and R2. Initially OFMSW was co-digested with manure with a successively higher concentration of OFMSW, at a hydraulic retention time (HRT) of 14 – 18 d and an organic loading rate (OLR) of 3.3 – 4.0 g-VS·l<sup>-1</sup>·d<sup>-1</sup>. Adaptation of the co-digestion process to a OFMSW:manure ratio of 50% (VS/VS) was established over a period of 6 weeks. This co-digestion ratio was maintained in reactor R2 while the ratio of OFMSW to manure was slowly increased to 100% in reactor R1 over a period of 8 weeks. Use of recirculated process liquid to adjust the organic loading to R1 was found to have a beneficial stabilization effect. The pH rose to a value of 8 and the reactor showed stable performance with high biogas yield and low VFA levels. The biogas yield from source-sorted OFMSW was 0.63 – 0.71 l/g-VS both in the co-digestion configuration and in the treatment of 100% OFMSW with process liquid recirculation. This yield is corresponding to 180 – 220 m<sup>3</sup> biogas per ton OFMSW. VS reduction of 69-74% was achieved when treating 100% OFMSW. None of the processes showed signs of inhibition at the free ammonia concentration of 0.45-0.62 g-N/l.

*Keywords: Anaerobic; Co-digestion; manure; Organic fraction of municipal solid waste; Process liquid; Recirculation*

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## 1. Introduction

Waste management has become of major concern around the world during the recent thirty years. Sustainable waste treatment concepts that favor waste recycling and the recirculation of nutrients back to soil will have the highest benefit for the environment (Lema and Omil, 2001, Sakai et al., 1996, Braber, 1995). Anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) offers the advantage of both a net energy gain by producing methane as well as the production of a fertilizer from the residuals (Edelmann et al. 2000, Sonesson et al. 2000, Hamzawi et al. 1999).

In Denmark, the aim is to use anaerobic digestion as the main waste treatment process in the future with a capacity of 100,000 tons of OFMSW by the year 2004 (Hartmann and Ahring, 2004). The existing 20 centralized biogas plants are the first option for the AD treatment of OFMSW in co-digestion with manure. In 2002, only

50,000 tons of OFMSW were treated per year in 9 biogas plants, where up to 10% (vol.) of OFMSW was added in co-digestion with manure (Hartmann and Ahring, 2004). For the realization of the goal to treat 100,000 tons by AD in 2004, the ratio of OFMSW added has to be increased in the existing plants and the installation of additional biogas plants for the treatment of OFMSW alone may be another option. Generally, OFMSW is a very attractive waste for the biogas plants as they are dependent on the addition of organic waste with a high biogas potential. The biogas yield from raw manure alone is only 20 – 30 m<sup>3</sup>/t and the operation of the plant is only economically feasible when biogas yields higher than 30 m<sup>3</sup> per ton of treated material can be achieved (Danish Energy Agency, 1995). As the amount of industrial organic waste is limited in Denmark, there will be a high demand for OFMSW with a biogas potential of more than 100 m<sup>3</sup>/t, especially with an expansion of the existing net of

biogas plants. Adding OFMSW will, however, change the process characteristics due to the different characteristics of OFMSW compared to manure: it has a low water content, a low pH and it can have low concentrations of nutrients, when it consists of high ratio of e.g. garden waste (Rivard et al., 1989, 1990). For high ratios of food waste, OFMSW can, however, also contain high concentrations of proteins, which can lead to inhibition by ammonia especially when process liquid is recirculated (Gallert and Winter, 1997). Furthermore, OFMSW can contain considerable amounts of heavy metals and xenobiotic compounds (Hartmann and Ahring, 2003, Braber, 1995).

The goal of the present work was to investigate how a thermophilic wet digestion system will react when adding OFMSW in a ratio of 50% (VS/VS) to the manure in the co-digestion process. Finally, the adaptation of the system to 100% of OFMSW using recirculated process liquid was investigated. Results of the reduction of xenobiotics have been previously studied (Hartmann and Ahring, 2003). The wet digestion system was preferred in order to achieve a well-mixed process in a conventional continuously stirred tank reactor (CSTR) and to make the results directly applicable in the Danish large-scale biogas reactors.

## 2. Methods

### 2.1 Waste characterization

OFMSW used in this investigation came from the municipality of Grindsted (Denmark) where OFMSW is source-sorted in the households in paper bags and co-digested together with sewage sludge at the municipal wastewater plant. Samples were taken after the on-site shredder device, further homogenized in an industrial meat mincer and stored at -18°C until used as feeding substrate. Two different batches of homogenized OFMSW were fed into the reactors R1 and R2, batch 1 before day 217 and batch 2 after day 217. Characterization of the waste was performed by analysis of TS, VS, and COD according to standard methods (APHA et al., 1992). The composition of the OFMSW with regard to hemicellulose, cellulose and lignin was determined in triplicates in batch 1 by sequential fiber analysis according to the method of Goehring and van Soest (1970). The biogas potential of OFMSW collected in batch 1 and cow manure in different co-digestion ratios were measured in triplicate batch experiments with inoculum from reactor R1, treating OFMSW in co-digestion with manure. OFMSW and cow manure, diluted to a concentration of 5% VS, was filled into 100 ml batch vials in different ratios equivalent to a total amount of 1 g-VS. After adding 15 ml inoculum and 10 ml of tap water the vials were flushed with a gas mixture of 80% N<sub>2</sub> and 20% CO<sub>2</sub> before closing the vials. The vials were

incubated at 55°C for 60 days. Methane production was monitored every 3–4 days by analysis of CH<sub>4</sub> concentration in the headspace using gas chromatography with flame ionization detection. The CH<sub>4</sub> production was standardized by sampling the same volume (0.2 ml) from the batch vials under pressure as from a 30% CH<sub>4</sub> standard under standard conditions (1 bar, 20°C). At a pressure higher than 2 bar in the vials, the pressure was released and the amount of CH<sub>4</sub> released was determined by the difference of the amount of CH<sub>4</sub> in the vials before and after release. The biogas potential was determined after 44 days of incubation, after which no significant increase in methane production was observed.

### 2.2 Reactor set-up

The treatment process was investigated in two 4.5 l lab-scale reactors R1 and R2 with an active volume of 3.0 l operated under thermophilic conditions (55°C). Each reactor was fed 3 times a day with a total feeding volume of 170 – 210 ml/d, resulting in a hydraulic retention time (HRT) of 14 – 18 d. OFMSW and manure were diluted in a ratio of 1:5 and 1:1.43, respectively, to reach an influent VS concentration of 6% for both substrates, resulting in an organic loading rate (OLR) of 3.3 – 4.0 g-VS·l<sup>-1</sup>·d<sup>-1</sup>. New influent was prepared every 3–4 days and stored in 1 l glass vessels, which were stirred for two minutes before feeding. The reactors were stirred for 15 minutes in intervals of 15 minutes. Effluent from the reactors was collected in 1 l Erlenmeyer vessels. For recirculation of process liquid in reactor R1 the effluent was collected during a period of 3–4 days, centrifuged at 4000 rpm for 30 minutes and the supernatant was decanted and used for dilution of OFMSW for the influent (figure 1). After centrifugation 92% ± 1% of the total effluent mass was recovered in the liquid phase, containing 34% ± 3% and 25% ± 4% of the total effluent TS and VS, respectively. Depending on volume loss by sampling and fluctuations in feeding volume, the ratio of the supernatant of the effluent, which was used as process liquid, to the whole liquid added for dilution of influent OFMSW varied between 23% and 100% and was in average 50% and 59% in the experimental phases, when recirculation was applied (table 1).

The reactor experiment was divided in four phases (table 1). In phase 1 (day 0–83) both reactors R1 and R2 were initially loaded with cow manure for ten days and then adapted to a higher load of OFMSW by an increase of the OFMSW ratio in 5% steps (on VS basis) every 3–4 days. After one month both reactors were running with 50% (VS/VS) OFMSW for a period of 42 days (2.7·HRT). R2 was further used in phase 2, 3 and 4 as control reactor maintaining a co-digestion ratio of 50% (VS/VS) OFMSW until the end of the experiment. From day 84 to 139 (phase 2) the OFMSW

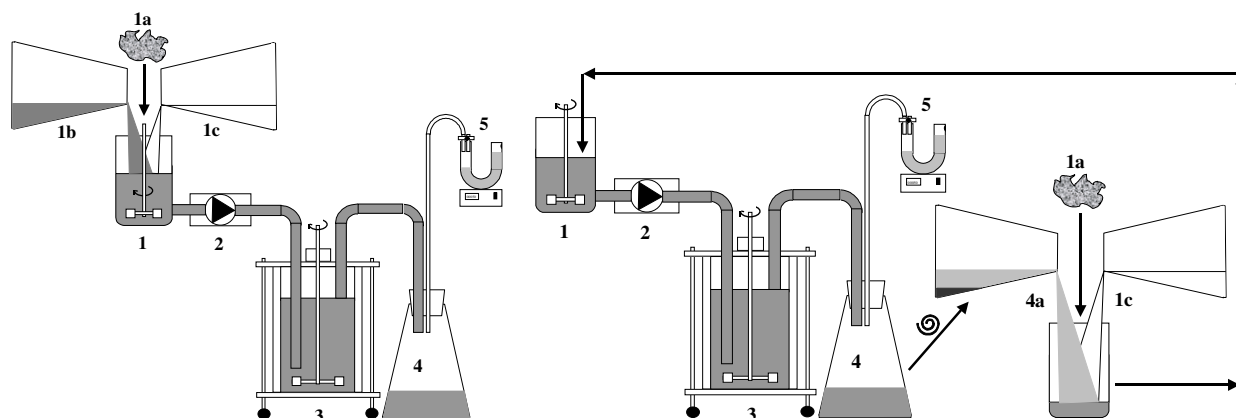


Fig. 1. Reactor set-up for co-digestion (left) and treatment of 100% OFMSW with recirculation of process water (right). 1: Influent storage vessel. 1a: OFMSW. 1b: Manure. 1c: Water. 2: Influent pump for reactor. 3: Thermophilic reactor with heating jacket and mechanical stirrer. 4: Storage vessel for effluent. 4a: Supernatant of effluent after centrifugation 5: Gas meter.

Table 1.  
Average process parameters in the different experimental phases

Parameter	Phase 1 (Days 0-83)	Phase 2 (Days 84-139)	Phase 3 (Days 140-216)	Phase 4 (Days 217-330)
	50% OFMSW R1, R2	100% OFMSW R1	Recirculation R1	Batch 2 OFMSW
HRT (d)				
R1	15.5 (2.2)	13.5 (2.8)	17.0 (5.5)	17.7 (7.7)
R2	15.3 (1.2)	17.5 (3.7)	17.9 (4.4)	16.0 (2.9)
OLR (g-VS/l/d)				
R1	3.5 (0.4)	4.0 (1.0)	3.3 (1.1)	3.4 (1.2)
R2	3.6 (0.3)	3.4 (0.7)	3.3 (0.8)	3.3 (0.6)
%Rec				
R1	-	-	50	59

%Rec.: ratio of effluent supernatant to total liquid volume used for dilution of influent OFMSW; standard deviation in brackets

ratio in reactor R1 was increased to 100% and from day 116 to 139 OFMSW was added after dilution with water. Use of the liquid fraction of the effluent for dilution of OFMSW before feeding of R1 was started on day 140. Since a new batch of OFMSW was used from day 217, the last experimental period was divided into phase 3 (day 140 – 216) and phase 4 (day 217 – 330). HRT and OLR were in average 13.5– 17.9 d and 3.3 – 4.0 g-VS·l<sup>-1</sup>·d<sup>-1</sup>, respectively. The variations were due to variations of the pumping volume caused by the inhomogeneity of the substrate. Process parameters are displayed in table 1 as averages of the whole period of phase 3 and 4 and of the periods of phase 1 and 2, when the reactors were fed with a constant mixture of 50% OFMSW: (VS/Vs) and 100% OFMSW, respectively.

### 2.3 Monitoring parameters

Biogas production was measured by liquid displacement gas measurement systems connected to the headspace of the effluent vessels, logging the gas production automatically in 10 ml intervals. The methane content of the biogas was analyzed by gas chromatography as previously described by Sørensen et al. (1991). The methane yield in the reactors was calculated as average over a period of 3–4 days as  $Y_{CH_4} = \frac{\sum(\text{ml } CH_4)_{\text{prod}}}{\sum(\text{g-VS})_{\text{feed}}}$ . The process performance was monitored by volatile solids (VS) reduction, volatile fatty acids (VFA) concentration, pH, and ammonia formation. VS reduction was determined as difference in VS concentration in the influent times influent volume and VS concentration in the effluent



times effluent volume. TS, VS, pH and ammonia in the influent and effluent of the reactor system were determined according to standard methods (APHA et al., 1992). The ratio of free ammonia to total ammonia was calculated according to Anthonisen et al. (1976):

$$\frac{\text{Free} - \text{NH}_3}{\text{Total} - \text{NH}_3} = \frac{10^{pH}}{10^{pH} + \frac{1}{K_a}} = \frac{10^{pH}}{10^{pH} + e^{\frac{6344}{273+T}}}$$

where T is the temperature in °C.

The single VFA's acetate, propionate, isobutyrate and butyrate were analyzed by gas chromatography as described by Sørensen et al. (1991).

### 3 Results and discussion

#### 3.1 Waste characteristics

VS concentration in the two batches of OFMSW used for the experiment was 31% with a VS/TS ratio of 86-91% and a COD/VS ratio of 1.4 (table 2). The collected waste was, furthermore, characterized by only 1% (w/w) of impurities (plastic, metal, glass). This high purity of the waste shows the high efficiency of the waste collection concept in the municipality of Grindsted. The total nitrogen content of OFMSW was higher than of the manure used, but lower per kg dry matter, meaning that manure contributed to more nitrogen during co-digestion of equal amounts of manure and OFMSW. The free ammonia concentration was three times lower for OFMSW than for manure.

In the batch experiment, a methane yield of 0.40 l/g-VS of OFMSW was found (figure 2), which was 82% of the maximal theoretical yield of 0.49 l/g-VS, calculated from the COD content of OFMSW. The methane yield in

the co-mixture of OFMSW and manure increased linearly with higher ratios of OFMSW, showing no signs of inhibition or nutrient deficiency at high OFMSW ratios (figure 2). With a methane content of 60% in the biogas, the maximal biogas yield was 0.82 l/g-VS. This was close to the theoretical biogas yield of 0.81 l/g-VS, which was calculated by Scherer et al. (2000), based on a composition of 3% fat (1.42 l/g-TS), 13% protein (0.89 l/g-TS), 17% cellulose (0.96 l/g-TS), 8.5% lignin (0.0 l/g-TS) and 58.5% carbohydrates (0.84 l/g-TS)..

The biodegradability of the OFMSW used, determined by the batch experiment, was much higher than the one, which can be calculated from the relationship between lignin content and biodegradable fraction found by Chandler et al. (1980) giving a biodegradable fraction of 38% of VS. This indicated that the lignin content was generally lower than the 19%, which was determined in the fiber analysis.

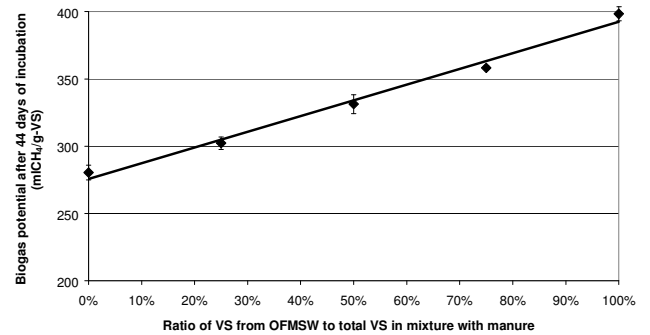


Fig. 2 Methane yield of OFMSW and manure in different mixtures in batch experiment after 44 days of incubation (55°C)

Table 2  
Characteristics of OFMSW and manure used in the reactor experiment

	TS (%)	VS (%)	COD (g/kg)	Total-N (g/kg)	Total-N (g/kg-TS)	NH <sub>3</sub> -N (g/kg)	NDF (non-soluble) (% of VS)	NDF-ADF (hemicellulose) (% of VS)	ADF-ADL (cellulose) (% of VS)	ADL (lignin) (% of VS)
OFMSW										
Batch 1	35.6 (0.10)	30.7 (0.17)	431 (9.3)	6.3 (0.46)	17.7	1.0 (0.10)	36.6 (2.1)	13.1 (3.5)	5.0 (0.4)	18.5 (0.9)
Batch 2	33.6 (0.49)	30.7 (0.16)	-	-	-	-	-	-	-	-
Manure	11.5 (0.45)	8.5 (0.03)	-	4.6 (0.06)	40.0	3.0 (0.02)	-	-	-	-

NDF: neutral detergent fiber fraction, ADF: acid detergent fiber fraction, ADL: acid detergent lignin fraction, standard deviation in brackets

### 3.2 Reactor experiment

#### 3.2.1 Phase 1: Start-up to a ratio of OFMSW:manure of 50%

The methane yield increased with higher ratios of OFMSW from 0.20 l/g-VS when feeding only manure, to 0.34 l/g-VS in the 50% co-digestion ratio (figure 3A1, 3A2). The methane yield was equivalent to the methane yield found in the batch test. Due to the acidity of OFMSW the pH of the influent dropped from 7.3 of pure manure to 6.3 in the 50% (VS/VS) co-digestion mixture (figure 3D1, 3D2). The pH in both reactors, however, dropped only from 8.5 to 8.0, showing that the co-digestion system was well buffered. Accordingly, the pH in the effluent stabilized at values of 7.6 – 7.8 at the end of phase 1. The VFA profile showed for both reactors a stable performance with total VFA concentrations below 8 mM after an initial transitory increase in VFA (figure 3C1, 3C2) which is typical for start-up of an anaerobic process when the balance of the hydrolytic bacteria, fermentative bacteria and methanogens has not stabilized yet (Ahring, 1994). The further increase of the ratio of OFMSW did not show signs of process instability. The fluctuation of the methane yield was due to fluctuation in the feed volume and the waste composition of the single waste loads.

#### 3.2.2 Phase 2: Increasing the OFMSW ratio to 100% in reactor R1

Loading R1 with a higher ratio of OFMSW showed an increase in methane yield and VS reduction up to an average value of 0.46 l/g-VS and 73%, respectively, on average in the last period of phase 2 (1.8-HRT) when 100% OFMSW diluted by addition of water, was fed to the reactor (figure 3A1, 3B1, table 3). These high values for the methane yield and the VS reduction were signs for a high content of biodegradable organic matter in the substrate. Parallel to the drop of the influent pH of R1 down to 4.0 – 4.5, the effluent pH declined to 7.0 (figure 3D1). Reactor R2 showed generally stable performance with low VFA concentration (figure 3C2), and about the same methane yield and VS reduction as in phase 1 (figure 3A2, 3B2). The biogas yield and the VS reduction in R1, operating on 100% OFMSW, were 28% and 23%, respectively, higher than during co-digestion with manure in R2 (table 3).

#### 3.2.3 Phase 3: Recirculation of process liquid in reactor R1

When starting the recirculation of process liquid in R1 on day 140, using exclusively the supernatant of the effluent for dilution of OFMSW, a slight increase of VFA concentration and a drop of methane yield below 0.40 l/g-VS was detected (figure 3C1, 3A1). The same process disturbance was, however, also seen in reactor R2 (figure

3A2, 3C2), indicating that the process disturbance was related to the feeding of both reactors rather than the start of recirculation in R1. In general, low VFA concentrations in R1 showed stable reactor performance. The methane yield and VS reduction showed some variations and were, in average, lower than at the end of phase 2. The average biogas yield was, however, still higher than in the batch experiment and biogas yield and VS reduction in R1 were 14% and 25%, respectively, higher than found in R2 (table 3).

Dilution of OFMSW with a high ratio of supernatant showed an instant buffering effect with an increase in the influent pH above 6.0 (figure 3D1). The effluent pH stabilized at a higher level of 7.2, showing beneficial effect of recirculation of the effluent for the pH stabilization of the process.

The ammonia load of R1 increased successively with recirculation of the effluent (figure 4) and the concentration in the effluent increased from 0.6 to 1.0 g/l, which corresponded to a level of 0.28 g/l of free ammonia in the reactor (55°C, pH 8.0).

#### 3.2.4 Phase 4: Using a second batch of OFMSW

The feed of a new batch of OFMSW in phase 4 (6.4-HRT for R1 and 7.1-HRT for R2) showed a lower average of 0.38 l/g-VS than in phase 3 (figure 3A1, table 3). The VS reduction, however, increased by 5% compared to phase 3 (figure 3B1, table 3). The same can be seen for the co-digestion in R2 (figure 3A2, 3B2), indicating that batch 2 of OFMSW had a lower content of high yielding organic matter (fat, protein, cellulose). VFA concentration fluctuated more during phase 4 than in the previous phases and showed a higher level than in phase 3 (figure 3D1). However, the concentration was always below 5 mM, indicating that the process was in balance. When using exclusively the supernatant of the effluent for dilution of OFMSW between day 235 and 255 (figure 4A), the influent pH was higher than 6.2 and the effluent pH rose to 7.5. During the whole period the pH in reactor R1 was stable around 8.0. Due to higher ratios of supernatant used for dilution of OFMSW in phase 4 (59%) compared to phase 3 (50%), the ammonia concentration in the effluent increased to values of 1.5 – 1.6 g-N/l, which was about the same level as for the co-digestion reactor R2 (figure 4B). Due to a lower pH in R1 compared to R2 (8.0 compared to 8.2), the free ammonia concentration can be calculated to 0.42 – 0.45 g-N/l in R1 and 0.58 – 0.62 g-N/l in R2.

Assuming that the ammonia loss is as much as the volume loss in the process, the effluent ammonia concentration was calculated according to the mass balance:

$$C_{NH_3, e_{j+1}} = C_{NH_3, OFMSW} \cdot r_{OFMSW} + C_{NH_3, e_j} (1 - r_{OFMSW}) \cdot r_{sn} + t_{org-N} \cdot (C_{TKN, OFMSW} - C_{NH_3, OFMSW}) \cdot r_{OFMSW}$$

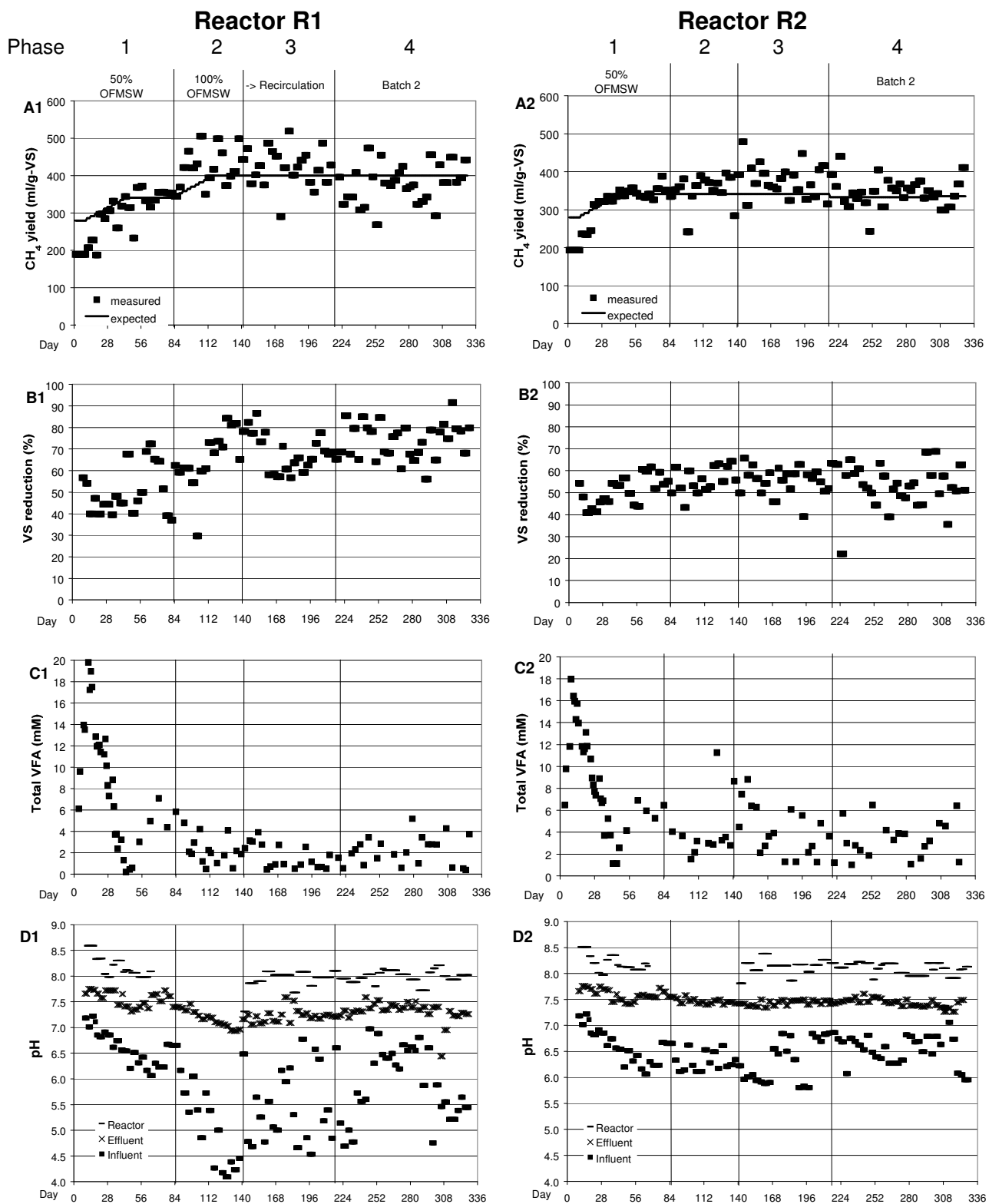


Fig. 3. Biogas yield (A1, A2), VS reduction (B1, B2), VFA concentration (C1, C2) and pH (D1, D2) in reactor R1 (left) and R2 (right); expected biogas yield in A1 and A2 is according to the methane yield found in the batch experiment (figure 2)

Table 3  
Average performance parameters in the different experimental phases

Parameter	Phase 1 (Days 0-83)	Phase 2 (Days 84-139)	Phase 3 (Days 140-216)	Phase 4 (Days 217-330)
CH <sub>4</sub> yield (l/g-VS)				
R1	0.34 (0.03)	0.46 (0.05)	0.42 (0.05)	0.38 (0.08)
R2	0.35 (0.01)	0.36 (0.03)	0.37 (0.04)	0.34 (0.04)
%CH <sub>4</sub>				
R1	64.2 (1.1)	59.7 (0.2)	59.4 (1.4)	60.6 (2.0)
R2	64.6 (0.6)	62.8 (1.6)	63.0 (1.3)	62.8 (1.9)
VS reduction				
R1	56.0 (12.8)	73.1 (7.0)	69.0 (8.6)	74.3 (8.2)
R2	54.2 (5.7)	59.5 (4.4)	55.3 (6.0)	56.4 (9.9)
pH Effluent				
R1	7.5 (0.1)	7.0 (0.1)	7.2 (0.1)	7.3 (0.2)
R2	7.5 (0.1)	7.4 (0.0)	7.4 (0.1)	7.2 (0.1)

%CH<sub>4</sub>: methane content in biogas; standard deviation in brackets

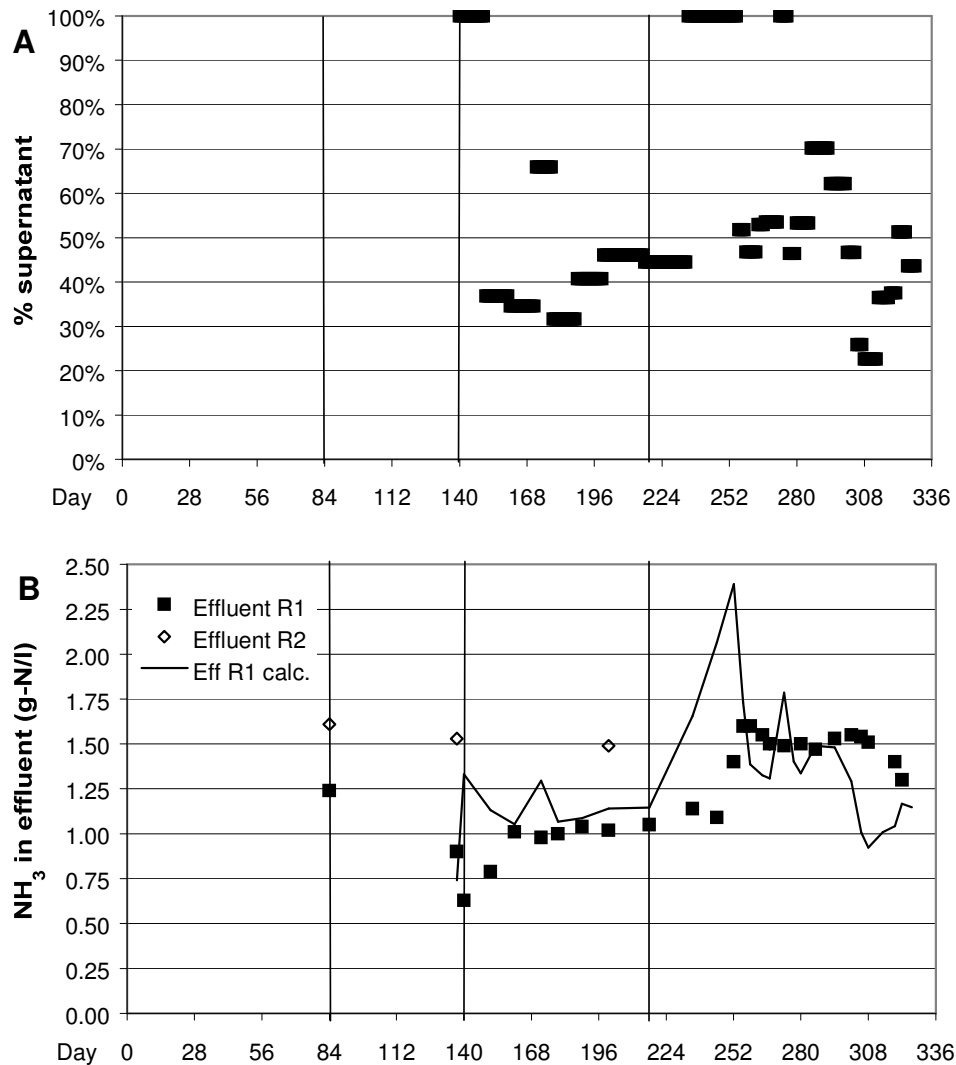


Fig. 4. Ratio of supernatant to total liquid volume used for dilution of influent OFMSW of R1 (A) and ammonia concentration in the effluent of R1 and R2 (B); Eff R1 calc. is the calculated NH<sub>3</sub> concentration in the effluent

where C = concentration (g-N/l), index i = influent, index e = effluent, index j = recirculation count, index NH<sub>3</sub> = total ammonia-N, index TKN = total Kjeldahl-N, r<sub>OFMSW</sub> = ratio of OFMSW in influent, r<sub>sn</sub> = ratio of supernatant:water used for dilution of OFMSW, t<sub>org-N</sub> = ratio for release of NH<sub>3</sub>-N from organic bound nitrogen (TKN)

$$\text{with } t_{org-N} = \frac{C_{NH_3,e} - C_{NH_3,i}}{C_{TKN,i} - C_{NH_3,i}}$$

Comparing the measured values with the calculated data, it can be seen that changes of the concentration followed the values predicted by the mass balance after about one retention time (figure 4B). The predicted increase on day 235, for example, is first apparent after 15 days and the fluctuations in the concentration as predicted are leveled out. This indicated that ammonia from organic bound nitrogen was not instantly released, but over the period of one retention time. With a constant ratio of the supernatant of 50% (phase 3) and 59% (phase 4), an effluent ammonia concentration of 1.2 g-N/l and 1.4 g-N/l, respectively, can be calculated from the mass balance. An effluent ammonia concentration of 3.7 g-N/l and a respective free ammonia concentration of 1.0 g-N/l could be predicted when recirculating 100% of effluent supernatant. This is in agreement with results found by De Laclos et al. (1997) who measured an increase of the effluent ammonia concentration in the Valorga process from 1.3 to 3 g-N/l over an operation period of 2 years.

### 3.2.5 Overall performance

The overall process performance of reactor R1 and R2 in phase 3 and 4 can be summarized as follows: Anaerobic treatment of OFMSW showed stable performance in a thermophilic wet digestion treatment system both when co-digested with manure in a ratio of 50% (VS/VS) and as sole substrate with recirculation of the effluent. The biogas yield from OFMSW was in both treatment configurations 0.63 – 0.71 l/g-VS, corresponding to 180 – 220 m<sup>3</sup>/t<sub>OFMSW</sub>, which is more than 50% higher than in comparable thermophilic dry digestion systems using source-sorted OFMSW (Kayhanian and Tchobanoglous, 1993, Six and de Baere, 1992) and more than 25% higher than in comparable mesophilic systems (Krzysek et al., 2001, Mtz.-Vituria et al., 1995). This gives evidence for both a high quality of the collected waste and for the advantage of the thermophilic wet digestion treatment of OFMSW. Similar biogas yields of OFMSW have, so far, only been found in a thermophilic wet digestion system by Scherer et al. (2000). Treating exclusively OFMSW with recirculation of process liquid in a ratio of 50-59% for dilution of influent OFMSW was beneficial and stabilized the process at a pH 8.0 in the reactor and with an ammonia level similar to the one found during co-digestion with manure. Stabilization of the process by recirculation of process liquid has been shown previously (Cecchi et al.

1990). Compared to other treatment processes with recirculation of process liquid, like the BTA and the Valorga process, the biogas yield in the present investigation was more than 50% higher (Kübler, 1994, de Laclos et al., 1997). The higher degradation efficiency is suspected to be due to a better contact of the microorganisms to the more homogenous substrate in the present process configuration. The results from the lab-scale system have to be verified in a large-scale process. The homogeneity of the substrate may be less in a large-scale process, the process fluctuations in the feed volume (i.e. the OLR) are, however, higher in the lab-scale system. Both the co-digestion and the recirculation process showed to be robust towards these fluctuations and no inhibition was detected at free ammonia levels as high as 0.62 g/l.

The co-digestion conditions with a ratio of 50% (VS/VS) of OFMSW could be achieved without addition of water in a mixture of 77.9% (v/v) manure together with 22.1% (v/v) of OFMSW. In this case, the resulting VS and TS concentration would be 13.2% and 16.6%, respectively. This would be at the limit of mechanical handling in a CSTR. Addition of higher ratios of OFMSW would make recirculation of the liquid effluent necessary. Large-scale separation of the liquid fraction from the effluent could be achieved in a continuous process using a decanter centrifuge as it is currently applied for manure (Møller et al. 2000).

## 4. Conclusions

Adaptation of the thermophilic anaerobic digestion process to OFMSW in co-digestion with manure was established at a ratio of 50% (VS/VS) over a period of 6 weeks. Addition of higher ratios of OFMSW and AD treatment solely of OFMSW was achieved after dilution with tap water and with recirculation of process liquid. Both the co-digestion process and the treatment of 100% OFMSW with recirculation of process liquid showed stable operation despite fluctuations in the feed volume. The biogas yield from the source-sorted OFMSW used was 0.63 – 0.71 l/g-VS in both configurations, corresponding to 180 – 220 m<sup>3</sup> biogas per ton waste. VS reduction of 69-74% was achieved when treating 100% OFMSW. Recirculation of process liquid showed a beneficial effect on the process performance with a stabilization of the pH. Using the liquid effluent of the process for dilution of the influent OFMSW in a ratio of 59% resulted in an ammonia level in the effluent of 1.5 g-N/l, which was similar to the values found during co-digestion with manure. Both reactor systems showed no signs of inhibition at the corresponding free ammonia concentration of 0.45-0.62 g-N/l.

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## **PAPER 5**

# **A novel process configuration for anaerobic digestion of source-sorted household waste using hyper-thermophilic post-treatment**

**Hartmann, H. and Ahring, B. K.**

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# A novel process configuration for anaerobic digestion of source-sorted household waste using hyper-thermophilic post-treatment

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**Abstract:** A novel reactor configuration was investigated for anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW). An anaerobic hyper-thermophilic (68°C) reactor R68 was implemented as a post-treatment step for the effluent of a thermophilic reactor R1 (55°C) in order to enhance hydrolysis of recalcitrant organic matter, improve sanitation and ease the stripping of ammonia from the reactor. The efficiency of the combined system was studied in terms of methane yield, volatile solids (VS) reduction and volatile fatty acid (VFA) production at different hydraulic retention times (HRT). A single-stage thermophilic (55°C) reactor R2 was used as control. VS reduction and biogas yield of the combined system was 78 – 89% and 640 – 790 ml/g-VS, respectively. While the VS reduction in the combined system was up to 7% higher than in the single-stage treatment, no increase in methane yield was observed. Shifting the HRT of the hyper-thermophilic reactor from 5 to 3 days resulted in a drop in the methanogenic activity in the hydrolysis reactor to a minimum. Operation of R68 at HRTs of 24 – 48 h was sufficient to achieve high VS conversion into VFAs. Removal of pathogens was enhanced by the hyper-thermophilic post-treatment. 7% of the ammonia load was removed in the hyper-thermophilic reactor with a flow of headspace gas through the reactor equivalent to four times the biogas flow produced in reactor R1.

**Keywords:** Hyper-thermophilic; anaerobic digestion; organic fraction of municipal solid waste; post-treatment; ammonia stripping; sanitation

## INTRODUCTION

Anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) is a proven technology for organic waste treatment (De Baere, 2000). Life cycle analysis has shown that AD is the most sustainable waste treatment method, generating energy in the form of biogas and a nutrient rich fertilizer (Edelmann et al., 2000). In search for the highest biogas yield and best applicability, the AD process for OFMSW has been applied in different configurations as low- and high-solids, mesophilic and thermophilic processes and single-stage and multi-stage processes with different outcomes (Mata-Alvarez et al.,

2000). Process stability, biogas yield, reduction of organic matter (volatile solids, VS) and the production of an environmentally safe fertilizer are the key parameters for AD of OFMSW. Hydrolysis of organic matter is the bottleneck for the degradation of complex organic matter found in OFMSW and a higher hydrolytic activity in a balanced biogas process will lead to a higher VS reduction and a higher biogas yield. An increase of hydrolytic and methanogenic activity by a shift from mesophilic (37°C) to thermophilic (55°C) operation in the AD treatment of manure, sewage sludge and OFMSW has been shown previously (Ahring, 1994; Del Borghi et al., 1999; Cecchi et al., 1992). Recent studies identified a further increase of hydrolytic activity under anaerobic conditions at 65°C (Ahring et al., 2001). Thermal hydrolysis at 70°C and above has been implemented as separate reactor stage before the anaerobic treatment (Rintala and Ahring, 1994; Bonmatí et al., 2000; Weisz and Solheim, 2000; Scherer et al., 2000). Hydrolytic pre-treatment of manure at 68°C has previously been studied (Nielsen et al., 2004). In the present study we investigated the implementation of a biologically active reactor at 68°C as a post-treatment step. This configuration has not previously been tested, although it has the advantage of a lower organic load and, thus, a smaller reactor volume compared to a pre-treatment configuration. Large parts of organic matter in OFMSW are easily degradable and will be degraded in a conventional thermophilic AD process. A post-treatment using the high capability of hyper-thermophilic conditions (>60°C) would be more suitable for the treatment of residual recalcitrant organic matter that has not been hydrolysed in the first stage. The scope of the separate hydrolysis reactor is to achieve a high degradation of complex organic matter into volatile fatty acids (VFAs), which then could be recycled with the process water into the first-stage reactor where they will contribute to an enhanced biogas yield. Furthermore, the hyper-thermophilic

reactor could be used for stripping of ammonia for recovering a nitrogen rich fertilizer product. According to the data by Katehis et al. (1998) the increase in ammonia removal from the reactor by a temperature increase from 55°C to 68°C can be quite significant, especially for pH<10. Finally, the high process-temperature would improve the sanitation of the waste. The temperature range >60°C is in this context denoted hyper-thermophilic to indicate that this is above the temperature range where most thermophilic methanogens have their growth optimum (Ahiring, 1994, Mladenovska, 1997) which means that fermentative bacteria are predominant in the hyper-thermophilic range.

## MATERIALS AND METHODS

### Waste characteristics

Four batches of source-sorted OFMSW from the municipality of Grindsted (Denmark) were used as feeding substrate. Samples of the source-sorted OFMSW were taken after the on-site shredder device, further homogenized in an industrial meat mincer and stored in 1 kg portions at -18°C. Influent batches were prepared every 2 weeks from the thawed waste portions, diluted 1:5 with tap and/or process water, and stored at 4°C before filling into the influent vessels every 3-4 days. Characterization of the waste was performed by analysis of TS, VS, and COD according to standard methods (APHA et al., 1992).

### Reactor set-up

The reactor experiment consisted of a thermophilic reactor R1 (3.5 l initial active volume) in combination with a hyper-thermophilic post-treatment reactor R68 (1 l initial active volume) (Fig. 1) and a thermophilic reactor R2 (3.5 l initial active volume), which served as control reactor. R1 had been previously adapted to 100% OFMSW with recirculation of process water and R2 to a co-digestion mixture of 50% (VS/VS) of OFMSW and manure. For start-up of reactor R68, it was inoculated with hyper-thermophilic inoculum from a lab-scale reactor (68°C) used for pre-treatment of cow manure (Nielsen et al., 2004). The feed volume of effluent from R1 into R68 was increased successively during the first 30 days from 60 ml/d to 200ml/d. The reactors were fed every 8 h by tube pumps, R1 and R2 from a 1-liter influent vessel (Watson-Marlow, 25 mm tube diameter), and R68 from the 1-liter effluent vessel of R1 (Watson-Marlow, 10 mm tube diameter). The temperature inside the reactors was monitored by the temperature of the

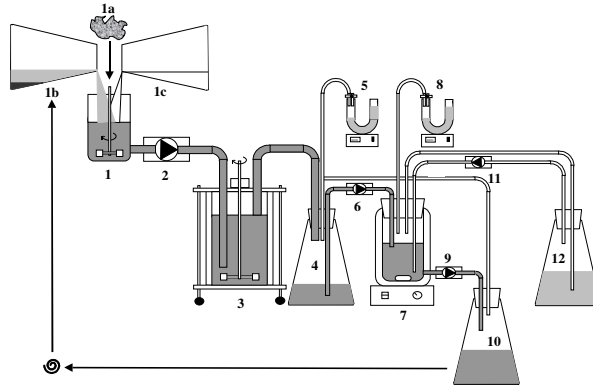
water of the heating jacket after calibrating to the temperature measured inside the reactor.

## Operation parameters and performance analysis

The experiment was divided into seven phases due to changes of the operation regime of the reactors (Table I). The designed HRTs of the respective reactors were adjusted by adjusting the active reactor volume. Deviations of the real to the designed HRT were due to variations in feeding volume. Table 1 displays the real HRT (Table 1), calculated as  $HRT = \frac{Volume_{reactor}}{Flow_{influent}}$ . In phase 1 and 2, R1 and R2 had the same designed HRT and R68 was implemented as additional treatment reactor for the effluent of R1 with a HRT of 6.0 – 6.8 d. During phase 2, R2 was adapted to 100% OFMSW with recirculation of process water and was in the following phases used control reactor for the combined system of R1 and R68. For recirculation of process water, the effluent of R68 and R2 was collected during a period of 3-4 days, centrifuged at 4000 rpm for 30 minutes and the supernatant was decanted and used for dilution of OFMSW for the influent for R1 and R2, respectively. Depending on volume loss by sampling and fluctuations in feeding volume, the ratio of the supernatant of the effluent, which was used as process water, to the whole liquid added for dilution of influent OFMSW varied in average between 42% and 86% (Table 1).

In phase 3–7, the combination of R1 and R68 was operated at the same overall HRT as the control reactor R2. In phase 4 – 7 the retention time in R68 was lowered to 5.3, 3.2, 2.6 and 1.5 d, respectively, by decreasing the active volume of reactor R68.

The performance of all three reactors was monitored by biogas production, VS reduction, VFA concentration, pH and ammonia concentration. Biogas production was measured by liquid displacement gas measurement systems connected to the headspace of the effluent vessels, logging the gas production automatically in 10 ml intervals. The methane content of the biogas was analyzed by gas chromatography as previously described by Sørensen et al. (1991). TS, VS, pH and ammonia in the influent and effluent of the reactor system were determined according to standard methods (APHA et al., 1992). The single VFAs acetate, propionate, isobutyrate and butyrate were analyzed by gas chromatography as described by Sørensen et al. (1991).



**Figure 1.** Set-up of reactor combination of R1 (55°C) and post-treatment R68 (68°C). 1: Influent storage vessel. 1a: OFMSW. 1b: Supernatant of effluent of R68. 1c: Water 2: Influent pump for reactor R1. 3: Thermophilic reactor R1 with heating jacket and mechanical stirrer. 4: Storage vessel for effluent from R1. 5: Gas meter for R1. 6: Influent pump for reactor R68. 7: Hyper-thermophilic reactor R68 with heating jacket and magnetic stirrer. 8: Gas meter for R68. 9: Effluent pump for R68. 10: Storage vessel for effluent of R68. 11: Pump for headspace gas of R68 through gas washing bottle 12. 12: Gas washing bottle with sulphuric acid

**Table I.** Average operation parameters in the different experimental phases

Parameter	Units	Phase 1 (0-106)	Phase 2 (107-223)	Phase 3 (224-309)	Phase 4 (310-334)	Phase 5 (335-374)	Phase 6 (375-402)	Phase 7 (403-443)
<b>OFMSW</b>	<b>TS</b>	% of tot mass	32.6 (1.0)	32.4 (1.1)	29.7 (0.1)	30.7 (2.7)	30.7 (2.7)	30.7 (2.7)
	<b>VS</b>	% of tot mass	29.2 (0.7)	28.9 (0.4)	26.3 (0.0)	27.4 (0.5)	27.4 (0.5)	27.4 (0.5)
<b>HRT</b>	<b>R1</b>	d	14.9 (22.8)	17.7 (25.3)	15.2 (2.3)	15.3 (1.8)	16.2 (1.7)	16.1 (2.3)
	<b>R68</b>	d	6.0 (3.6)	6.8 (3.8)	6.5 (1.6)	5.3 (0.9)	3.2 (1.3)	2.6 (1.9)
	<b>R2</b>	d	16.2 (20.0)	17.5 (32.7)	20.9 (2.9)	22.2 (2.5)	18.3 (2.3)	18.5 (3.2)
<b>OLR</b>	<b>R1</b>	g-VS l <sup>-1</sup> d <sup>-1</sup>	3.5 (1.7)	2.8 (1.3)	3.3 (0.4)	2.9 (0.5)	3.1 (0.3)	3.1 (0.5)
	<b>R2</b>	g-VS l <sup>-1</sup> d <sup>-1</sup>	3.2 (1.1)	3.0 (1.6)	2.3 (0.3)	2.4 (0.3)	2.7 (0.3)	2.8 (0.4)
<b>%Rec.</b>	<b>R1</b>	%	44 (24)	42 (29)	67 (33)	44 (35)	86 (33)	71 (16)
	<b>R2</b>	%	-	-	-	44 (35)	86 (33)	71 (16)

%Rec.: ratio of effluent supernatant to total liquid volume used for dilution of influent OFMSW; standard deviation in brackets

## Ammonia stripping

In phases 1 and 2 the efficiency of the hyper-thermophilic reactor for ammonia stripping was investigated. Headspace gas from R68 was pumped through 500 ml of a 20% H<sub>2</sub>SO<sub>4</sub> solution and recycled back into the bottom of the reactor (Fig. 1). The gas flow was maintained at 20 ml/min, which was about four times the biogas flow of reactor R1. NH<sub>3</sub>-N content in the H<sub>2</sub>SO<sub>4</sub> solution was determined according to standard methods (APHA et al., 1992) and compared to the total NH<sub>3</sub>-N load of the reactor during the respective periods in order to determine the stripping efficiency of the system. The actual ammonia concentration was compared to the predicted

concentration for a constant recirculation ratio according to the following mass balance without stripping loss:

$$C_{NH_3,e_{j+1}} = C_{NH_3,OFMSW} \cdot r_{OFMSW} + C_{NH_3,e_j} (1 - r_{OFMSW}) \cdot r_{sn} + t_{org-N} \cdot (C_{TKN,OFMSW} - C_{NH_3,OFMSW}) \cdot r_{OFMSW}$$

where C = concentration (g-N/l), index i = influent, index e = effluent, index j = recirculation count, index NH<sub>3</sub> = total ammonia-N, index TKN = total Kjeldahl-N, r<sub>OFMSW</sub> = ratio of OFMSW in influent, r<sub>sn</sub> = ratio of supernatant:water used for dilution of OFMSW, t<sub>org-N</sub> = ratio for release of NH<sub>3</sub>-N from organic bound nitrogen (TKN)

$$\text{with } t_{org-N} = \frac{C_{NH_3,e} - C_{NH_3,i}}{C_{TKN,i} - C_{NH_3,i}}$$

## Batch experiments

Biogas and VFA production under thermophilic and hyper-thermophilic conditions were investigated in triplicate batch experiments. OFMSW equivalent to an amount of 0.4 g-VS was filled into 100 ml batch vials with 20 ml buffered medium and 30 ml inoculum added. Two batch experiments were performed with inoculum taken from the thermophilic and the hyper-thermophilic reactor and different buffer concentrations. The buffer concentration in the second batch test was increased from 2.6 g/l NaHCO<sub>3</sub>, 0.6 g/l K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (inoculum taken on day 252), to 3.1 g/l NaHCO<sub>3</sub>, 0.9 g/l K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (inoculum taken on day 283) in order to counteract pH drop due to high VFA accumulation under hyper-thermophilic conditions. The vials were flushed with a gas mixture of 80% N<sub>2</sub> and 20% CO<sub>2</sub> before closing and incubated at 55°C and 68°C, respectively, for 25 days. Methane production was monitored every 2–3 days by analysis of CH<sub>4</sub> concentration in the headspace using gas chromatography with flame ionization detection. VFA concentration was measured at the start and after 20 days according to Sørensen et al. (1991). A third batch experiment was performed to investigate the course of VFA production under hyper-thermophilic conditions. 6 ml effluent from the thermophilic reactor R1 was filled together with 20 ml buffer medium (2.6 g/l NaHCO<sub>3</sub>, 0.6 g/l K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O) and 30 ml hyper-thermophilic inoculum from R68 into 100 ml vials in duplicates. VFA samples were withdrawn from the vials every hour during the first 12 hours and every 24 – 48h during 6 days of experiment.

## Sanitation

The sanitation effect of the thermophilic and the hyper-thermophilic treatment was evaluated using fecal enterococcus as indicator organism. This method was based on a method commonly used for the examination of food and has proved its value for monitoring reduction of pathogens in Danish biogas plants (Bendixen, 1994). Enterococcus agar media with the following composition per 1000 ml was used: 10.0g agar, 20.0g peptone, 5.0g yeast extract, 2.0g glucose, 4.0g disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O), 0.4g sodium azide (NaN<sub>3</sub>) and 0.1g tetrazolium (2,3,5 triphenyl tetrazolium chloride). All ingredients except tetrazolium were dissolved in 1000 ml water, adjusted to pH 7.2±0.1 and autoclaved at 121°C for 15 minutes. Tetrazolium was added immediately before use of the agar from an aseptically prepared solution. 10-15 ml of the substrate

was poured into sterile Petri dishes. For dilution of the samples a media containing 8.5 g/l NaCl and 1.0 g/l peptone was prepared, adjusted to pH 7.2±0.1 and autoclaved at 121°C for 15 minutes. Dilution rows were prepared for 1 ml of sample from influent to reactor R1 (55°C), effluent from R1 and effluent from reactor R68, respectively. For each dilution a duplicate of agar dishes was inoculated by transferring 0.1 ml of medium and distributing it using a sterile glass rod. The Petri dishes were incubated for 2 days at 44°C. Enterococcus colonies were registered as pink to dark red in color, often surrounded by a narrow uncolored zone.

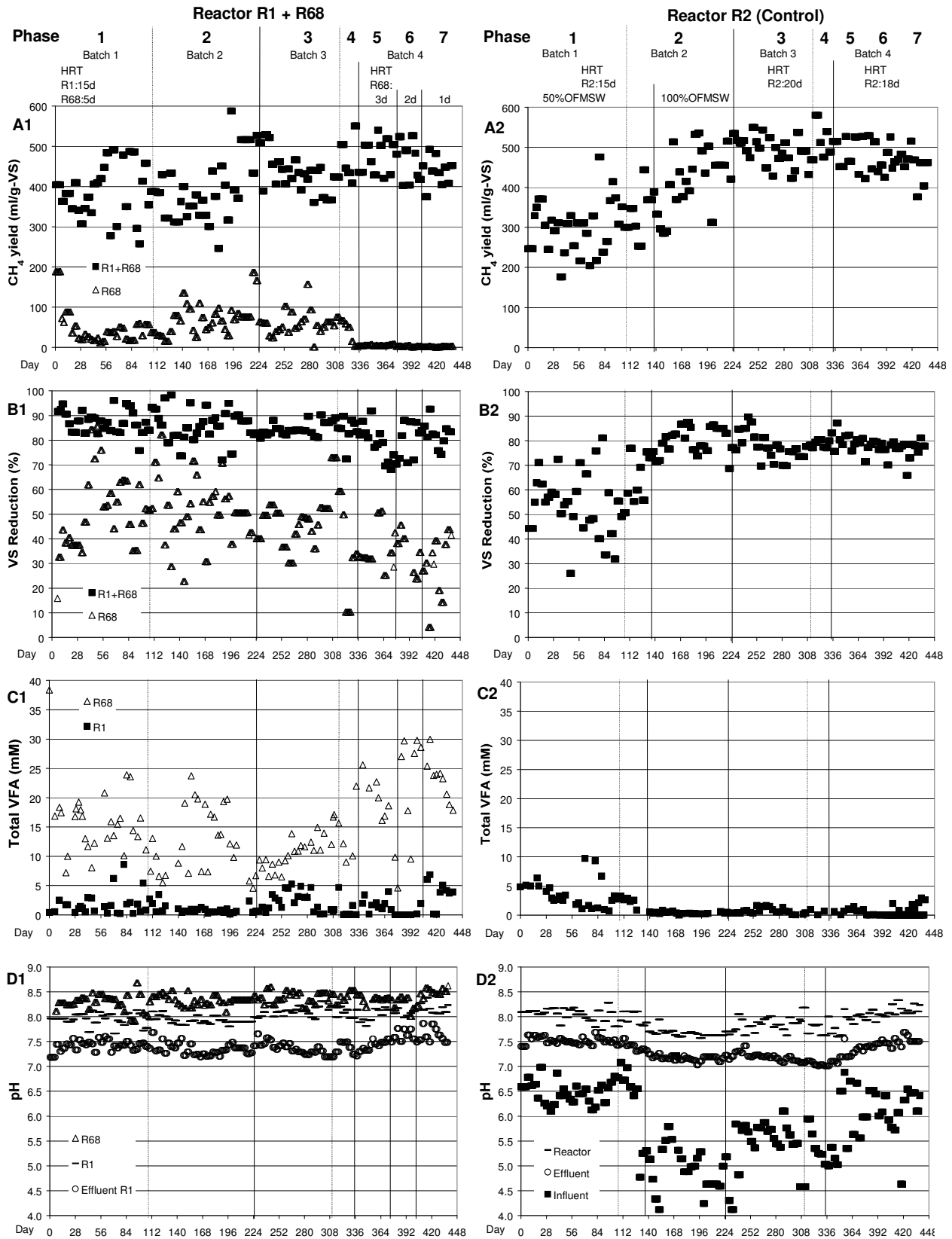
## RESULTS

### Reactor experiment

#### Phase 1 and 2: Hyper-thermophilic reactor R68 as additional treatment

When introducing the hyper-thermophilic reactor as additional post-treatment, the overall VS reduction increased from 74% of R1 (data not shown) to 89% of the combined system of R1+R68 (Fig. 2B1, Table II). On average, 52% of the organic matter from the effluent of R1 was degraded in R68. A relatively high VFA concentration of 10 – 25 mM and methane production with an average yield of 70-110 ml/gVS in R68 indicated both hydrolytic and methanogenic activity under hyper-thermophilic conditions at 6.0-6.8 d retention time (Fig. 2C1, 2A1, Table II).

The higher VS reduction in the combined treatment was, however, not reflected as an increase of the overall biogas production, since the methane yield (before 380 ml/gVS) did not significantly change after the implementation of R68 (390 ml/gVS, Table II). The methane yield of the combined two-stage treatment of R1 and R68 was, moreover, lower than in the control reactor after it was adapted to 100% OFMSW in phase 2, diluted with water (Fig. 2A1, 2AB, Table II). Adaptation of R2 to 100% OFMSW lead to significant rise in methane yield from 280 ml/g-VS to 410 ml/g-VS while the methane concentration in the biogas decreased from 64% to 57%, which indicated a higher ratio of carbohydrates in the composition of OFMSW compared to manure. The processes in R1 and the control reactor R2 showed VFA concentrations below 10 mM, indicating stable process performance (Fig. 2C1, 2C2). Fluctuations of the methane yield and VS reduction were, therefore, considered due to variations of the feed volume and not as a sign of process



**Figure 2.** Methane yield (A1, A2), VS reduction (B1, B2), VFA concentration (C1, C2) and pH (D1, D2) in reactor R1 and R68 (left) and control reactor R2 (right); CH<sub>4</sub> yield and VS reduction of R1+R68 refers to the influent VS of R1, of R68 refers to the influent of R68 (effluent of R1)

**Table II.** Average process parameters in the different experimental phases

Parameter	Units	Phase 1 (0-106)	Phase 2 (107-223)	Phase 3 (224-309)	Phase 4 (310-334)	Phase 5 (335-374)	Phase 6 (375-402)	Phase 7 (403-443)
<b>CH<sub>4</sub> yield</b>	<b>R1+R68</b>	l/g- VS 0.39 (0.09)	0.38 (0.07)	0.43 (0.05)	0.46 (0.03)	0.47 (0.04)	0.46 (0.05)	0.44 (0.03)
	<b>R68</b>	l/g- VS 0.07 (0.04)	0.11 (0.04)	0.05 (0.03)	0.09 (0.03)	0.03 (0.00)	0.02 (0.00)	0.02 (0.00)
	<b>R2</b>	l/g- VS 0.28 (0.07)	0.41 (0.08)	0.49 (0.04)	0.51 (0.04)	0.49 (0.05)	0.47 (0.03)	0.46 (0.04)
<b>%CH<sub>4</sub></b>	<b>R1</b>	%	58.5 (2.8)	59.5 (1.8)	61.3 (1.5)	61.3 (2.1)	61.8 (2.9)	63.5 (1.5)
	<b>R68</b>	%	51.6 (8.7)	54.5 (5.7)	54.3 (5.8)	40.1 (22.5)	16.3 (3.7)	11.5 (3.2)
	<b>R2</b>	%	63.5 (3.5)	57.2 (3.3)	59.4 (1.4)	58.5 (0.9)	60.8 (1.8)	63.0 (1.4)
<b>VS reduction</b>	<b>R1+R68</b>	%	89.0 (4.5)	87.4 (6.3)	84.4 (2.6)	84.9 (5.2)	80.0 (7.0)	78.2 (7.5)
	<b>R68</b>	%	51.7 (15.4)	52.1 (12.6)	46.7 (9.2)	40.3 (23.3)	31.3 (16.9)	18.7 (29.8)
	<b>R2</b>	%	55.0 (12.4)	79.7 (5.3)	77.7 (5.3)	78.9 (1.6)	79.8 (3.8)	77.5 (2.8)

CH<sub>4</sub> yield and VS reduction of R1+R68 and R2 refers to the influent VS of R1 and R2, respectively; the values for R68 refer to the influent VS to R68 (i.e. effluent from R1); %CH<sub>4</sub>: methane content in biogas; standard deviation in brackets

imbalance. The pH in the hyper-thermophilic reactor was generally about 0.5 higher than in the thermophilic reactor R1 due to further ammonia release (Fig. 2D1). In the control reactor the pH decreased in phase 2 from around 8.0 to 7.6 due to the use of 100% OFMSW diluted with water (Fig. 2D2).

### Phase 3 and 4: Combined thermophilic – hyper-thermophilic treatment compared to single stage treatment

The HRT of the control reactor was adjusted to 20 days in order to achieve a total retention time equivalent to the combined treatment of R1 and R68. The average methane yield in the control reactor was significantly higher than the overall yield from reactor R1 and R68 (Fig. 2A1, 2A2, Table II). Higher methane yields in both reactor systems compared with phase 1 and 2 indicated a higher biogas potential of batch 3 and 4 of OFMSW. Start of recirculation of process water into the control reactor could be another reason for an improved reactor performance of the control reactor. Lower fluctuations of the biogas yield in both reactors were due to a more continuous pumping of the feed after installation of new pumps. Lower VFA concentrations in R68 than in phase 1-2 gave evidence of further establishing of the methanogenic consortia.

### Phase 5 to 7: Decreasing the retention time in R68

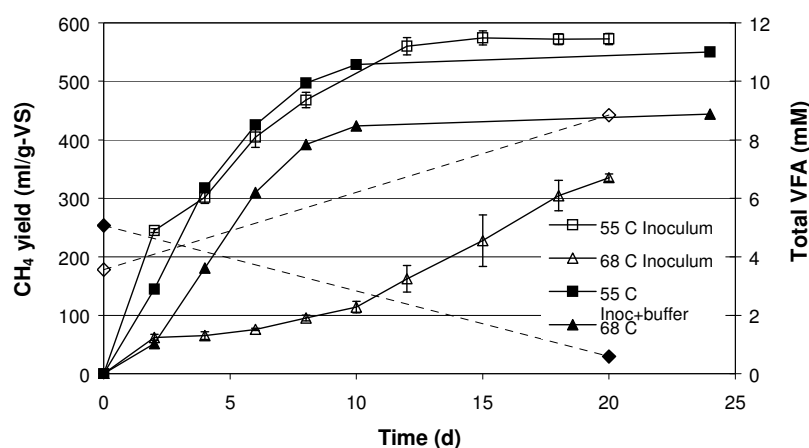
The change of retention time from 5 days to 3 days in R68 caused a significant decrease in the methane production in

the hyper-thermophilic system (Fig. 2A1). Total VFA concentrations in R68 more than doubled from 10 mM up to 25 mM (Fig. 2C1), indicating that the hydrolytic activity became dominant while methanogenic activity declined to a minimum when changing to a shorter retention time. In the course of phase 5, however, the total VFA concentration in R68 decreased to values below 10 mM, and the VS reduction of the combined system decreased to 70% at the end of phase 5 (Fig. 2B1). This indicated lower performance of the system under these operation conditions. Decreasing the HRT further to 2.6 days in phase 6, the VFA concentration increased again up to 30 mM and the system showed again higher VS reduction of 78% in average (Table II). At HRT of 1.5 days in phase 7 the VFA concentration fell again, but was always above 15 mM. VS reduction of the combined system was, on average, 5.5% higher than in the thermophilic single stage treatment.

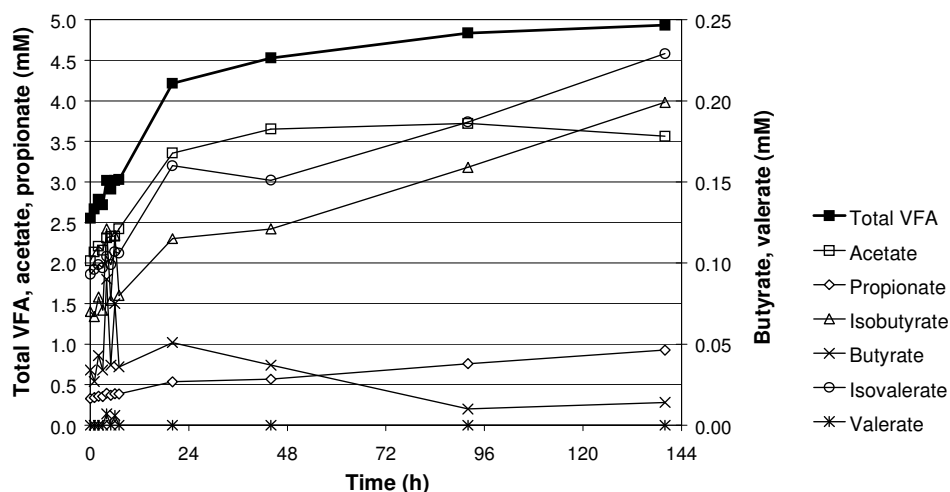
### Batch experiments

Batch tests revealed high VFA production under hyper-thermophilic conditions that lead to inhibition of the methanogenic activity when the buffer concentration was low. (Fig. 3). The ultimate biogas yield was, however, also for the buffered system significantly lower under hyper-thermophilic (444 ml/g-VS) than under thermophilic conditions (550 ml/g-VS).

Another batch test revealed that 72% and 80% of the total VFA was released after 24h and 48h, respectively (Fig. 4). This confirmed that HRT below 3 days is sufficient to gain most of the hydrolytic



**Figure 3.** Course of methane yield and VFA concentration under thermophilic and hyper-thermophilic conditions with low and high buffer capacity (see methods)



**Figure 4.** Course of VFA production under hyper-thermophilic conditions

activity. In both the reactor and batch experiments, acetate was the predominant VFA produced (66-82% of total VFA) followed by propionate.

## Ammonia

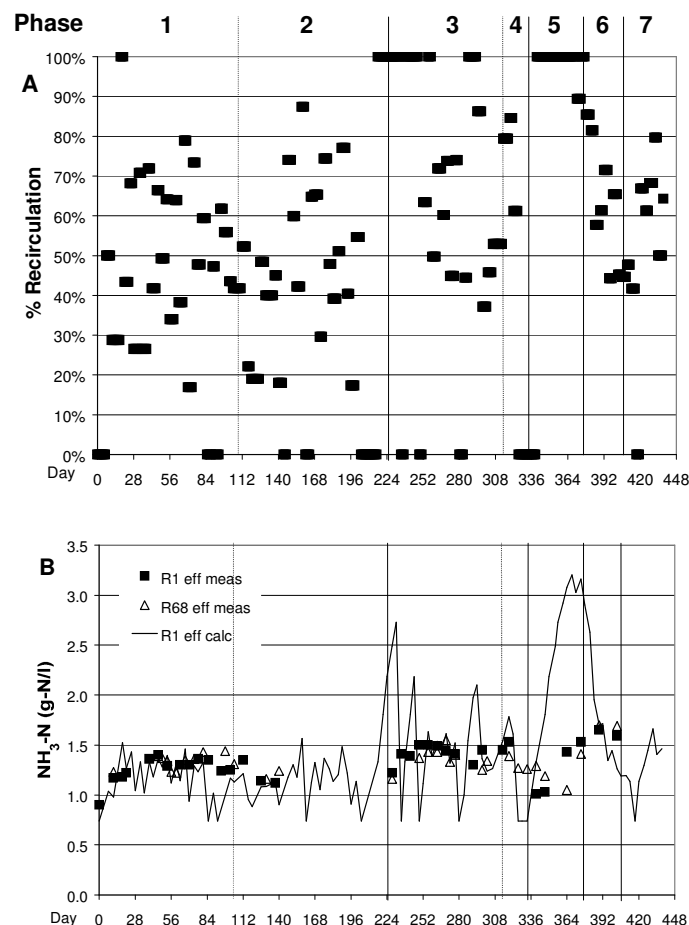
With a recirculation ratio of the effluent of 42-44% in phases 1 and 2 and 67% in phase 3, the ammonia concentration in the thermophilic reactor was, on average, 1.25 g-N/l in phase 1-2 and 1.42 g-N/l in phase 3 (Fig. 5). The measured ammonia concentration was not as much affected by fluctuations in the recirculation ratio for process water as it was predicted by the calculated ammonia concentration, indicating that the ammonia release was not instant. The ammonia concentration in the

hyper-thermophilic reactor was, on average, 1.31 and 1.35 g-N/l in the respective phases.

## Sanitation effect of hyper-thermophilic treatment

The numbers of enterococcus colonies before and after thermophilic (15 d HRT) and hyper-thermophilic treatment (1 d HRT) are shown in Table III. The thermophilic treatment reduced the number of colony forming units (CFU) by 4 orders of magnitude and the hyper-thermophilic treatment by one more order of magnitude. In the effluent of the hyper-thermophilic reactor only one single colony was detected..





**Figure 5.** Recirculation ratio of process water (A) and ammonia concentration in effluent of R1 and R68 (B); eff: effluent; meas: measured; calc: calculated; %Recirculation: ratio of effluent supernatant to total liquid volume used for dilution of influent OFMSW

**Table III.** Reduction of enterococcus colony counts by thermophilic and hyper-thermophilic treatment

Sample	CFU/ml	CFU/g-TS
Influent OFMSW	$1.1 \cdot 10^6$	$1.8 \cdot 10^7$
Effluent R1 (55°C, 15 d HRT)	$2.0 \cdot 10^2$	$9.8 \cdot 10^3$
Effluent R68 (68°C, 1 d HRT)	$0.5 \cdot 10^1$	$2.6 \cdot 10^2$

CFU: colony forming units

## DISCUSSION

The process data of the reactors showed a separation between the thermophilic and the hyper-thermophilic reactors. While low VFA concentrations in the thermophilic reactors R1 and R2 indicated a well-balanced process of hydrolytic bacteria and methanogens, operation of the separate hyper-thermophilic reactor showed a predominant hydrolytic activity at 68°C with high VFA production and low methanogenic activity. This is in accordance with the observations by Ahning et

al. (2001) who reported a decrease in methanogenic activity and an increase in VFA concentration when shifting the operation temperature of a manure-treating anaerobic reactor from 55°C to 65°C. In the combined system and the control reactor, VS reduction and methane yield of 78-89% and 380 – 510 ml/g-VS, respectively, were significantly higher than previously reported (for example de Laclos et al.; 1997, Kübler, 1994; Scherer et al., 2000). Introducing the hyper-thermophilic reactor as additional post-treatment lead to a significant increase in the overall VS reduction of up to 89%. In the combined system of the thermophilic R1 and the hyper-thermophilic reactor R68 with the same total HRT as the single-stage thermophilic treatment system R1, the VS reduction was 6 – 7% higher in the combined system for HRT of R68 of 5.3 – 6.5 d. Lowering the HRT in R68 to 3.2 d and 2.6 d did not show a benefit compared to the single-stage thermophilic treatment. At HRT of 1.5 d of R68 the VS reduction of the combined system was, however, again 7% higher than of the treatment at 55°C. This showed together with the results from the batch experiments

that a hydraulic retention time in the hyper-thermophilic reactor of 24 – 48 h is sufficient when operating the reactor exclusively for hydrolysis without considerable methanogenic activity. The methane yield in the combined system did not increase in the same way as the VS reduction. Neither VS accumulation in the reactor nor hydrogen production could account as a significant VS sink. Similar observations were made by Scherer et al. (2000) who investigated the combination of a hyper-thermophilic (60 - 70°C) first stage reactor and a thermophilic (55°C) second stage.

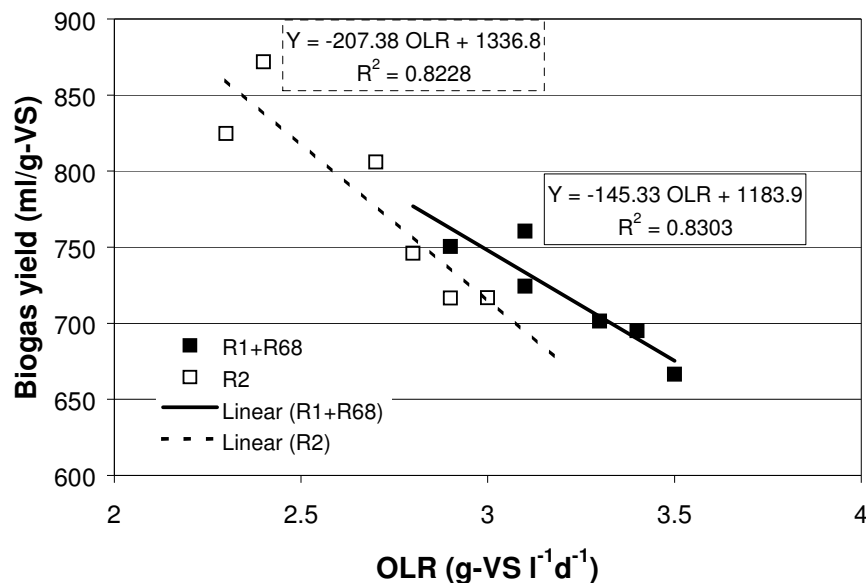
A good correlation was found for the biogas yield and the OLR of the combined treatment R1+R68 and the single-stage control reactor R2 (Fig. 6). It revealed almost the same tendency for both treatment systems (the value for the combined system in phase 2, 0.64 ml<sub>biogas</sub>/g-VS at 2.8 g/l/d, was excluded due to uncertainties because of high fluctuations of the biogas yield). No substantial difference was found in the biogas yield of both systems. The lower biogas yield in R1+R68 was, thus, due to a higher loading of the thermophilic reactor R1 than R2. In the investigated range of OLR the sharp decrease of the biogas yield was indicating, that the process efficiency was quite sensitive to an increase of the OLR. For the same OLR applied for the thermophilic reactors, the combination of R1+R68 showed, however, a slightly higher biogas yield. Consequently, the hyper-thermophilic reactor showed clear benefits as additional post-treatment of OFMSW, but only small benefits when the combined system is operated at the same total HRT as the single-stage thermophilic system. One reason for the low benefit of the additional hyper-thermophilic treatment could be the high degradability of 76 – 80% of the OFMSW used, also under thermophilic (55°C) conditions, which

indicated a low content of poorly degradable organic matter in the OFMSW used.

The ammonia concentration of the effluent measured in phase 1-2 and 3 was in average in accordance to the values of 1.14 and 1.59 g-N/l, calculated from the mass balance shown in materials and methods.

A free NH<sub>3</sub> concentration of 0.4 g-N/l in the thermophilic (pH 8.0, 55°C) and 0.9 g-N/l in the hyper-thermophilic reactor (pH 8.4, 68°C) was calculated according to Anthonisen et al. (1976). Thus, the stable process performance in the thermophilic reactors showed that AD of OFMSW in the investigated low-solids digestion treatment tolerated much higher ammonia concentrations than described for high-solids systems, where free ammonia concentration of 0.125 g-N/l was reported to induce process failure (Kayhanian, 1994). Low VFA concentration and high biogas production in the present thermophilic process indicated adaptation to higher ammonia levels as described by Angelidaki and Ahring (1993), who found stable reactor performance at free ammonia levels of up to 0.65 g-N/l. A free ammonia concentration of 0.9 g-N/l in the hyper-thermophilic reactor could, however, be the reason for low methanogenic activity in reactor R68.

Ammonia concentration measured on day 68 and 253 in the H<sub>2</sub>SO<sub>4</sub> absorption bottle revealed that 3% and 7% of the total ammonia load of the first 2 months and the following 6 months, respectively, had been removed by the applied stripping method. The low efficiency in the first two months was due to operational problems with the gas recirculation, which



**Figure 6.** Biogas yield versus OLR for the combined treatment of R1 and R68 and for the control reactor R2

made continuous operation impossible. A removal of 7% of the ammonia was in accordance with the difference in the measured total nitrogen concentration in the influent ( $2.14 \pm 0.20$  g-N/l) and effluent ( $1.92 \pm 0.14$  g-N/l) of R68, which accounted for 10%, measured in the respective period. This showed that ammonia was removed with the gas flow applied. An ammonia concentration in the thermophilic reactor of 2.38 g-N/l could be calculated for a removal rate of 10% and continuous 100% recirculation of the effluent. This would correspond to a free ammonia concentration of 0.66 g-N/l, which is at the limit of ammonia inhibition. This means, the 10% removal would be an effective means to avoid ammonia inhibition. For higher ammonia removal, which can be estimated at the given conditions (pH 8.5, T 68°C) to about 30% (Katehis et al. 1998; Liao et al., 1995), a higher gas stream would be necessary in order to enhance the contact between gas and liquid phase. Applying this removal ratio, the total ammonia and the free ammonia concentration could be lowered to 1.18 and 0.33 g-N/l, respectively.

Sanitation was enhanced by hyper-thermophilic post-treatment at 68°C and leads to almost complete sanitation of the waste. This can have major impact on the use of the effluent from the treatment process. Furthermore, we have previously shown that hyper-thermophilic conditions enhanced the degradation of phthalic acid esters found in OFMSW (Hartmann and Ahring, 2003).

## CONCLUSIONS

The implementation of an additional hyper-thermophilic (68°C) post-treatment to a conventional thermophilic (55°C) AD treatment of OFMSW increased the total VS reduction to 89%. VS reduction in the combined treatment system was 7% higher than in the thermophilic single-stage treatment and a biogas yield of 640 – 790 ml/g-VS was achieved, corresponding to a biogas yield of 185 – 216 m<sup>3</sup>/m<sup>3</sup><sub>OFMSW</sub>. Hydrolytic activity was dominating in the hyper-thermophilic system and lowering the HRT from 6 to less than 3 days resulted in a drop of the methanogenic activity to a minimum. Operation of the hyper-thermophilic reactor exclusively for hydrolysis, a HRT of 24 – 48 h was sufficient to gain a high VS reduction. An ammonia removal of 7% was obtained by running a low gas stream of headspace gas from the hyper-thermophilic reactor through a sulphuric acid solution. Sanitation was enhanced by the hyper-thermophilic treatment with almost complete destruction of fecal enterococcus used as indicator organism for pathogens.

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## **PAPER 6**

# **Phthalic acid esters found in municipal organic waste: Enhanced anaerobic degradation under hyper-thermophilic conditions**

**Hartmann, H. and Ahring, B. K.**

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# PHTHALIC ACID ESTERS FOUND IN MUNICIPAL ORGANIC WASTE: ENHANCED ANAEROBIC DEGRADATION UNDER HYPER-THERMOPHILIC CONDITIONS

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## ABSTRACT

Contamination of the organic fraction of municipal solid waste (OFMSW) with xenobiotic compounds and their fate during anaerobic digestion was investigated. The phthalic acid ester di-(2-ethylhexyl)phthalate (DEHP) was identified as the main contaminant in OFMSW in concentrations more than half of the threshold value for the use as fertilizer on agricultural soil in Denmark. Analysis of DEHP in samples before and after large-scale anaerobic digesters revealed higher concentrations of DEHP per kg dry matter in the effluent than in the influent. The concentration of DEHP and DBP (dibutylphthalate) in OFMSW was monitored in the influent and effluent of anaerobic thermophilic (55°C) and hyper-thermophilic (68°C) lab scale reactor systems. In the thermophilic reactors with a hydraulic retention time (HRT) of 15 days 38%-70% of DBP was removed, but no consistent removal of DEHP was observed. However, after treatment of the effluent from the thermophilic reactor in a hyper-thermophilic digester (HRT: 5 days) 34%-53% of the DEHP content was removed and the DBP removal was increased to further 62%-74%. Removal rates ( $k_h$ ) of DEHP and DBP were found to be  $0.11 - 0.32 \text{ d}^{-1}$  and  $0.41 - 0.79 \text{ d}^{-1}$ , which is much higher than in previous investigations. It can be concluded that the higher removal rates are due to the higher temperature and higher initial concentrations per kg dry matter. These results suggest that the limiting factor for DEHP degradation is the bioavailability, which is enhanced at higher temperature and higher degradation of solid organic matter, to which the highly hydrophobic DEHP is adsorbed. The investigated reactor configuration with a thermophilic and a hyper-thermophilic treatment is, therefore, a good option for combining high rate degradation of organic matter with high biogas yields and efficient reduction of the phthalic acid ester contamination.

## KEYWORDS

Anaerobic digestion; bioavailability; DEHP; hyper-thermophilic; organic fraction of municipal solid waste; phthalic acid esters



## INTRODUCTION

Biological waste treatment concepts need to compete with incineration. The extra costs for separation of the organic fraction of municipal solid waste (OFMSW) for biological treatment can only be justified if a more sustainable concept can be realized by the biological treatment. Consequently, the energy gain should be higher and emission of pollutants should be lower than by incineration. Anaerobic digestion of OFMSW offers the advantage of a higher net energy gain than by incineration from the production of methane. Furthermore, the end product of the process can be used as fertilizer. However, for using the effluent of the process as fertilizer it has to be ensured that the content of xenobiotics and heavy metals is below the levels found to be of environmental risk. The Danish government has set the aim to treat 150,000 tons of OFMSW (40%-42% of the total amount of municipal solid waste) biologically by the year 2004. Here, anaerobic digestion is the major choice. Since the effluent of the biogas plants should be used as a fertilizer, OFMSW has to comply with thresholds for heavy metals and xenobiotics. The threshold values for xenobiotic compounds are listed in table 1.

Table1: Threshold values of xenobiotic compounds in organic waste for the use as fertilizer in Denmark (since 01-07-2002)

	Xenobiotic compound	Threshold (mg/kg-TS)
LAS	(Linear alkyl benzene sulphonates)	1,300
PAH	(Polycyclic aromatic hydrocarbons as sum of acenaphthene, phenanthrene, fluorene, fluoranthene, pyrene, benzfluoranthene (b+j+k), benz(a)pyrene, benz(ghi)perylene, indeno(1,2,3-cd)pyrene)	3
NPE	(Nonyl phenols + ethoxylates with 1-2 ethoxy groups)	10
DEHP	(Di-(2-ethylhexyl)phthalate)	50

TS: total solids

Previous investigations identified the concentration of DEHP as the major concern in OFMSW in Denmark (Kjølholt et al. 1998, Møller 1999). This is suspected to be due to a widespread collecting system using plastic bags followed by insufficient plastics separation. The DEHP concentration in the collected waste has often been close to the threshold value (50 mg/kg-TS). Since the organic matter (VS) and thus the total solids (TS) content decrease during anaerobic digestion, the concentration of DEHP per kg dry matter of fertilizer product would exceed the permitted level if no removal of DEHP occurs.

In the development of a new treatment concept for the anaerobic digestion of OFMSW (Hartmann et al. 2001) the present work had two aims with respect to xenobiotic contamination of OFMSW: first, to identify the level of xenobiotic contamination in OFMSW of different origin in Denmark and its variation over time and second to determine the fate of phthalic acid esters contamination in OFMSW throughout the anaerobic treatment process.

The contamination of OFMSW with phthalic acid esters (PAEs) and its fate during anaerobic digestion processes is only rarely investigated (Ejlertsson et al. 1996). Most investigations concerning the degradation of PAEs are based on aerobic and anaerobic sludge treatment and their fate on sludge-amended soil (for example Roslev et al. 1998, Madsen et al. 1999, Banat et al. 1999, Merkel and Appuhn 1996). From these studies it is well known that among all PAEs DEHP is one of the compounds that is most recalcitrant towards both aerobic and anaerobic degradation (Staples et al. 1997). The recalcitrant characteristics of DEHP are suspected to be due to two physical properties: (1) its low water solubility and (2) its three dimensional branched structure which prevents hydrolytic enzymes from binding (Ejlertsson et al. 1997). Ejlertsson and co-workers (1997) suspected the water solubility being the major limiting factor for degradation of hydrophobic PAEs. Most reliable measurements indicate that the water solubility of DEHP and DBP is in the

range of 0.0006 – 0.0026 mg/l and 1.5 – 13.0 mg/l, respectively, with a log  $K_{OW}$  in the range of 7.0 – 7.8 and between 3.74 and 5.15, respectively (Staples et al. 1997). The difference in water solubility could explain why degradation of lower molecular weight phthalates like DBP is relatively rapid also under anaerobic conditions, while experiments with DEHP show little or no degradation (Staples et al. 1997, Ejlerthsson et al. 1997). Investigations of the degradation of PAEs show furthermore a higher variability in anaerobic biodegradation suggesting that the nature of the inoculum influences test results (Ejlerthsson et al. 1997). Several investigations have also shown that the degradation of DEHP is temperature dependent (Madsen et al. 1999, Banat et al. 1999). The hypothesis for the present investigation was therefore that a higher degradation efficiency could be established at higher temperatures due to enhanced water solubility and hence a higher bioavailability and biodegradability.

## METHODS

**Sampling.** For analysis of xenobiotic contamination of OFMSW from different collection sites, samples were taken from the wastewater treatment plant in Grindsted, the biogas plant in Studsgård, and the composting plant Noveren near Holbæk. In Grindsted and Studsgård samples were taken of untreated OFMSW and from different stages of the treatment process to follow the xenobiotic contaminants. At Noveren only the collected OFMSW was analyzed. In Grindsted OFMSW is source sorted, collected in paper bags and treated in a mesophilic anaerobic digester in co-digestion with sewage sludge. The effluent is dewatered by a ribbon press after addition of a polymer solution. The solid fraction is sold as fertilizer. In Studsgård OFMSW is collected in plastic bags, plastic is removed by mechanical separation on roller sieves and the organic waste fraction is treated in the biogas plant in co-digestion with manure under thermophilic conditions. The solids in the effluent are removed using a separator consisting of a brush sieve and a screw press. The solid fraction is incinerated. For representative sampling 20 kg untreated OFMSW was collected from the three sites, each. In Grindsted and Studsgård 10 l of mixture with the co-substrate was collected over a period of 7 days and of the effluent of the process after the hydraulic retention time of the reactor.

**Reactor set-up.** OFMSW collected for the co-digestion plant in Grindsted was used as substrate for laboratory reactor set-up. The waste was homogenized using a meat-mincer and diluted to a slurry of 6% TS (w/w) by addition of tap water, cow manure or liquid fraction of the reactor effluent, respectively. A thermophilic (55°C) continuously stirred tank reactor (CSTR) R1 with an active volume of 3 l was operated solely on OFMSW in a wet digestion process after acclimation from cow manure to a successive higher ratio of OFMSW. A second thermophilic reactor R2 (3 l active volume) was stabilized to a (50:50%VS) co-digestion process of OFMSW and cow manure. The hydraulic retention time (HRT) was 15 days for R1 and R2. Influent for both reactors was prepared as described with the same portions of OFMSW; 200 g OFMSW was used per liter of influent for R1 and 100 g OFMSW per liter for influent of R2. Both reactors were fed every 8 hours with an organic loading rate (OLR) of 4 gVS l<sup>-1</sup> d<sup>-1</sup>. After day 140 the liquid fraction of the effluent from R1 was recycled for dilution of OFMSW used for influent of R1. Due to a volume loss by sampling additional tap water was used for dilution of OFMSW. The ratio between recycled liquid effluent and tap water was, on average, 49% (v/v). Effluent from R1 was in a second experimental phase after day 340 treated in a subsequent hyper-thermophilic (68°C) CSTR R68 with an active volume of 1 l and a HRT of 5 days. The inoculum for start-up of R68 originated from a laboratory-scale hyper-thermophilic reactor treating cow manure. In this experimental phase, the liquid fraction of the effluent from R68 was used for dilution of influent OFMSW for R1. Process performance was monitored by VS-reduction, methane production, VFA (volatile fatty acids) concentration, ammonia formation and concentration of PAEs in the reactor influent and effluent. It has to be

pointed out that OFMSW was not spiked with phthalic acid esters, so only the original contamination was measured.

Analytical procedure. For chemical analysis the untreated OFMSW collected from the three treatment plants was homogenized using a meat mincer. Xenobiotics were analyzed according to a method recommended by the Danish Environmental Protection Agency. A sample amount equivalent to 10 g-TS was transferred to 500 ml serum bottles. 10 µg deuterium-labeled phenanthrene d10, fluoranthene d10, benzo(a)pyrene d12 and 25 µg DEHP d4, all dissolved in 10 ml dichloromethane (DCM) was added as internal standard prior to extraction. After adjusting the pH to 10-12 using NaOH, 150 ml DCM was added as extracting agent. The serum bottles were sonicated for 5 minutes and shaken for 2 h at 250 rpm at room temperature. The DCM phase was harvested after centrifugation and DCM was evaporated at 70°C. The residue was dissolved in 10 ml DCM and analyzed by GC-MS equipped with a HP-5 column (25 m x 0.2mm x 0.3µm). Helium was used as carrier gas with a flow of 0.8 ml/min. GC oven temperature was 50°C for 2 minutes, increased with 12°C/min up to a final temperature of 310°C, which was held for 10 min. Injector temperature was 280°C, and 270°C of the MS interface. Detection limit for DEHP was 0.005 mg/l. For analysis of PAEs in the influent and effluent samples of the laboratory reactor set-up a sample amount of 40-60 ml was taken, 60 µg DEHP d4 was added as internal standard dissolved in 3 ml DCM and the amount of DCM used for extraction was reduced to 100 ml. After extraction and evaporation of the DCM phase as described above, the residue was dissolved in 3 ml DCM. GC-MS analysis was performed as previously described.

## RESULTS AND DISCUSSION

Xenobiotic contamination of OFMSW at different treatment sites. Analysis of xenobiotic compounds in the OFMSW samples from the different sites revealed concentrations of NPE and LAS below detection limits at all sites. PAH concentration (as sum of PAH's listed in table 1) in OFMSW was below detection limits at Studsgård and Grindsted while OFMSW from Noveren contained 2.6 mg/kg-TS. The DEHP concentration, however, revealed a significant level of 10-28 mg/kg-TS in all OFMSW samples and, therefore, the present investigation focused on the fate of DEHP during anaerobic treatment processes (figure 1). At Studsgård, the DEHP concentration per kg dry matter decreased significantly in the mixture with manure (from 25 mg/kg-TS to 2 mg/kg-TS) while the sewage sludge in Grindsted (36 mg/kg-TS) contributed to an increase of the DEHP concentration from OFMSW (10.4 mg/kg-TS) to 26 mg/kg-TS. In the effluent of both plants the concentration per kg-TS increased, at Studsgård by a factor of 11 (from 2 to 23 mg/kg-TS) and at Grindsted by a factor of 2 (from 26 to 50 mg/kg-TS). For the samples at Grindsted, this corresponds to the reduction of the TS concentration of 50% (from 4.1% to 1.9%). The increase of the DEHP concentration per kg-TS measured in the effluent from Studsgård is, however, higher than the TS reduction, which is about 80% (from 12.7% to 2.5%). This means that the concentration in mg per liter was higher in the effluent than in the influent, which suggests a higher extractability of DEHP in the effluent than in the influent sample. This is in accordance with previous investigations. Møller (1999) found DEHP concentrations of 28 mg/kg-TS in OFMSW collected in Zealand, Denmark, and levels of up to 160 mgDEHP/kg-TS in the effluent after treatment in a biogas plant near Ålborg (Møller 1999). It is, therefore, impossible to state whether DEHP degradation occurred in the anaerobic digesters or not. Fact is that the DEHP concentration in the effluent from the digester in Grindsted was as high as the threshold value. The lower value at Studsgård was only due to that OFMSW was diluted with manure. Analysis of the effluent samples from Studsgård show, furthermore, that DEHP was efficiently separated with the solid fraction of the effluent.

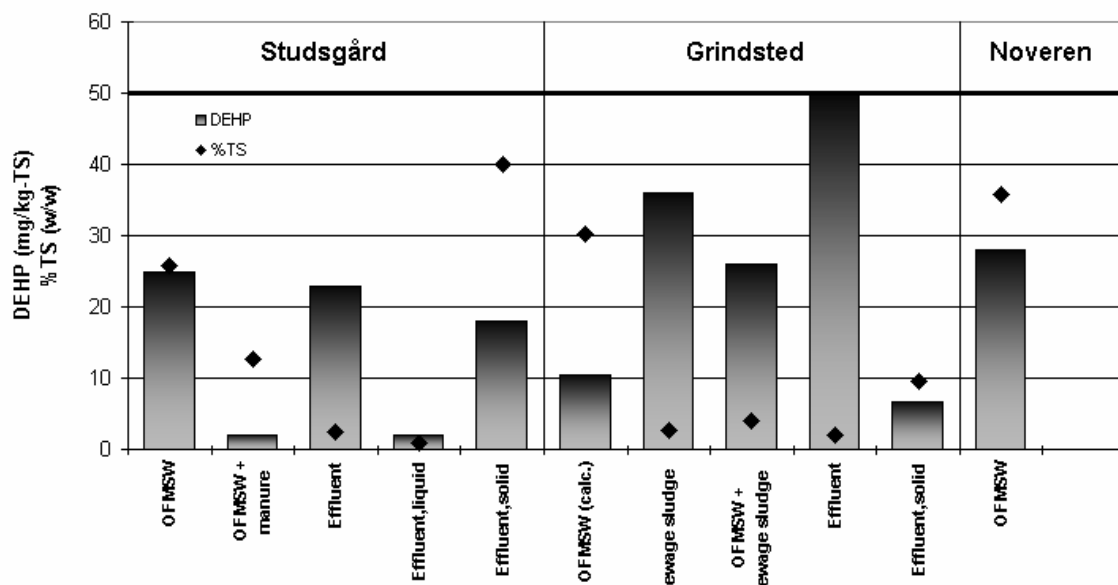


Figure 1: DEHP and TS ratio in OFMSW from Studsgård biogas plant, Grindsted wastewater treatment plant, Noveren composting plant and in co-substrates and along the different stages of the biogas process at Studsgård and Grindsted; the concentration of DEHP in OFMSW from Grindsted was calculated from a mass balance based on the DEHP and TS values found in sewage sludge and the mixture of sewage sludge and OFMSW

Phthalic acid esters in lab-scale reactor experiments. The phthalic acid esters DEHP and DBP were chosen as model compounds to monitor the fate of high and low molecular weight phthalic acid esters during the anaerobic degradation process. DEHP and DBP were both found in significant concentrations, but we decided to focus on DEHP since its concentration was generally higher and its degradation is reported to be restricted during anaerobic processes. The origin of the phthalate contamination in OFMSW remained unclear since the waste showed only low content of plastic material and analysis of phthalates in the paper bags used for collection of the waste revealed low values of 0.4 mg/kg-TS and 0.9 mg/kg-TS for DEHP and DBP, respectively.

Concentrations of DEHP and DBP in the influent and effluent of R1 are given in figure 2, of R2 in figure 3 and of R68 in figure 4. The concentrations are given in mg/l for a better comparison of the total in- and output of phthalic acid esters of the reactors. The threshold value of 50 mg/kg-TS corresponds to 3.0 mg/l in the influent (with a TS average of 6%), to 1.5 mg/l in the effluent of R1 (with a TS average of 3%), to 1.7 mg/l in the effluent of R2 (with a TS average of 3.5%) and 0.75 mg/l in the effluent of R68 (with a TS average of 1.5%).

The concentration of DEHP in the influent of R1 showed high fluctuations (figure 2) while the DEHP concentration in the mixture with manure in the influent of R2 was, except for the measurements around day 200, generally below the threshold value of 3 mg/l (figure 3). DBP concentration of the influent to both reactors was except for one measurement on day 182 (R1) lower than 0.6 mg/l. Thus the reactor results confirm DEHP as the main contaminant of interest compared to DBP. High DEHP concentrations in both reactors around day 200, more than 10 mg/l in the influent of R1 and more than 5 mg/l in the influent of R2, are suspected to be due to a higher DEHP contamination of the OFMSW used in this period. The higher contamination could, however, not be visually estimated by an obvious appearance of plastic material. In the period of recycling the liquid fraction of the effluent of R1 (between day 140 and 340) the concentration of DEHP and DBP in the influent of R1 was more than twice the concentration of the influent to R2. This indicates that both PAEs were partly recycled with the liquid fraction of the effluent of R1. When the effluent of R68 was recycled as part of the influent of R1 after day 340, the influent DEHP and DBP concentration of R1 was not more than twice of the concentration in R2,

suggesting that recycling the liquid fraction of the effluent of R68 did not increase the DEHP and DBP concentration. After day 440 the influent DEHP concentration of R1 was again higher, which is suspected to be due to a higher level of DEHP in a new batch of OFMSW.

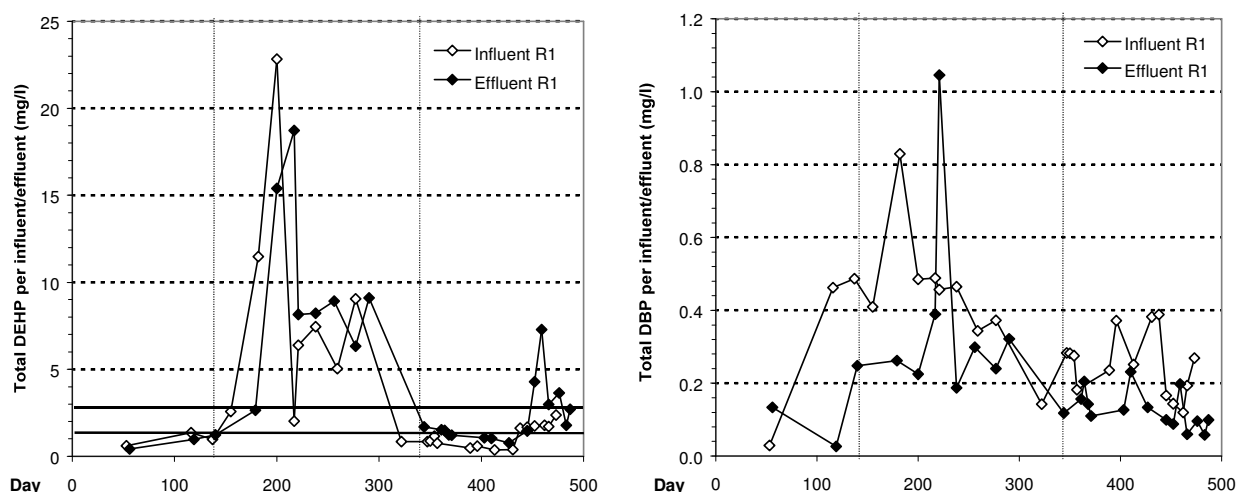


Figure 2: DEHP (left) and DBP (right) in influent and effluent of thermophilic reactor R1 (100% OFMSW) and threshold concentrations for influent (3 mg/l) and effluent (1.5 mg/l) for use as fertilizer

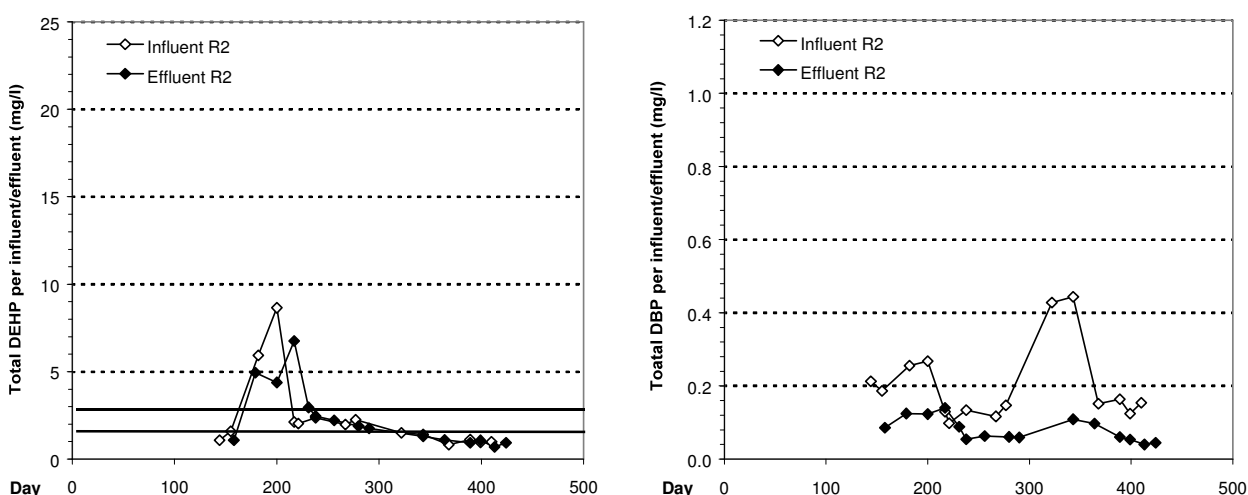


Figure 3: DEHP (left) and DBP (right) in influent and effluent of thermophilic reactor R2 (50%(VS/Vs) OFMSW in co-digestion with manure) and threshold concentrations for influent (3 mg/l) and effluent (1.7 mg/l) for use as fertilizer

The fluctuation pattern of the DEHP and DBP concentration in the influent to both reactors was generally well reflected in the effluent concentration of DEHP, when comparing the concentrations after one hydraulic retention time (15 days). This can be seen, for example, in the high concentration peaks around day 200 in both reactors followed by high concentration peaks in the effluent and the dynamics in influent concentrations of R1 in the period between day 200 and 300 followed by the same pattern in the effluent concentrations of R1. In the effluent of reactor R2 the concentration in mg/l was, except for two measurements around day 200, roughly the same as in the influent (figure 3). In the effluent of reactor R1 the measured DEHP concentration was even higher than in the influent (figure 2). This was still true when taking into account the volume loss in R1 due to evaporation and mineralization, assuming that DEHP was not part of this loss. The reason for the higher value in the effluent than the influent is, therefore, suspected to be a higher extractability

of DEHP after biological degradation of particulate organic matter in the anaerobic digester. In both reactors the effluent concentration was, except for the period between day 350 and 440 for R1 and day 330 to 440 for R2, above the threshold values of 1.5 mg/l for R1 and 1.7 mg/l for R2. DBP concentration was both for R1 and R2 lower in the effluent than in the influent. Assuming first order kinetics and steady state conditions for the removal of DEHP and DBP, the kinetic constant for removal by hydrolysis  $k_h$  was calculated according to equation (1).

$$k_h = \frac{1}{HRT} \cdot (C_{in} - C_{out}) \cdot \frac{1}{C_{out}} \quad (1)$$

where  $C_{in}$  is the influent concentration (mg/l);  $C_{out}$  the effluent concentration (mg/l) and HRT the hydraulic retention time ( $d^{-1}$ )

$k_h$  values are shown in table 2. DEHP removal in the thermophilic reactors could only be detected for reactor R2 in the period between day 340 and 442. The concentration was, on average, 9.6% lower in the effluent and the calculated  $k_h$  value was  $0.009 d^{-1}$ . Removal of DBP was observed in both reactors, with a range of 38% - 49% and 46% - 70% for R1 and R2, respectively. Removal rates for DBP in the range of  $0.044 - 0.112 d^{-1}$  and  $0.065 - 0.163 d^{-1}$  for R1 and R2, respectively, were about 10 times higher than the observed DEHP removal rate in reactor R2.

After treatment of the effluent from reactor R1 in the hyper-thermophilic reactor R68 the effluent concentration of DEHP and DBP was consistently lower than the influent concentration (figure 4). The reduction was 34% - 53% for DEHP and 62% - 74% for DBP. In the period between day 400 and 450 the effluent concentration was below the respective threshold value of 0.75 mg/l.  $k_h$  values reveal removal rates in the range of  $0.21 - 0.47 d^{-1}$  and  $0.55 - 1.09 d^{-1}$  for DEHP and DBP, respectively (table 2). In this calculation accumulation of DBP and DEHP was considered. Accumulation was determined by extraction of the phthalic acid esters from the residue found in R68 at the end of the experiment. The accumulated amount per total volume of influent throughout the whole experimental period accounted for an accumulation of 0.029 mg/l DEHP and 0.002 mg/l DBP. Thus the accumulation was negligible considering the influent concentrations of 1.25 - 3.45 mg/l DEHP and 0.10 - 0.15 mg/l DBP.

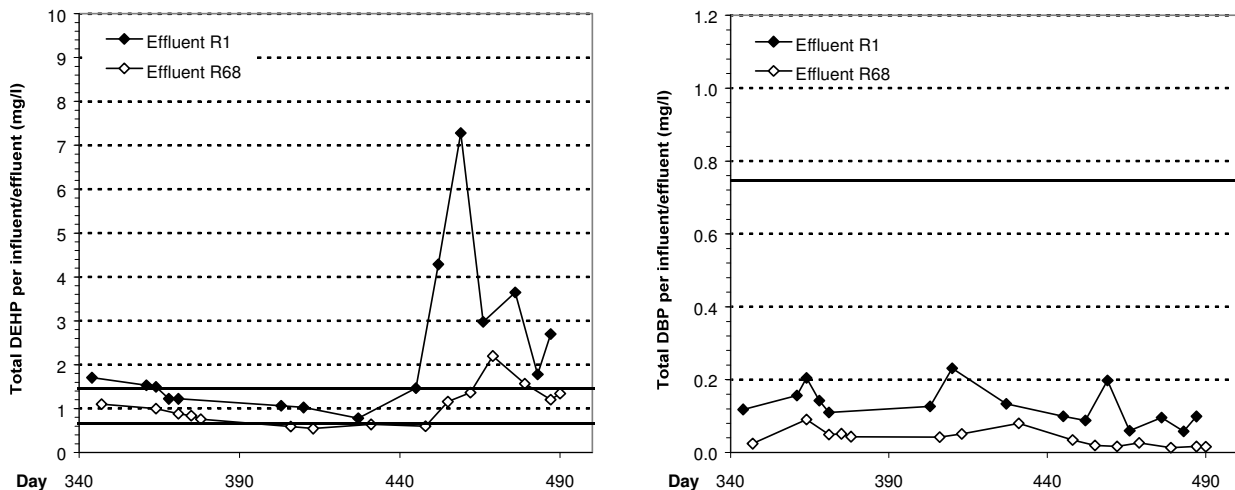


Figure 4: DEHP (left) and DBP (right) in influent and effluent of hyper-thermophilic reactor R68 and threshold concentrations for influent (1.5 mg/l) and effluent (0.75 mg/l) for use as fertilizer

Table 2: Removal rates of DEHP and DBP in thermophilic reactors R1 and R2 and in hyper-thermophilic reactor R68

Period	Reactor	DEHP				DBP			
		Initial conc.		Reduction	$k_h$	Initial conc.		Reduction	$k_h$
		mg (kg-TS) <sup>-1</sup>	mg l <sup>-1</sup>	%	d <sup>-1</sup>	mg (kg-TS) <sup>-1</sup>	mg l <sup>-1</sup>	%	d <sup>-1</sup>
0 - 140	R1	20.6	0.98	n.o.	n.o.	5.02	0.33	49.1	0.0643
141 -	R1	121.7	7.51	n.o.	n.o.	7.24	0.44	45.6	0.0463
339	R2	48.7	3.16	n.o.	n.o.	3.02	0.20	47.8	0.0652
340 -	R1	13.3	0.78	n.o.	n.o.	4.98	0.29	38.4	0.0443
442	R2	16.2	1.06	9.6	0.009	3.12	0.21	69.9	0.1632
	R68	53.1	1.25	33.8	0.107	6.29	0.15	62.2	0.4067
443 -	R1	35.0	1.86	n.o.	n.o.	3.34	0.18	49.1	0.1122
490	R68	163.6	3.45	53.1	0.3207	4.78	0.10	74.0	0.7930

n.o.: not observed

The consistently lower effluent concentrations of both DEHP and DBP after the hyper-thermophilic treatment revealed high-rate removal of both phthalic acid esters during biological anaerobic treatment at 68°C. The benefit of DEHP reduction was, furthermore, proved in the significantly lower DEHP concentration in the influent of R1 when recycling the liquid fraction of the effluent of R68 (figure 2).

Relatively rapid degradation of lower molecular weight phthalates like DBP under anaerobic conditions has been demonstrated before, but the reduction of DEHP in the range of up to 53% during the hydraulic retention time of 5 days in reactor R68 is much faster than in most previous anaerobic degradation experiments where this high degradation efficiency was reached in batch test after duration of 100 days (Staples et al. 1997). Accordingly,  $k_h$  values of the observed DEHP removal are quite high and can be compared to aerobic removal rates (Madsen et al. 1999). Madsen and co-workers (1999) investigated the kinetics of DEHP mineralization mainly under aerobic conditions at temperatures ranging from 5–20 °C and with initial concentrations of 1.6 – 35.1 mg/kg-TS. For sludge amended soil with an initial concentration of 1.6 mg/kg-TS the  $k_h$  value at 20°C was 0.0127 d<sup>-1</sup> in the initial degradation phase. In the temperature range of 5-20 °C the results showed linear correlation between temperature and removal rate ( $k_h$ ). Furthermore, the initial mineralization rate was increasing with higher initial DEHP concentration and  $k_h$  was for an initial concentration of 35.1 mg/kg-TS 10 times higher than at 9.9 mg/kg-TS. Taken into account that in the present hyper-thermophilic treatment the temperature and the initial DEHP concentration were, respectively, 3.5 times and 2–4 times higher than reported by Madsen and co-workers (1999), the removal rates found in the present investigation are in the range of extrapolated aerobic kinetic values at higher temperature and higher initial concentrations. The benefit of high temperature treatment for DEHP reduction was also shown by Banat and co-workers (1999), who demonstrated 70% DEHP reduction within 3 days in aerobic thermophilic treatment of sewage sludge at 68°C (Banat et al. 1999). The present work reveals that this effect can almost be reached also under anaerobic conditions.

The high-rate removal of DEHP observed in the present study indicates that degradation potential under anaerobic conditions can be in the same range as under aerobic conditions. Since the initial phase of biodegradation of phthalic acid esters is expected to be both under aerobic and anaerobic conditions an enzymatic ester hydrolysis to form phthalic acid (Staples et al. 1997), this does not explain why DEHP is less biodegradable than DBP under anaerobic degradation. It can be

speculated that the low degradation of DEHP rather is a result of its low water solubility and thus its lower bioavailability compared to DBP. The present results suggest that bioavailability is significantly enhanced at hyper-thermophilic conditions and at higher concentrations per kg dry matter. They indicate that a higher concentration per kg dry matter is achieved during degradation of organic matter and the bioavailability is enhanced since DEHP adsorbed to solids is released. Therefore, the high degradation of DEHP in the hyper-thermophilic reactor can be suspected to be also a result of the lower TS content of the effluent from the thermophilic reactor R1 that is treated in reactor R68. This means that the high removal rates of DEHP in the investigated reactor system are a result of the combination of thermophilic and hyper-thermophilic treatment. It is likely that no or much lower degradation of DEHP was observed in the thermophilic treatment of R1 and R2 compared to the hyper-thermophilic treatment due to two phenomena: First, the initial concentration of DEHP per kg dry matter was lower in the influent to R1 and R2 than to R68 and, second, the higher extractability of DEHP in the effluent concealed the degradation of DEHP in the thermophilic reactors.

It can be assumed that the observed high rate degradation of highly hydrophobic phthalic acid esters like DEHP is limited down to a certain concentration per kg-TS in the effluent also for higher temperatures. This can be seen in the lowest concentration of the effluent of R1 and R68, which are in the same range of 40 mg/kg-TS. Further degradation below this concentration will be much slower since a certain amount of DEHP will be bound strongly to the particulate matter and will not be available for enzymatic attack.

## CONCLUSIONS

The present study reveals that among organic contaminants found in the organic fraction of municipal solid waste (OFMSW) in Denmark phthalic acid esters and namely di-(2-ethylhexyl)phthalate (DEHP) is the most critical. In conventional anaerobic digesters treating solely OFMSW the concentration per kg-TS will exceed the threshold value for the use as fertilizer on agricultural soil in Denmark if no removal of DEHP occurs. In thermophilic lab-scale reactors treating OFMSW at 15 days hydraulic retention time no significant degradation of DEHP was observed while removal of DBP was between 38% and 70%. Effluent concentration of DEHP was even higher than in the influent due to a higher extractability after degradation of solid organic matter. However, after treatment of the effluent from the thermophilic treatment in a hyper-thermophilic reactor at 5 days hydraulic retention time 34-53% of the DEHP content could be removed and further 62-74% of DBP. High removal rates are obviously due to the high treatment temperature and high degradation of organic matter, which both enhance the bioavailability of DEHP. The results suggest that under anaerobic conditions enzymes are present for the degradation of DEHP as well as for DBP and that it is the low water solubility of DEHP that limits its degradation. DEHP made bioavailable by the treatment is obviously degraded. For treatment of 100% OFMSW the DEHP per kg dry matter will, therefore, be in the same range as in the influent concentration and the combination of a thermophilic and a hyper-thermophilic treatment will comply with the threshold values for use as fertilizer for OFMSW that shows DEHP contents below 50 mg/kg-TS.

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