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Wet oxidation technologies for integrated bioconversion of organic waste

Natte oxidatietechnologieën voor geïntegreerde biologische omzetting van organisch afval

door

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...if Nature had given a scope for things
To be forever broken more and more,
By now the bodies of matter would have been
So far reduced by breakings in old days
That from them nothing could, at season fixed,
Be born, and arrive its prime end of life.

– Lucretius, *Rerum Natura* (50 B.C.)

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LIST OF ABBREVIATIONS

A	ampere
AD	anaerobic digestion
Ah	ampere hour
AOP	advanced oxidation process
AOX	adsorbable organic halogens
AWO	alkaline wet oxidation
BHA	biodegradeerbaar huishoudelijk afval
BMP	biochemical methane potential
B_v	reactor loading rate
BDD	boron-doped diamond
BMW	biodegradable municipal waste
BOD	biological oxygen demand
COD	chemical oxygen demand
CSTR	continuous stirred tank reactor
DHEP	di-ethylhexyl-phtalate
DM	dry mass
DNS	dinitrosalicylic acid
DRANCO	Dry Anaerobic Composting
DSA	dimensionally stable anode
E	cell potential
EAOP	electrochemical advanced oxidation process
EC	European Commission
ECC	enzymatic convertible cellulose
EDTA	ethylenediaminetetraacetic acid
EEA	European Environment Agency
EPA	Environmental Protection Agency
ESA	European Space Agency
EU	European Union
FID	flame ionization detector

FPU	filter paper unit
GC	gas chromatography
HF CVD	hot filament chemical vapour deposition
HMF	hydroxyl methylfurfural
HPLC	high-pressure liquid chromatography
HRT	hydraulic retention time
I	cell current
ICE	instantaneous current efficiencies
IE	inhabitant equivalent
kWh	kilo watt-hour
LAS	linear alkyl benzene sulfonates
LCA	life cycle analysis
LEC	ligand exchange chromatography
LSS	Life Support System
MELiSSA	Micro-Ecological Life Support System Alternative
MS-OFMSW	mechanically sorted organic fraction of municipal solid waste
MSW	municipal solid waste
NTA	nitrotriacetic acid
OFMSW	organic fraction of municipal solid waste
OLR	organic loading rate
PAH	polyaromatic hydrocarbons
ppi	pores per inch
RDF	refused derived fuel
rpm	rounds per minute
RT	retention time
SC-OFMSW	separately collected organic fraction of municipal solid waste
SCP	single cell protein
SEC	specific energy consumption
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SRT	solids retention time
SSF	simultaneous saccharification and fermentation
SS-OFMSW	source-sorted organic fraction of municipal solid waste
TAN	total ammonia nitrogen

TCD	thermal conductivity detector
TIC	total inorganic carbon
TKN	total kjeldahl nitrogen
TOC	total organic carbon
TS	total solids
TVS	total volatile solids
UASB	upflow anaerobic sludge blanket
V	cell voltage
VFA	volatile fatty acids
VFG	vegetable, fruit, garden
VOC	volatile organic compounds
VS	volatile solids
VSS	volatile suspended solids
WO	wet oxidation
XOC	xenobiotic organic compounds

Chapter 1

OUTLINE OF THE THESIS

In this work, the development and demonstration of novel oxidation processes in combination with existing biological treatments (anaerobic digestion and fermentation) was aimed at for the enhanced valorisation of renewable organic waste. This valorisation is situated both at the level of biofuel production from renewable materials as well as the reuse of industrial process waters. The total concept of the dissertation is given in Figure 1.1.

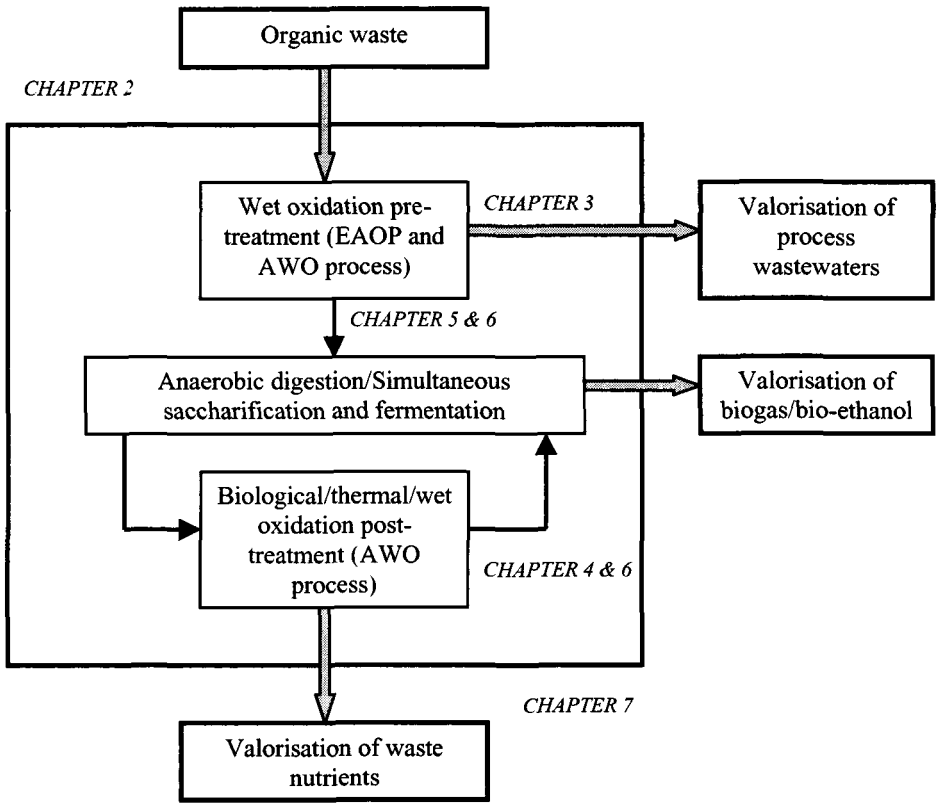

Figure 1.1. Conceptual framework of the thesis

Chapter 2 summarizes all relevant literature with regard to both existing treatment technologies and management options for organic waste with main emphasis on biowaste. Particularly non-biological pretreatments and post-treatments are discussed in the light of the existing biological treatment technologies for solid biowaste.

In a first experimental phase, an electrochemical wet oxidation method based on newly developed boron-doped diamond electrodes (Electrochemical Advanced Oxidation Process or EAOP process, Figure 1.1) was investigated for its ability to partially or completely mineralise biologically recalcitrant organic compounds. The results of this work are given in **Chapter 3**, where the electrochemical degradation of chelating agents (EDTA, NTA) and surfactants (sodium dodecylbenzenesulfonate and hexadecyltrimethyl ammonium chloride) - commonly occurring pollutants in organic waste- is highlighted.

The main theme in **Chapters 4, 5 and 6** was the advanced energy recovery from biowaste under the form of biogas or bio-ethanol (Chapter 5) by employing existing fermentation processes in combination with new thermal treatment methods either under oxidative (Alkaline Wet Oxidation or AWO process, Figure 1.1) (Chapters 5 and 6) or non-oxidative (Chapter 4) conditions.
In **Chapter 5**, the AWO process was investigated as a pre-treatment for the simultaneous saccharification and fermentation of biowaste into ethanol. In **Chapters 4 and 6**, it was hypothesized that the biogas production from biowaste can considerably be increased (> 25% increase) when conventional anaerobic digestion is coupled to advanced thermal treatment methods. The main emphasis here was the enhancement of both the enzymatic and anaerobic biodegradability of the lignocellulose fraction contained in the waste. In Chapter 4, this hypothesis was placed in the context of a life support programm for space applications whereas Chapter 6 aimed at developing a novel integrated process for increased and sustainable biogas recovery from biowaste on earth.

The general discussion in **Chapter 7** focuses in first instance on the technical merits of the work and an estimation of the economical costs involved in the proposed EAOP and AWO process is given. Second, the potential applications of both technologies are discussed in the light of sustainable integrated waste management. Finally, some future perspectives for sustainable organic waste management relative to the Kyoto agreements are proposed with anaerobic digestion as a key technology.

Chapter 2

LITERATURE REVIEW

2.1. INTEGRATED ORGANIC WASTE MANAGEMENT

Organic solid waste is an inevitable product of human society. As far in history as the first living creatures on earth appeared, the earth resources have been exploited by living organisms to support life with the resulting disposal of wastes. The assimilation process or return of organic wastes to nature is fundamental to sustain the elemental cycles of life and largely depends on the amount of land, air and water available per capita or living organism (Tchobanoglous et al., 1993). The increasing population worldwide and the subsequent increased pressure on the natural resources in a technologically-based society have caused an exceedance of the natural assimilative capacity in many places. In this regard, integrated waste management is an essential tool to save the environment for the future generations.

This chapter provides an insight into the principles and practices of integrated waste management applied to organic waste generation. The goals of the various aspects of integrated waste management will be discussed with special emphasis on the need for valorisation of organic waste under the form of energy and materials recycling in European perspective. In a second part, the solid waste sources and their composition are given and the currently applied waste transformation processes into biofuels (biogas and bio-ethanol mainly) are explained. Special attention will be given to existing pre-and post-treatments in addition to anaerobic digestion of organic waste.
To conclude, the current European policy on renewable energy from biomass is clarified.

2.1.1. Definitions

2.1.1.1. Organic waste

The EEA (European Environment Agency) defines *waste* as "materials that are not prime products for the market for which the generator has no further use in terms of his/her own

purposes of production, transformation or consumption, and of which he/she wants to dispose".

Waste can also shortly be defined as "materials with lack of use or value" (White et al., 1995). This definition underlines the most important aspect of dealing with waste, namely the fact that once value is restored to waste, it is no longer "waste". In fact, waste has in many cases a similar (elementar) composition as the useful products from which it is derived but in a less appealing or less safe form (e.g., due to mixing or due to the unknown composition). In this regard, separation of waste is an important processing step to restore the value of waste.

According to the EEA, organic waste is "waste containing carbon compounds". Because of the broadness of the term *organic waste*, *municipal solid waste (MSW)* is more often used which is "solid waste from households, as well as other solid waste which, because of its nature or composition, is similar to solid waste from households". Due to its very heterogenous composition (glass, metal, paper, plastics and organics), the *organic fraction of municipal solid waste (OFMSW)* is then defined as the organic or *biodegradable* fraction of municipal solid waste.

2.1.1.2. Integrated solid waste management

Integrated environmental management is according to the EEA officially defined as "a philosophy that prescribes a code of practice for ensuring that environmental considerations are fully integrated into all stages of the development process in order to achieve a desirable balance between conservation and development". This definition can be applied to *integrated waste management*, which is a waste management practice which integrates all types and sources of solid wastes, is market-oriented, is flexible to meet social, economic and environmental conditions and is applied on a large scale and regional basis (White et al., 1995). This implies that conversion technologies are chosen which restore the value of the waste (*waste valorisation*) by the production of marketable products.

2.1.1.3. Biodegradable waste

"Any waste that is capable of undergoing anaerobic or aerobic decomposition" is defined as biodegradable waste. *Bioconversion* is the microbial transformation and upgrading of various organic wastes to products of high(er) value (Gajdos, 1998).

2.1.1.4. Waste recovery

Under *waste recovery* is understood "the act of regaining energy from waste". Related to but different from *recovery* are the terms *reuse* and *recycling*. Both terms imply the use of a waste product for use as raw material in the same production process. In waste management, *reuse* of waste is however preferred above *recycling* since the former does not require structural changes to the waste product.

2.1.2. Environmental impacts of organic waste

The management and sustainable disposal of solid organic waste is needed for two major reasons: conservation of resources and the prevention of pollution of the environment (White et al., 1995). Today, the conservation of our natural resources is confined in *sustainable development*, defined in the Brundtland Report (WCED, 1987) as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs". This concept meets the overall objectives of integrated waste management, namely to further increase the economic wellfare and well-being of society while, at the same time, reducing resource requirements to a level consistent with the natural carrying capacity of ecosystems (EEA, 2003).

The most important effects of solid waste on the environment can be summarized as follows (Sonesson et al., 2000):

- acidification and eutrophication potential
- climate change and greenhouse effect
- human health and pollution of natural resources

2.1.2.1. Acidification and eutrophication potential

Acidification and eutrophication of soils and groundwaters is a process caused by air photo-oxidants and acidifying pollutants such as NO_x, SO_x and NH_3 which are emitted mainly from agriculture, energy industries and transport and to a lesser extent from the waste sector (Barton and Atwater, 2002 ; EEA, 2003). Contributions of the waste sector are for example flue-gas compounds from waste incineration and landfill emissions. Acidification leads to acid rain, one of the most important environmental concerns in this regard (EEA, 2002a).

Another important environmental concern is the excessive enrichment of water resources with nutrients derived from organic waste (e.g., MSW) or *eutrophication*. This effect partially originates from organic waste landfills due to the high nitrogen loading of leachates (Jokela et al., 2002).

2.1.2.2. Climate change and greenhouse effect

Due to the emissions of greenhouse gases, the global mean temperature on earth has increased by 0.6°C (in Europe even by 1.2°C) over the past 100 years. There is stronger and stronger evidence that the temperature rise over the past 50 years is attributable to human activities and that global warming will continue increasing by 1.4-5.8°C from 1990 to 2100 (EEA, 2003). This change will have large impacts on natural resources and world economy.

The generation and disposal of solid waste contributes to global climate change by the emission of greenhouse gases such as water vapour, CO_2, N_2O and CH_4. However, the most significant man-made greenhouse gas emission contributing to global warming is carbon dioxide (CO_2) that is released into the atmosphere when fossil fuels are burned. Contrary to fossil fuels which have been formed over thousands of generations, biomass or organic waste is *carbon neutral* because the amount of carbon which is released during processing or degradation is equal to the amount of carbon adsorbed during the life time of the biomass (or the raw materials from which the waste is derived) (Figure 2.1). Hence, the relative contribution of organic waste in the release of net CO_2 in the atmosphere is only minor compared to the emissions caused by the use of fossil fuels (Wuebbles and Hayhoe, 2002).

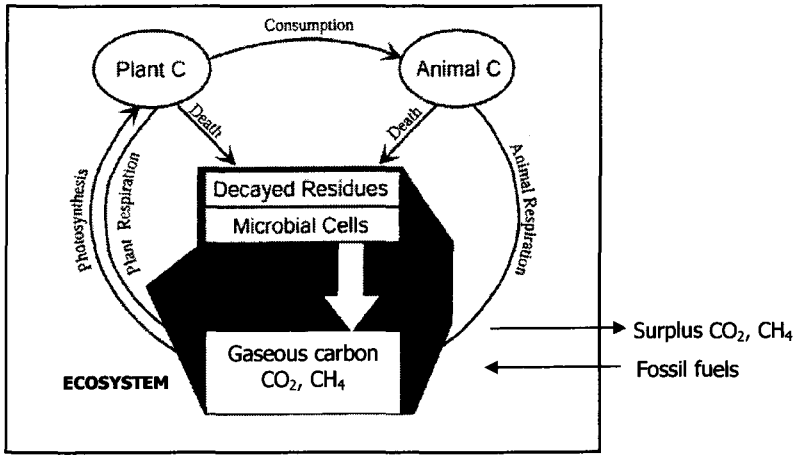

Figure 2.1. The elemental carbon cycle and the relationship with carbonous greenhouse gas emissions

The waste sector contributes with 3-5% to the total greenhouse gas emissions in Europe of which the main source is methane resulting from solid waste disposal on land (EEA, 2003). Methane gas (CH_4) is the most abundant greenhouse gas in the troposphere after water vapour and CO_2. Furthermore, CH_4 is much more effective as a greenhouse gas than CO_2 due to its reactivity with OH radicals leading to other greenhouse and oxidative gases (e.g., CO_2, O_3). Based on current estimates, worldwide human-related biogenic and fossil fuel-related sources for methane are 43.3 tons and 16.2 tons CH_4/I.E.year while total natural sources are around 160 Tg CH_4/year or corresponding to 25.2 tons CH_4/I.E.year (Wuebbles and Hayhoe, 2002). The contribution of organic waste decomposition to the waste-related CH_4 is shown in Figure 2.2.

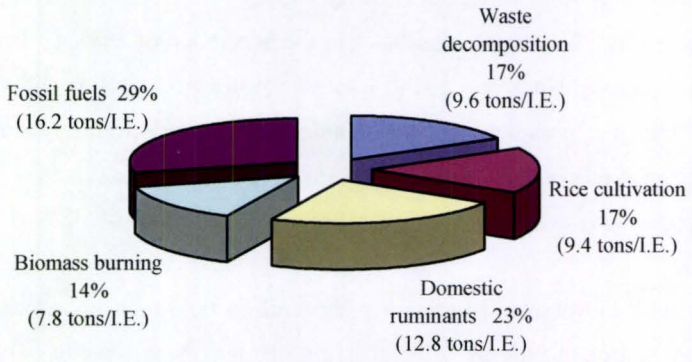

Figure 2.2. Contribution of individual sources to total anthropogenic methane emissions on a yearly basis (Wuebbles and Hayhoe, 2002)

In order to decrease CH_4 and other gaseous emissions to the atmosphere from organic waste generation, sustainable waste processing technologies are needed. It is predicted that methane emissions from the waste sector will decrease much further by increasing the use of methane and energy recovery and the diversion of biodegradable waste from incineration to composting or anaerobic treatment (EEA, 2003). It should however be remarked that waste transformation processes require extra energy and hence use of fossil fuels. It is therefore assumed that the risk of increased CO_2 production is acceptable to defined levels provided that other more powerfull greenhouse gases such as CH_4 can be curbed down (Verstraete, 2002).

2.1.2.3. Human health and pollution of natural resources

The increased urbanization in many parts of the world has resulted in increased waste generation at a small available surface (Moore et al., 2003). Inefficient waste management can place human health at risk because the natural assimilative capacity for pollutants and pathogens associated with the waste is exceeded.

Pollutants present in organic waste affect air, soil and water quality. Numerous examples of dangerous pollutants exist of which heavy metals, dioxines and chlorinated compounds are among the most investigated. Other pollutants which commonly occur in source separated MSW are di-ethylhexyl-phtalate (DHEP), polyaromatic hydrocarbons (PAH) and linear alkyl benzene sulfonates (LAS) (Moeller and Reeh, 2003).

Biodegradable waste is a major contributor to the generation of leachate, landfill gas, odour and other nuisances in landfills. Landfill leachate for instance contains pollutants that can be categorized into four groups (dissolved organic matter, inorganic macrocomponents, heavy metals, and xenobiotic organic compounds). Most recent studies in this field have shown that release of ammonia constitutes one of the major problems related to MSW landfills (Kjeldsen et al., 2002).

Organic waste is known to contain many pathogenic bacteria such as *Salmonella* species and other microorganisms mainly from faecal origin that may pose a health risk for both people and animals. The biosecurity risk associated with the handling and reuse of treated waste as fertiliser can therefore not be neglected (Sahlström, 2003).

2.1.3. Integrated waste management: the holistic approach

A waste management system typically consists of several steps: waste collection and sorting, pre-processing, treatment and final disposal. An integrated system includes waste collection and sorting, followed by one or more treatment options (White et al., 1995):

- recovery of secondary materials or recycling
- biological treatment of organics
- thermal treatment
- landfilling

The sustainable handling and treatment of waste can mostly not be guaranteed by a single treatment but a range of the above treatment options. Hence, several interconnected waste treatment steps are needed which affect each other significantly. It is therefore necessary to consider the whole management system in a holistic way, whereby an overall system that is economically and environmentally sustainable can be reached (Figure 2.3).

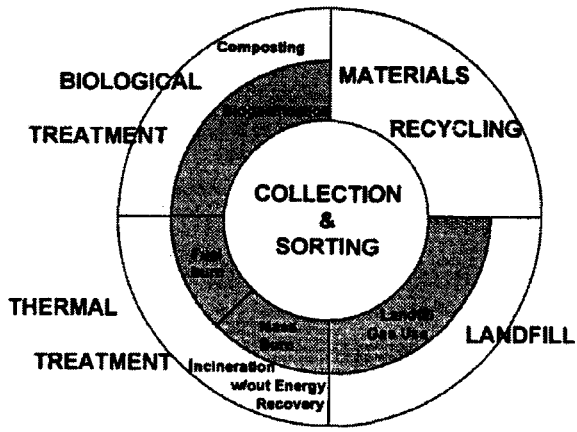

Figure 2.3. The interconnection of an integrated solid waste management system. Shaded area represents waste-to-energy technologies (White et al., 1995)

The global thinking on dealing with waste follows a priority listing of waste management options in decreasing order of priority: waste minimisation, reuse, recycling, energy recovery, incineration and landfilling (White et al., 1995).

Considering organic waste, recycling and energy recovery by biological treatment is considered to be the most promising treatment leading to sustainability. The high amount of plant nutrients and bioenergy (biochemically bound energy) in organic waste can be upgraded in bioconversion systems, whereby plant nutrients can be recycled and bioenergy can be used (Gajdos, 1998).

The cultivation of raw materials for food production, being based on the consumption of fossil fuels, has a great impact on the environment. By recycling organic waste, a considerable amount of fossil-fuel derived energy could be saved and replaced by nutrients and energy derived by direct recycling (Figure 2.4). This way, the elements contained in

organic waste could be efficiently recycled in completely closed local bioconversion systems, thereby decreasing pollution and saving waste materials. The concept shown in Figure 2.4 forms a real challenge since municipal waste is one of the hardest waste sources to manage due to its very heterogenous composition (Gajdos, 1998).

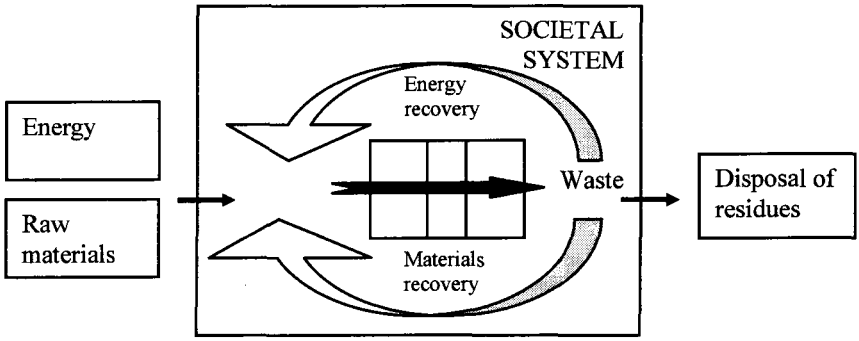

Figure 2.4. Integrated waste management applied to organic waste

2.2. MUNICIPAL SOLID WASTE MANAGEMENT IN EUROPE

2.2.1. General overview

Total waste quantities continue to increase worldwide. In Western Europe, the major waste producing sectors with their relative percentage are: energy production (4%), municipal waste (14%), industrial waste (15%), mining and quarrying (24%), construction and demolition (31%) and not declared waste (2%) (EEA, 2003).

According to recent statistics of the European Environment Agency, about 1.3 billion tons of municipal waste is generated annually within the European Union of which at least 40 million tons are of hazardous nature. This represents a daily municipal solid waste (MSW) production of 400,000 tons in Europe (Mata-Alvarez et al., 2000). Besides, 700 million tons of agricultural wastes are produced yearly within the EU. Another troublesome waste stream is thickened municipal sewage sludge, of which yearly 9.4 million tons dry matter are to be disposed of by 2005. Finally, grey waste or residual refuse make up a relatively new waste stream for AD and encompasses all waste fractions that remain after source separation (e.g.,

sludge and fibers). These fractions are currently mostly landfilled or incinerated. All these abundantly produced waste streams represent a challenge for sustainable and cost-effective disposal.

2.2.2. Municipal solid waste management in European perspective

Municipal solid waste production in Europe is large and still continues to increase. In 2000, estimations showed that on average 550 kg/capita was produced in Western Europe which corresponds to 14% of the total waste production in the EU. More than 306 million tonnes are estimated to be collected each year, or an average of 415 kg/capita over the whole of Europe. From the collected MSW, about 44% is landfilled, 30% is incinerated with energy recovery and the remaining 26% is recovered (EEA, 2002b).

From the total MSW production in the year 2000, about 107 million tons or 330 kg/capita of biodegradable waste were generated in the EU and Norway. It is expected that the organic waste production in Europe will continue to increase with 10% every 5 years.
Most European countries and regions still employ traditional "bagged mixed waste" collection whereas only a limited number of countries separately collect OFMSW. In fact, only in Belgium (Flanders), Austria, the Netherlands, Denmark and Norway, more than 30% of the biodegradable fraction of MSW is separately collected and treated (EEA, 2001). In these countries, the separately collected OFMSW is currently treated by incineration, composting or recycling.

The majority (66%) of OFMSW in Europe is still being landfilled. Other employed management routes for OFMSW are incineration without or with energy recovery, central composting, recycling, anaerobic digestion and mechanical-biological pretreatment. Despite the increasing amount of MSW that is recycled in the EU (11% during 1985-90 up to 29% in 2000), plenty of recycling and recovery opportunities still exist in almost all European countries (EEA, 2003). As a result, the creation of market opportunities and increased public acceptance of biodegradable MSW is expected to increase dramatically in the near-future.

2.2.3. European landfill directive targets for biodegradable municipal solid waste

To decrease the quantities of biodegradable municipal waste (BMW) going to landfill, a new European Directive has been defined (1999/31/EC) which obliges the member states to challenge increased recycling of organic municipal waste. The Directive states that based on the BMW produced in 1995, the BMW going to landfill must be reduced to 75% by 2006, to 50% by 2009 and to 35% by 2016 (EEA, 2001a). Today, most countries still send the majority of their BMW to landfill and thus have a long way to go to reach the targets. Only Denmark, Austria and the Netherlands have constituted sufficient landfill diversion capacity to the point that the targets set by the Directive have been met.

Importantly, the chosen treatment options as an alternative to landfilling of BMW largely depend on the way in which the waste is collected. Table 2.1 summarizes the alternative treatments of BMW for different waste sources as recommended by the EEA (EEA, 2001a).

Table 2.1. Alternative treatment options for diverting biodegradable MSW away from landfill (EEA, 2001a)

Waste stream	Incineration	Gasification	Pyrolysis	Central composting for mass reduction	Composting	Anaerobic digestion	Recycling	Re-use	Manual or mechanical sorting
Bagged mixed waste	√			√		√			√
Refuse Derived Fuel (RDF)	√	√	√						
Food and garden					√	√			
Food					√	√		√	
Garden					√	√			
Paper	√	√	√		√	√	√		
Textiles	√	√	√				√	√	
Wood	√	√	√				√	√	

It can be deducted from Table 2.1 that the amount of alternative treatments with high recycling potential is mostly larger for separately collected waste streams. However, in the light of integrated waste management, the final decision on the most appropriate treatment technology does not only depend on the collection technology and its environmental impact but also on the availability of the markets for the recovered materials.

2.3 MUNICIPAL SOLID WASTE SOURCES AND CHARACTERISTICS

2.3.1. Composition and properties of municipal solid waste

2.3.1.1. Main waste fractions of municipal solid waste

Municipal solid waste composition is largely variable from country to country due to inherent differences in collection and sorting procedures. The main components of MSW are: paper, paperboard and paper products, plastics, glass, metals, food and garden waste and other undefined sources. Overall, packaging waste represents about 1/3 of the MSW content in the EU, with paper and cardboard (63 kg/capita) being the largest fraction followed by glass (35 kg/capita), plastics (29 kg/capita) and metals (9 kg/capita). The other 2/3 of the MSW amount generated in the EU consitutes the biodegradable fraction, with an average production of 160-560 kg/capita per year (EEA, 1999).

2.3.1.2. Physicochemical characteristics of the organic fraction of municipal solid waste

The composition of OFMSW is highly dependent on the collection and separation procedure. Cecchi et al. (2003) reviewed the literature on the composition of three OFMSW sources: mechanically sorted from unsorted municipal waste (MS-OFMSW), separately collected OFMSW (SC-OFMSW) (e.g., food waste from markets, canteens...) and domestic source-sorted OFMSW (SS-OFMSW). The average physicochemical characteristics of the three waste streams are compared in Table 2.2.

Mechanically sorted OFMSW

Due to the mixed waste collection approach in the past, mechanical sorting technology was predominantly used the past 20 years to separate the organic fraction and a highly calorific RDF fraction (Refuse Derived Fuel) from MSW streams. As can be expected, the MS-OFMSW characteristics largely depend on the sorting plant. Overall, the MS-OFMSW still

contains 33% of inerts and 1.8% of plastics on TS basis. The readily biodegradable fraction or putrescible fraction has been reported to be only 59% on TS basis (Cecchi et al., 2003).

Due to the incomplete separation of OFMSW from inert materials, the total solids content (TS) of MS-OFMSW is much higher while the TVS content is much lower (< 50% of TS) compared to OFMSW from other sources (Table 2.2). This results in a comparatively lower anaerobic biodegradability of MS-OFMSW (on average 0.3-0.38 m^3 CH_4/kg of TVS) compared to separately collected OFMSW (0.4-0.5 m^3 CH_4/kg TVS) (Cecchi et al., 2003).

Table 2.2. Physicochemical characteristics of MS-OFMSW, SC-OFMSW and SS-OFMSW (Cecchi et al., 2003)

Parameter*	MS-OFMSW	SC-OFMSW[a]	SC-OFMSW[b]	SS-OFMSW
TS (g/kg)	763.0	256	81.8	200
TVS (%TS)	43.9	96.5	81.9	88
TCOD (TS)	596	307	81.8	220
TOC (%TS)	19.3	-	-	-
IC (%TS)	1.3	-	-	-
TKN (%TS)	2.2	3.2	2.1	3.2
P (%TS)	0.11	0.2	2.8	0.4

*TS = total solids; TVS = total volatile solids; TCOD = total chemical oxygen demand; TOC = total organic carbon; IC = inorganic carbon; TKN = total Kjeldahl nitrogen; P = total phosphorus.
[a] SC-OFMSW food waste, [b] SC-OFMSW fruit and vegetable waste

Separately sorted OFMSW

The typical total solids content of separately sorted OFMSW is in the range of 15-25% while the total volatile solids content varies from 70-90% on TS basis (Table 2.2).

The nutrient content of mechanically sorted OFMSW and separately collected OFMSW is relatively similar and varies from 2.5-3.5% TS for total nitrogen and 0.5-1% TS for total phosphorous (Cecchi et al., 2003). The average production of at least 280 kg of OFMSW per European citizen per year then corresponds to a nutrient content of 1.5-4 kg of nitrogen, 1-2.5 kg of potassium and 0.2-0.5 kg of phosphorous (Gajdos, 1998).

2.3.1.3. Microbiological aspects of the organic fraction of municipal solid waste

The biosafety risks associated with biowaste (municipal waste and animal waste) should be carefully considered in case the recycling of the treated residue is envisaged. Since raw organic waste contains considerable numbers of (opportune) pathogenic bacteria, the ability

of the waste treatment technology to reduce the pathogenic bacteria to acceptable levels is of major importance (Sahlström, 2003).

Pathogenic bacteria in biowaste originate from both infected sources (e.g., diseased people) but also from the excreta (faeces, urine and exudates) of healthy organisms. The most important pathogenic organisms present in solid organic waste are enteric pathogens derived from soil and excreta from living organisms (Santamaria and Toranzos, 2003). They are summarized in Table 2.3.

Table 2.3. Concentration range and infectious dose of pathogenic agents potentially present in raw organic municipal waste (adapted from Sahlström, 2003 ; Santamaria and Toranzos, 2003 ; Hassen et al., 2001 ; Gaspard and Schwartzbrod, 2003)

Agent	Concentration (number/g waste dry weight	Infectious dose	Disease
Bacteria	10^7-10^8		
Salmonella spp.		10^4-10^7	Salmonellosis
Listeria monocytogenes		unknown	Listeriosis
E. coli		10^6-10^{10}	Gastro-enteritis
Shigella		10-200	Dysentery
Mycobacterium paratuberculosis		unknown	Crohn's disease
Vibrio cholerae		10^3-10^7	Cholera
Campylobacter jejuni		400-500	Campylobacteriosis
Staphylococcus aureus		1-10^{10}	Toxic infections
Clostridium spp.		1-10^{10}	Perfringens
Yersinia enterolitica		10^6	Gastro-enteritis
Enteric viruses	10-10^3	1-10	
Yeasts and fungi	10^6-10^7	unknown	Pneumonia
Protozoa	10^2-10^4		
Entamoeba histolytica		20	Amebiasis
Giardia intestinalis		< 10	Giardiasis
Cryptosporidium parvum		1-10	Cryptosporidiosis
Helminths			
Ascaris lumbricoides	up to 1.3 eggs	1-10	Ascariasis

Viruses are the most hazardous infectious agents and have some of the lowest infectious doses of any of the enteric pathogens. Examples are hepatitis A, hepatitis E, enteric adenoviruses, pollovirus types 1 and 2, multiple strains of echoviruses and coxsackievirus (Santamaria and Toranzos, 2003). Other hazardous agents are spore-forming bacteria such as *Clostridium*

perfringens, which have been reported to survive mesophilic anaerobic digestion and subsequent storage of the residue (Bujoczek et al., 2002). Finally, ascaris eggs have been reported to be one of the most persistent pathogens and can hence be used as a hygienic indicator of treated excreta (Gaspard and Schwartzbrod, 2003). As a result, the biosafety of compost from digested MSW cannot be guaranteed for reuse purposes if no other post-treatments are considered.

Another emerging biosafety issue on biowaste concerns the risks associated with BSE (Bovine Spongiform Encephalopathy) contaminants related to category 1 waste materials. Due to the very persistent character of BSE infected material, a new EU Directive 1774/2002 has been implemented since May 2003 which defines the criteria of an alkaline hydrolysis treatment. Only after this treatment, recycling of the potentially infected material is possible (European Commission Regulation, 2003).

2.3.1.4. Lignocellulose composition and biodegradability of municipal solid waste

Lignocellulose is a collective term for the main building blocks of plant material. It consists of three major biopolymers, namely cellulose, hemicellulose and lignin (Figure 2.5).

Due to its abundance in nature and its use in many daily life products (e.g., paper), lignocellulose forms the main matrix of municipal solid waste. On average, MSW contains 40-50% cellulose, 5-20% hemicellulose and 10-27% lignin by dry weight (Chynoweth and Pullammanappallil, 1996). The main sources of lignocellulose in MSW are paper, paperboard, yard waste and food waste. Theoretically, cellulose and hemicellulose make up over 90% of the biochemical energy (or roughly corresponding to 90% of the TVS content) contained in MSW. Other constituents that are determining for the biochemical energy content of MSW are lipids (0-7%), proteins (3-10%), pectins (< 4%), starch (0.5-1%) and other soluble sugars (< 1%) (Chynoweth and Pullammanappallil, 1996).

The biodegradability of lignocellulose is the major factor determining the biodegradability of MSW and thus crucial for the amount of energy that can be gained from it. While pure cellulose and hemicellulose can be easily biologically converted and the energy recovered, their bioavailability in lignocellulose is generally low due to the architectural design of the lignocellulose matrix. The rate and extent of utilization of the embedded polysaccharides present in lignocellulose is severely limited due to the intense cross-linking of cellulose with hemicellulose and lignin (Lynd et al., 2002). The cell walls of plants consist of cellulose

microfibrils embedded in a layer of hemicellulose and lignin defined as the *middle lamella*. Individual cells are glued together by a 1-2 micron thick layer of lignin that also serves as a barrier to microbial and enzymatic attack on the carbohydrate portion of the cell wall. Moreover, the crystalline structure of cellulose also largely prevents penetration by enzymes or microorganisms and even by small molecules such as water (Lynd et al., 2002).

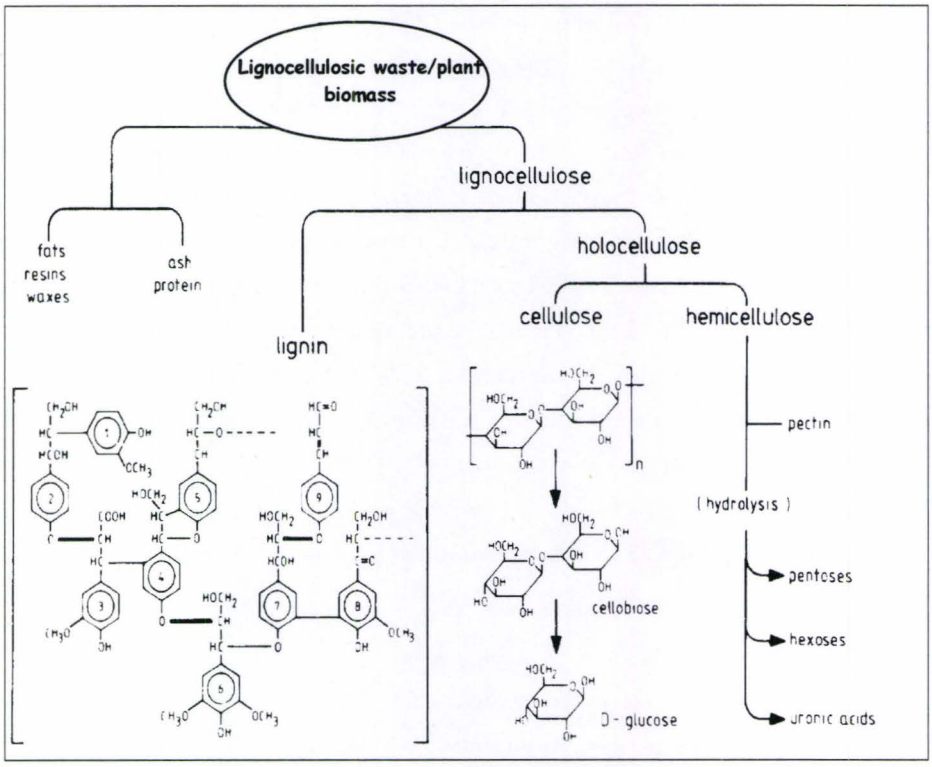

Figure 2.5. Composition of lignocellulose, the principal building block of municipal solid waste

While cellulose is a homogenous linear high molecular weight polymer (10,000 units on average) of β-1,4 linked glucose, hemicellulose is much shorter (< 200 units) and has a much more heterogenous nature which is represented in the different sugars, side-branches and substituted sugars. Bacterial hydrolases degrade cellulose to yield a soluble disaccharide called cellobiose which on further hydrolysis results in D-glucose (Figure 2.5). Cellulose hydrolyzing-enzymes from different microbial species have been isolated and investigated.

The most abundant sugars in hemicellulose are the xylan chains of β-1,4 linked xylose units. Depending on the kind of biomass, the xylan chains can be acetylated (e.g., up to 70% of the

xylans in wood). Beside acetylation, the xylan is substituted with different side-groups of which arabinose- and glucuronic derivatives are the most important (Bjerre et al., 1996). The hemicellulose fraction also contains pectines, which are dominantly present in young plant tissues. *Clostridia* species have been described to be the most important cellulose and hemicellulose degrading organisms in bioconversion processes. Despite its branched structure, hemicellulose is more rapidly degraded than cellulose in anaerobic bioconversion processes (Chynoweth and Pullammanappallil, 1996).

Lignin is considered to be a 3-dimensional network of phenolic compounds mainly based on three aromatic alcohols, namely coniferyl, sinapyl and p-coumaryl alcohol. Lignin is attached to cellulose and hemicellulose by mainly ether linkages with the hydroxyl groups of the cellulose and hemicellulose polysaccharides. Because lignin does not consist of repeating monomeric units, this lignocellulose fraction is the most heterogenous and most difficult to characterize (Dorrestijn et al., 2000). Though anaerobic bacteria are capable of degrading the monomeric units that make up the lignin molecule, it is assumed that lignin depolymerization (or degradation) under anaerobic conditions in digesters is low or even non-existing (Chynoweth and Pullammanappallil, 1996). Lignin can only be degraded by fungi and is therefore limited to aerobic conditions (Sanders et al., 2003).

2.3.2. Sources, properties and biodegradability of hazardous components in municipal waste

2.3.2.1. Heavy metal recycling and chelating agents

Heavy metals are one of the major environmental concerns with regard to the reuse and recycling of treated muncipal solid waste under the form of compost. The frequent application of compost to soil systems is of great concern because it can lead to accumulation of heavy metals in the soil and hence cause harmfull effects to humans and the environment (Veeken and Hamelers, 2002).

Heavy metals in organic municipal waste are derived from a variety of sources such as food products, plant material and soil organic matter (Veeken and Hamelers, 2002) but also from xenobiotics such as detergents and plastics. Due to the relative loss of organic material during most waste treatment technologies (e.g., composting or incineration), the heavy metal content of the waste is enriched for certain metals (e.g., Zn, Cd and Pb). This often leads to an exceedance of the legal metal concentrations in the end-product (e.g., compost and fly ashes) (Veeken and Hamelers, 2002 ; Hong et al., 2000 ; Zorpas et al., 2000).

Efforts for the recycling of heavy metals present in municipal solid waste are only minor sofar due to the fact that source separation of MSW is still uncomplete. Moreover, the heavy metal content of MSW is rather low (as low as 1 mg to few grams/kg of dry solids waste) compared to industrial waste streams and hence too diluted to recover metals in a cost-effective way for most metal recovery technologies (EU report, 2002).

Generally, if heavy metal recovery from MSW is envisaged, heavy metals are extracted from the waste by leaching and electrokinetic technologies. Organic and inorganic acids, bases, chelating agents and tensio-active agents (surfactants) are usually used to leach out the metals. Several researchers found that EDTA (ethylenediaminetetraacetic acid) (Figure 2.6) has the greatest potential for heavy metal recovery from soils and solid waste due to its stability and superior chelating properties (reviewed by Korolewicz et al., 2001). Hence, EDTA or other chelating agents are often used to lower the heavy metal content of both compost and fly ashes to make them suitable for recycling or to meet the guidelines for landfilling (Hong et al., 2000). Electrokinetic methods are based on the solubilization of metals by EDTA and the subsequent recovery of the metals at an anode (Korolewicz et al., 2001).

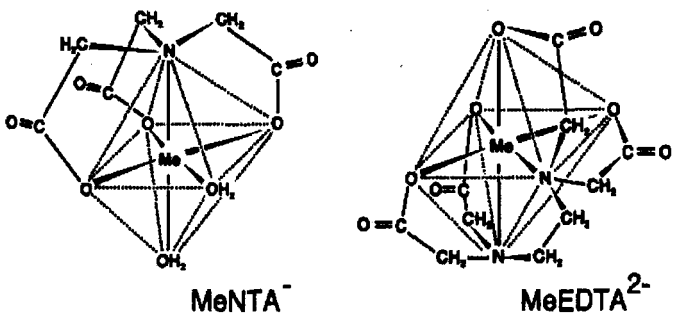

Figure 2.6. Ideal octahedral structure of metal-NTA and metal-EDTA complexes (Bucheli-Witschel and Egli, 2001)

Besides its use in soil and solid waste remediation, chelating agents are widely used in household and industrial applications where concentrations of metal ions have to be controlled or undesirable metal contaminants have to be inactivated (e.g., in detergents) (Henneken et al., 1995 ; Bucheli-Witschel and Egli, 2001). The annual EDTA consumption in Western-Europe alone was about 32,550 tonnes in 1997 and is expected to further increase

worldwide (Nörtemann, 1999). Besides its use in pharmaceuticals, detergents and food conservatives, the main consuming sectors of EDTA are the paper and pulping industry, textile and photography industry, electro-plating processes and nuclear industry (Bucheli-Witschel and Eggli, 2001 ; Eklund et al., 2002).

The main drawback of chelating agents such as EDTA is its limited biodegradability. EDTA has been reported to be the organic compound occuring at the highest concentrations (up to 2.5 g/L in wastewater effluent) in many surface waters, thereby leading to eutrophication and disturbing the natural metal cycles (Bucheli-Witschel and Egli, 2001). Although a number of recent studies showed that biodegradation of EDTA in wastewater treatment plants is possible, the reaction conditions need to be well-defined such as a long sludge retention time and a pH > 7. Furthermore, the initital cleavages of EDTA are considered to be the rate-limiting step in biological EDTA breakdown (Sillanpää and Pirkanniemi, 2001; Nörtemann, 1999). As a result, EDTA is a recalcitrant compound that is normally not removed by conventional biological or physicochemical treatment technologies used in municipal waste treatment (Henneken et al., 1995).

2.3.2.2. Other organic pollutants in municipal organic waste

Other important hazardous compounds in municipal organic waste are DEHP (di-ethylhexyl-phthalate) and polyaromatic hydrocarbons (PAH) derived from plastics and linear alkylbenzene sulfonates (LAS) derived from detergents (Hartmann and Ahring, 2003 ; Moeller rand Reeh, 2003).

LAS are the most widely used (anionic) surfactants worldwide and have many domestic and industrial applications with an estimated consumption of 2 million tonnes per year worldwide (Jensen, 1999). Their basic structure is depicted in Figure 2.7.

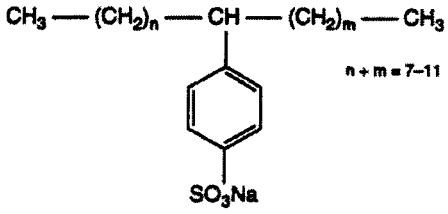

Figure 2.7. Structure of linear alkylbenzene sulphonate (LAS)

LAS tend to easily adsorb onto organic matter (e.g., MSW) and to primary sludge in wastewater treatment plants. As a result, LAS concentrations in solid wastes from surfactant rich wastewater tend to be high (up to 30-35% of the LAS present in sewage) (Jensen, 1999). Although LAS in MSW can be significantly degraded during oxidative aerobic conditions (e.g., during composting and subsequent land application), their biodegradation during anaerobic treatment is mostly limited or they even show inhibitory effects towards the degrading bacteria (reviewed by Jensen, 1999). Gavala and Ahring (2002) and Mensah and Forster (2003) showed that LAS present in primary sludge from municipal wastewater exhibited inhibition to anaerobic digestion of the sludge. It was proposed that the biomass specific LAS concentration of 14 mg LAS/g TVS should not be exceeded in the anaerobic digestion of primary sludge (Gavala and Ahring, 2002).
Despite the high concentrations of LAS in compost and primary sewage sludge, the rapid biological aerobic degradation of LAS (1-3 weeks) will most likely prevent that LAS will pose a threat to terrestrial ecosystems on a long term basis (Jensen, 1999). The threat rather comes from the toxicity the LAS exhibit towards methanogens in the anaerobic digestion of solid wastes (Gavala and Ahring, 2002).

2.4. CURRENT TECHNOLOGIES FOR MSW TREATMENT

2.4.1. Composting and anaerobic digestion of municipal solid waste

Composting is the controlled aerobic biological degradation of organic material to stabilise organic waste and to convert it into humus-like material for fertilizer purposes. Apart from this, a significant mass reduction (~50%) of the waste is provided (EEA, 2001b). During composting, the temperature in the piled waste becomes thermophilic (55-75°C) within a few days which provides a sanitation effect for most pathogens and weed seeds.
In practice, composting can be carried out *without* or *with* forced aeration for a period of 3-18 months. Furthermore, composting is subdivided in *static* and *agitated* composting, whereby in the latter case the compost is turned weekly or monthly.

Composting can be applied as sole treatment or as post-treatment to anaerobic digestion. Sofar, industrial anaerobic digestion facilities for the treatment of biodegradable municipal waste have mainly relied upon a short-term anaerobic digestion phase (typically 15-20 days),

followed by composting of the remaining non-digested solids (Verstraete et al., 2000; De Baere, 2000; Lissens et al., 2001; Van Lier et al., 2001). Hence, mostly one or more (aerobic) post-treatments are necessary to obtain a high-quality digestion product that can be reused for agricultural purposes (Mata-Alvarez et al., 2000).

Composting bears the advantage that the digested residue mostly has a very slow biological turnover, given adequate soil conditions (Mata-Alvarez et al., 2000). This way, the soil can function as a sink of highly sequestered carbon. However, despite its suitability as an option to divert MSW away from landfills, composting has several drawbacks. One of them constitutes the fact that the post-composting step counteracts the advantages of AD in a way that composting is a net energy consumer that moreover results in high emission of VOC (volatile organic compounds), high nutrient losses (20-40% of nitrogen as ammonia) and carbon dioxide release. Moreover, the lack of quality of the compost often hinders the application of compost for fertilizer purposes (EEA, 2001b). Edelmann et al. (2001) showed that, based on LCA (Life Cycle Analysis) tools applied to biowaste treatment, AD has the advantage over composting, incineration or combination of digestion and composting because of the much better energy balance of AD. The overall energy and product yields of AD and composting are illustrated in Figure 2.8. Due to the high capital costs, AD is however still a factor 1.2-1.5 more expensive than composting, one of the main reasons for the common practice of composting.

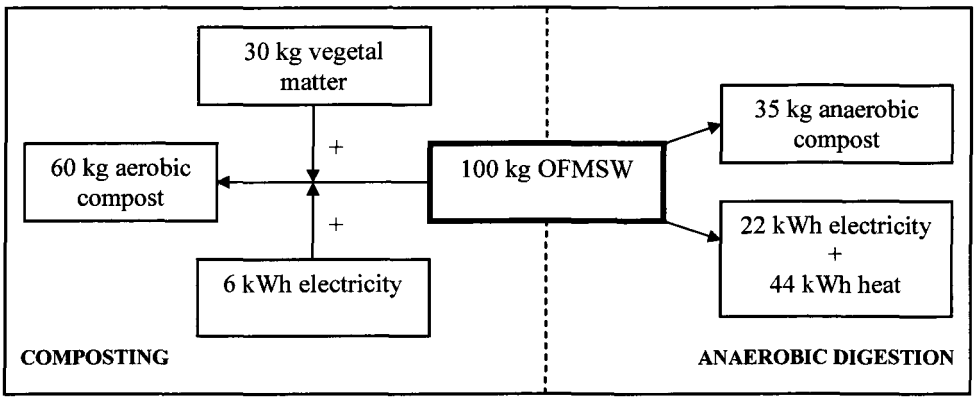

Figure 2.8. Product and energy yields of composting versus anaerobic digestion in OFMSW treatment (Mata-Alvarez, 2003a)

2.4.2. Thermal treatment methods and landfilling

2.4.2.1. Thermal treatment methods

The most known thermal treatment methods for MSW are *incineration*, *gasification* and *pyrolysis*.

Incineration of MSW proceeds in a furnace at a temperature of at least 850°C, thereby reducing the MSW to about 2-5% of its original weight. Obviously, besides the generation of flue gas, fly ashes are produced which have to be deposited by landfilling. Both waste streams contain pollutants (toxic air emissions and heavy metals, respectively) and hence have to be treated before ultimate disposal. Although energy can be efficiently recovered (~85% of the heat) during incineration, neither nutrients nor organic matter are recovered since incineration aims at a total destruction and sanitation of the waste. Other disadvantages of the process are the extensive capital costs (EEA, 2001b).

As indicated in Table 2.1, thermal treatments are generally not applied to the biodegradable fraction of MSW but preferably to the high-calorific components of MSW (e.g., wood, plastics). This is due to the high moisture content (e.g., 5-35% dry matter) of biodegradable waste in general and their concomitantly relative low energy content, leading to low incineration efficiency and higher emissions. Therefore, incineration of OFMSW requires extensive energy-input prior to incineration and the energy yield is low.

Pyrolysis and *gasification* are *refined* incineration processes and have in common that they transform the waste into a gas as energy carrier for the powering of boilers or gas engines. Pyrolysis involves the thermochemical conversion of the waste into hydrocarbons (gas and oil) and solid char (carbon residue) in the absence of air at temperatures between 500-700°C and a retention time of 0.5-1 h. In gasification, temperatures of 800-1100°C are applied whereby also the carboneous fraction is gasified to a syngas by carefully controlling the amount of oxygen present. Similar to incineration, in both processes nutrients and organic matter are not recovered, high capital costs are involved and only pre-dried waste streams (in absence of oxygen) can be treated (e.g., wood chips). Another main drawback is the formation of carcinogenic and toxic compounds in the oil, gas and char fractions (EEA, 2001b).

2.4.2.2. Landfilling

Landfilling is the deposition of waste for long-term storage of inert materials along with the relatively uncontrolled decomposition of biodegradable waste. The main advantage of

landfilling is that it can deal with all solid waste materials. The three essential outputs of a landfill are landfill gas, leachate and (inert) solid waste. Although methane formed during the (anaerobic) degradation of the waste can be partially recovered, in a number of studies landfills have been shown to be the least sustainable disposal method for biodegradable municipal solid waste (Ni et al., 2002 ; Mendes et al., 2003).

2.5. ANAEROBIC BIOCONVERSION TECHNOLOGIES FOR RECYCLING AND ENERGY RECOVERY FROM MUNICIPAL WASTE

2.5.1. Anaerobic digestion key principles

2.5.1.1. Fundamentals of anaerobic digestion

Biodegradation pathways

Anaerobic digestion (AD) is a biological process in which organic matter (either in liquid or solid phase) is decomposed by a syntrophic association of bacteria in the absence of oxygen. The main products formed during AD are methane gas (~65%) and carbon dioxide (~35%), the main constituents of biogas. Although AD as a treatment for waste was known already in the 19th century, significant progress in anaerobic digestion as an energy recovery method from waste only started since the 1970's, stimulated by the energy crises in that period (Mata-Alvarez, 2003b). Since then AD has become a mature technology for the treatment of a whole variety of domestic, agricultural and industrial wastes such as manure, wastewaters, sludge, etc.

Generally, the amount of organic matter present in the waste expressed as COD (Chemical Oxygen Demand) converted into biogas lies in between 50 and 75% for full-scale digesters while only a few percent of the organic matter is used for the growth of new biomass (Verstraete et al., 1996). Figure 2.9 shows the conversion pathway of particulate organic material during anaerobic digestion into eventually methane (and carbon dioxide).

Hydrolysis of complex polymers (mainly lignocellulose, proteins and lipids) by hydrolytic organisms is the first and one of the most important steps in the bioconversion of organic waste. Despite the hydrolytic capabilities of many anaerobic bacteria by secretion of exocellular enzymes or attachment of the concerned bacteria to the solid substrate, this step is considered to be most rate-limiting for the digestion of solid waste and is mostly also yield-

limiting in AD (Mata-Alvarez et al., 2000). This is particularly true for lignocellulosic substrate due to its inherent rigid structure. As a result, the hydrolysis of organic waste and hence the bioconversion into methane is mostly incomplete at normal retention times (15-20 days) in anaerobic digesters (Sanders et al., 2000).

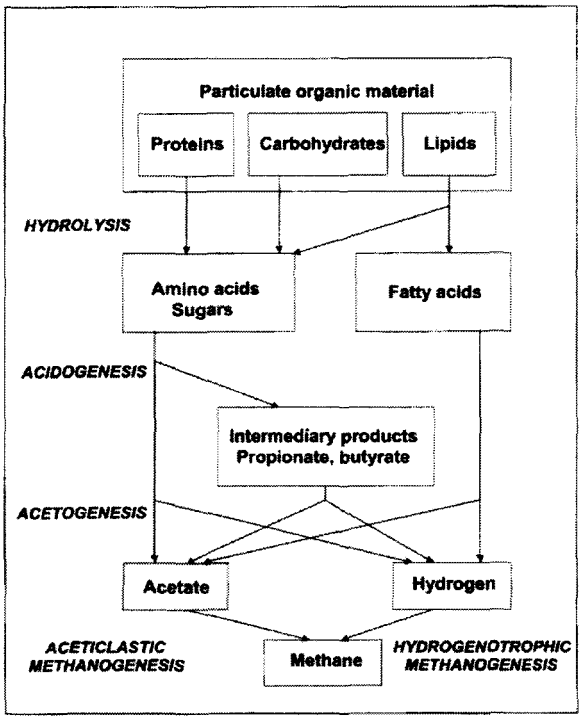

Figure 2.9. Overview of the biodegradation steps of complex organic matter in anaerobic digestion (Mata-Alvarez, 2003a)

The subsequent step in AD is the fermentation of monomeric soluble organic substances (e.g., sugars) into volatile fatty acids (VFA), acetate, hydrogen and carbon dioxide (Figure 2.9). Besides, ammonia and amines are produced as a hydrolysis product from proteins. This step is one of the fastest conversion steps in AD. The long chain fatty acids (LCFA) and VFA produced are subsequently converted by the obligate hydrogen producing acetogens (OHPA) into three sole products, namely acetate, carbon dioxide and hydrogen. The final step then consists of the conversion of acetate and hydrogen gas into methane gas by acetoclastic and hydrogenotrophic methanogens (Garcia-Heras, 2003). Syntrophic interactions of acetate-, H_2-,

and formate-producing bacteria with methane-producing archaea are known to be one of the most thermodynamically difficult reactions in anaerobic bioconversion of organic matter. Hence, this symbiotic interaction, which is absolutely required to sustain the thermodynamically unfavourable reactions of the syntrophs, is another important rate-limiting step in the process and its balance is decisive for the stability of the reactor (Verstraete et al., 1996). Most of the methane (~70% of the total production) is generated by the methanogenic acetoclastic bacteria (AMB) such as *Methanosarcina* and *Methanothrix* (Mata-Alvarez et al., 2003a).

Hydrolysis kinetics in anaerobic digestion

The rate of conversion of solid organic waste into methane and carbon dioxide largely depends on the rate of depolymerization (Chynoweth and Pullammanappallil, 1996).

Several researchers calculated the first order hydrolysis constants (k values) of several waste components (reviewed by Mata-Alvarez et al., 2000) (Table 2.4). It should be remarked that the carbohydrate fraction needs to be separated in glucose, starch and cellulose, of which the hydrolysis constants can vary with a factor of 8 (Table 2.4).

Apart from the reactor configuration, the hydrolysis rate of solid organic waste mainly depends on intrinsic process parameters such as the digestion temperature, pH and hydraulic retention time (HRT). Since an increase of the hydrolysis rate generally results in increase in biodegradability, it has been suggested that the rate of hydrolysis of particulate matter is determined by the adsorption of hydrolytic enzymes to the biodegradable surfaces (Mata-Alvarez et al., 2000).

Table 2.4. First order kinetic constant values for hydrolysis of different biowaste materials (after Mata-Alvarez et al., 2000)

Component	Hydrolysis constants
	k values (d^{-1})
Lipids	0.005-0.010
Proteins	0.015-0.075
Carbohydrates	0.025-0.200
Food wastes	0.4
Solid wastes	0.012pH – 0.042
Biowaste components	0.03-0.15 (20°C), 0.24-0.47 (40°C)

2.5.1.2. Operational and stability parameters in the control of anaerobic digesters

The most important operational parameters in AD are the hydraulic retention time (HRT) in [days], the solids retention time (SRT) in [days], the organic loading rate (OLR) in [kg substrate/m^3.day], the specific gas production or biogas yield (SGP) in [m^3 biogas/kg substrate], the gas production rate (GPR) in [m^3 biogas/kg substrate.day] and the substrate removal efficiency in [% TVS removed]. These parameters largely influence the performance of the digester in terms of biogas yield and reactor stability.

The HRT is related to the reactor volume (V) and the feed flow rate (Q). Furthermore, the reactor volume is also related to the OLR as summarized by equation 2.1:

$$OLR = \frac{Q.S_0}{V} = \frac{S_0}{HRT} \tag{2.1}$$

In practice, the biogas yield and hence the substrate removal efficiency of a substrate will increase with increasing HRT untill a maximum biogas yield is reached (*ultimate biogas potential*). The unconverted organic fraction in the effluent then corresponds to the non-biodegradable fraction of the influent. The OLR criterion is important due to its relationship with the substrate concentration S_0, affecting both physical performance (substrate viscosity) and biochemical performance (reactor stability) of the reactor (Garcia-Heras, 2003). Both the HRT and OLR are selected by taking into account the digester volume of the reactor.

Following parameters are usually monitored to determine the stability of the AD process :

- reactor pH and temperature
- alkalinity and VFA concentration
- biogas production and composition

The interrelated pH, alkalinity and VFA concentration are of major importance with regard to the stability of the AD process. Since methanogenic microorganisms have a much lower growth rate compared to fermentative bacteria, an increase in VFA concentration (e.g., caused by an increase in OLR) could provoke an unbalanced development of the trophic chain. Whether the reactor pH and hence also the biogas yield will eventually drop or not is largely determined by the alkalinity of the digester, the latter being function of the presence of buffering species in the reactor such as (bi)carbonates and their counterions (e.g., Ca^{2+}, Mg^{2+}, NH_4^+) (Cecchi et al., 2003).

The digestion temperature can be either mesophilic (~34°C) or thermophilic (~55°C). The hydrolysis rate of solid waste materials (e.g., cellulose) is generally higher under thermophilic conditions. Hence, most studies with OFMSW have been carried out with thermophilic reactors although this phenomenon is not reflected in full-scale applications.

2.5.2. Biogas utilization for renewable energy production

The energy content of biogas, with a calorific value of 17-25 MJ/m^3 (or about 10% lower than natural gas), is usually recovered by means of diesel stationary engines or dual-fuel engines with a thermal efficiency in the range of 30-38% (Bilcan et al., 2003; Henham and Makkar, 1998). Smaller engines (< 200 kWh) generally have an electrical conversion efficiency of less than 25% while larger engines (> 600 kWh) can reach efficiencies as high as 38%. However, in case hot water and steam from the engine's exhaust and cooling systems is recovered, an overall conversion efficiency of more than 80% can be reached (Ross et al., 1996). Possible alternatives for the production of electricity from biogas are gas turbines, direct carbonate fuel cells (Katikaneni et al., 2002) or solid oxide fuel cells (Staniforth and Ormerod, 2002).
If it is assumed that on average 250 m^3 biogas is produced from 1 ton TVS waste (50% bioconversion efficiency) and 2 kWh can be produced from 1 m^3 biogas, then 500 kWh per ton dry solids waste can be generated or approximately 160 kWh/ton wet waste.

2.5.3. Anaerobic digestion reactor configurations for full-scale municipal waste processing[1]

ABSTRACT

The most common types of anaerobic digesters for solid wastes have been compared based on biological and technical performance and reliability. Batch systems have the simplest designs and are the least expensive solid waste digesters. They have high potential for application in developing countries. Two-stage systems are the most complex and most expensive systems. Their greatest advantage lies in the egalisation of the organic loading rate in the first stage, allowing a more constant feeding rate of the methanogenic second stage. Two-stage systems with biomass accumulation devices in the second stage display a larger resistance toward toxicants and inhibiting substances such as ammonia. However, the large majority of industrial applications use one-stage systems and these are evenly split between 'dry' systems (wastes are digested as received) and 'wet' systems (wastes are slurried to about 12 % total solids). Regarding biological performance, this study compares the different digester systems in terms of organic loading rates and biogas yields considering differences in input waste composition. As a whole, 'dry' designs have proven reliable due to their higher biomass concentration, controlled feeding and spatial niches. Moreover, from a technical viewpoint the 'dry' systems are more robust and flexible than 'wet' systems.

Keywords: *biogas yield, biological performance, grey waste, inhibition, OFMSW, organic loading rate, total solids*

[1] Redrafted after:
Lissens, G., Vandevivere, P., De Baere, L., Biey, E.M. and Verstraete, W. (2001) Solid waste digestors: process performance and practice for municipal solid waste digestion. *Water Science and Technology* **44** (8): 91-102.

INTRODUCTION

The discussion and evaluation of reactor designs generally depend on biological, technical, environmental and last but not least, economical aspects. This paper strives to address the technical and biological viewpoints in depth and highlights a few environmental and financial issues.

The scope of this paper is limited to feedstocks consisting mainly of the organic fraction of municipal solid wastes (OFMSW) sorted mechanically in central plants or organics separated at the source, referred to here as biowaste (the vegetable-fruit-garden, or VFG fraction). Necessary pretreatment steps may include magnetic separation, comminution in a rotating drum or shredder, screening, pulping, gravity separation (dry separation) or pasteurization (Figure 2.10). As post-treatment steps, the typical sequence involves mechanical dewatering, aerobic maturation, and water treatment but possible alternatives exist such as biological dewatering or wet mechanical separation schemes wherein various products may be recovered.

The two main parameters chosen to classify the realm of reactor designs are the number of stages and the concentration of total solids (% TS) in the fermenter because these parameters have a great impact on the cost, performance and reliability of the digestion process. Of each of the discussed reactor systems, a short general theoretical approach will be given. Subsequently, practical considerations will be made with respect to reactor performance and compared with expected results from literature. Finally, future perspectives for the digestion of OFMSW are given.

ONE-STAGE SYSTEMS

The biomethanization of organic wastes is accomplished by a series of biochemical transformations, which can be roughly separated into a first step where hydrolysis, acidification and liquefaction take place and a second step where acetate, hydrogen and carbon dioxide are transformed into methane. In one-stage systems, all these reactions take place simultaneously in a single reactor, while in two- or multi-stage systems, the reactions take place sequentially in at least two reactors.

About 90 % of the full-scale plants currently in use in Europe for anaerobic digestion of OFMSW and biowastes rely on one-stage systems, approximately evenly split between 'wet'

and 'dry' operating conditions (De Baere, 1999). This is probably due to the lower cost of one-stage systems compared to two-stage systems.

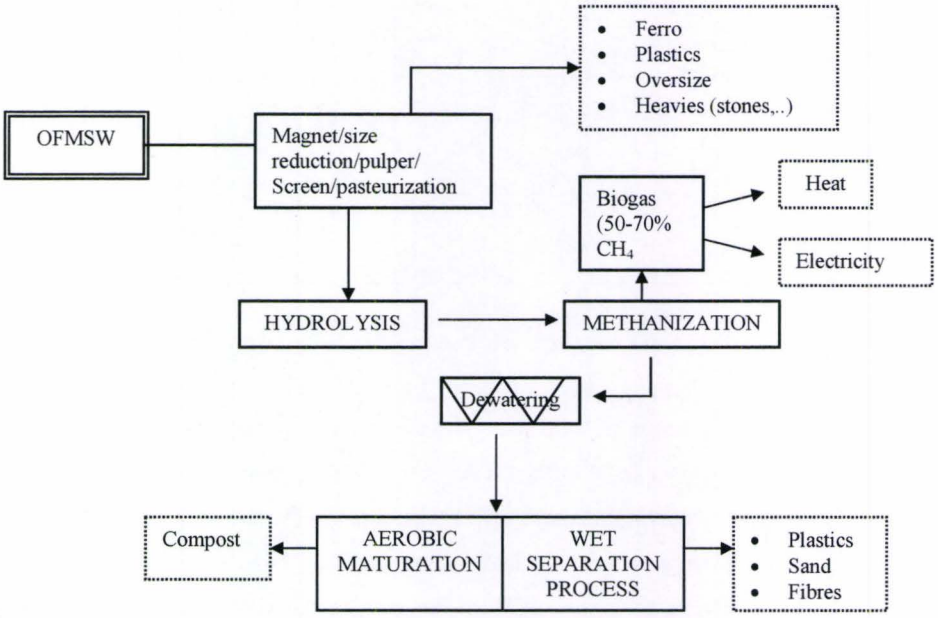

Figure 2.10. Overview of possible pre- and post-treatment technologies in OFMSW digestion

One-stage 'wet' complete mix systems

Technical evaluation

Under the term 'solid waste', one generally understands organic biodegradable waste with more than 15% TS. In 'wet' complete mix systems the organic solid waste is diluted with water via pulping and slurrying to less than 15% TS. Consequently, digesters of the CSTR-type (completely stirred tank reactor) are mostly used in this type of application.

One of the first full-scale plants for the treatment of biowastes, built in the city of Waasa, Finland, in 1989, is based on this principle (Figure 2.11).

A pulper with three vertical auger mixers is used to shred, homogenize and dilute the wastes in sequential batches. To this end, both fresh and recycled process water are added to attain 10-15 % TS. The obtained slurry is then digested in large completely mixed reactors where the solids are kept in suspension by vertical impellers (Figure 2.11).

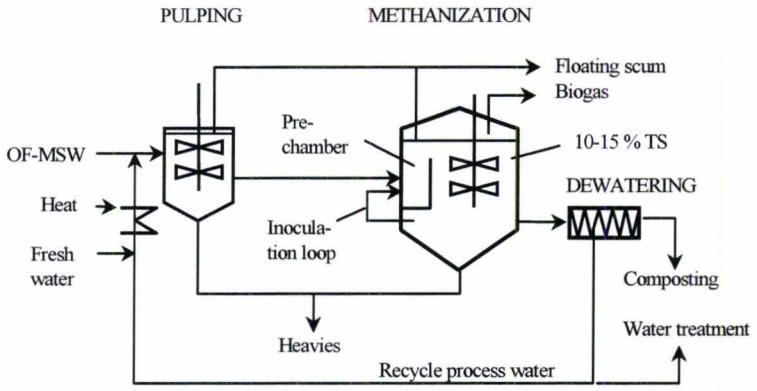

Figure 2.11. Typical design of a one-stage 'wet' system

Many technical aspects need actually be taken into account and solved in order to guarantee a satisfactory process performance (Westergard and Teir, 1999; Farneti et al., 1999). First of all, one should realise that the origin and kind (composition) of organic solid waste have a significant influence on biodegradability and consequently on biogas yields. Moreover, the selective removal of coarse contaminants from the mainstream can be difficult to achieve. Therefore, a complicated plant is required involving the use of screens, pulpers, drums, presses, breakers, and flotation units. These pretreatment steps inevitably result in a 15-25 % loss of volatile solids, with a consequent proportional drop in biogas yield (Farneti et al., 1999). Secondly, slurried wastes do not always keep a homogenous consistency because heavier fractions and contaminants tend to sink. A floating scum layer generally forms during the digestion process due to foam producing substances present in plant materials. This results in the formation of three layers of distinct densities in the reactor. It is therefore necessary to foresee means to extract periodically the light and heavy fractions from the reactor to avoid damage to pumping equipment.

A final technical drawback of the complete mix reactor is the occurrence of short-circuiting, i.e. the passage of a fraction of the feed through the reactor with a shorter retention time than the average retention time of the bulk stream. This generally results in a decreased biogas production and less kill-off of microbial pathogens.

Biological performance

A useful tool for the characterisation of biological performance is the maximum sustainable reaction rate, which can be expressed as a rate of substrate addition, i.e. the maximum organic

loading rate (OLR_{max} expressed in kg VS/m^3 reactor.d), or as a rate of product formation, i.e. the volume of dry biogas or, better, of methane (under standard conditions of pressure and temperature) produced per unit time per unit reactor volume (m^3 CH_4/m^3 reactor.d). Another parameter of use to quantify the rate is the retention time, which is roughly the inverse of the OLR when the OLR is expressed as mass wet substrate instead of mass substrate (VS). The best way to compare the biological performance of different reactor designs requires however the use of all three indicators simultaneously.

Typical OLR_{max} values for one-stage 'wet' digestion of OFMSW are in the range of 5-10 kg VS/m^3.d. These values are particularly dependent on the origin and composition of the biowaste. As a whole, the pulping of the solid waste results in a better hydrolysis and homogenisation of the waste (Stroot et al., 2001). Consequently, one may expect higher biogas yields applying one-stage 'wet' digestion in comparison with one-stage 'dry' digestion since bacteria have better access to the substrate. However, the technical drawbacks (loss of biodegradable material when removing coarse materials, scum layer and heavies) compensate this effect resulting in a similar or even lower biogas yield compared to one-stage 'dry' systems for the same solid waste feed.

Economical and environmental issues

The slurrying of the solid wastes brings the economical advantage that cheaper equipment may be used (e.g., pumps and piping) relative to solid materials. This advantage is however balanced by the higher investment costs resulting from larger reactors with internal mixing, larger dewatering equipment, and necessary pre- and post-treatment steps. Overall, investment costs are comparable to those for one-stage 'dry' systems.

One drawback of ecological and economical significance is the incomplete biogas recovery due to the loss of biodegradable organics with the removal of the floating scum layer and the heavy fraction. Another one is the relatively high water consumption necessary to dilute the wastes (about 1 m^3 tap water per ton solid waste).

One-stage 'dry' systems

Research during the 80's demonstrated that biogas yield and production rate were at least as high in systems where the wastes were kept in their original solid state, i.e. not diluted with water (Spendlin and Stegmann, 1988; Baeten and Verstraete, 1993; Oleszkiewicz and Poggi-

Varaldo, 1997). The new plants erected during the last decade are evenly split between the wet and the dry systems (De Baere, 1999).

Technical evaluation

In dry systems, the fermenting mass within the reactor is kept at a solids content in the range 20-40% TS. Consequently, only very dry substrates (> 60% TS) need to be diluted with process water (Oleszkiewicz and Poggi-Varaldo, 1997). The physical characteristics of the wastes at such high solids content impose technical approaches in terms of handling, mixing and pretreatment which are fundamentally different from those of wet systems.

Transport and handling of the wastes is carried out with conveyor belts, screws, and powerful pumps especially designed for highly viscous streams. This type of equipment is more expensive than the centrifugal pumps used in wet systems. However, it is also more robust and flexible since wastes with solid contents between 20 and 50 % can be handled and impurities such as stones, glass or wood do not cause any hindrance. The only pretreatment which is necessary before feeding the wastes into the reactor is the removal of the coarse impurities larger than ca. 40 mm. This makes the pretreatment of dry systems somewhat simpler than that of their wet counterparts and very attractive for the biomethanization of OFMSW which typically contains 25 % by weight of heavy inerts.

Due to their high viscosity, the fermenting wastes move via plug flow inside the reactors, which offers the advantage of technical simplicity as no mechanical devices need to be installed within the reactor. At least three designs have been demonstrated effective for the adequate mixing of solid wastes at industrial scale (Figure 2.12).

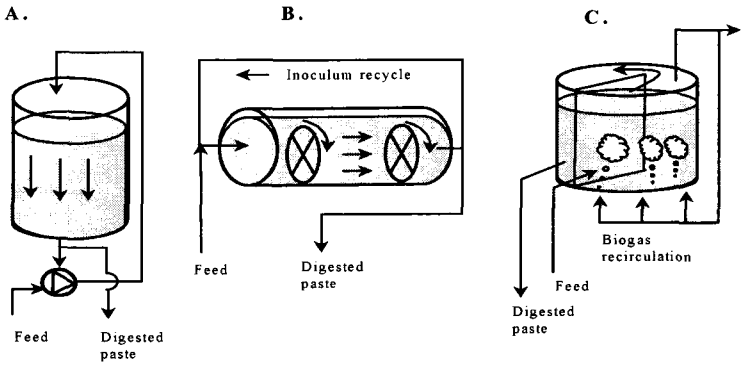

Figure 2.12. Different digester designs used in 'dry' systems (A illustrates the Dranco design, B the Kompogas and BRV designs, and C the Valorga design)

In the Dranco process, the mixing occurs via recirculation of the wastes extracted at the bottom end, mixing with fresh wastes (one part of fresh waste for six parts of digested waste), and pumping to the top of the reactor. This simple design has been shown effective for the treatment of (bio) wastes ranging from 20 to 50 % TS.

The Kompogas process works similarly, except that the plug flow takes place horizontally in cylindrical reactors. The horizontal plug flow is aided by slowly-rotating impellers inside the reactors, which also serve for homogenization, degassing, and resuspending heavier particles. This system requires careful adjustment of the solid content around 23 % TS inside the reactor. At lower values, heavy particles such as sand and glass tend to sink and accumulate inside the reactor while higher TS values cause excessive resistance to the flow.

The Valorga system is quite different in that the horizontal plug flow is circular in a cylindrical reactor and mixing occurs via biogas injection at high pressure at the bottom of the reactor. This biogas injection takes place every 15 minutes through a network of injectors (Fruteau de Laclos et al., 1997). Due to mechanical constraints, the volume of the Kompogas reactor is fixed and the capacity of the plant is adjusted by building several reactors in parallel, each one with a treatment capacity of either 15,000 or 25,000 tons/year (Thurm and Schmid, 1999). Possible drawbacks of this system are the clogging of the gas injection ports and the overall maintenance.

Biological performance

In terms of extent of VS destruction, the three 'dry' reactor designs discussed above perform very similarly, with biogas yields ranging from 90 m^3/ton fresh garden waste to 150 m^3/ton fresh food waste (Fruteau de Laclos et al., 1997; De Baere, 1999). These yields correspond to 210-300 m^3 CH_4/ton VS, i.e. 50-70 % VS destruction.

Differences among the dry systems are more significant in terms of sustainable OLR. The Valorga plant at Tilburg, The Netherlands, treats waste peaks of 1,000 ton VFG wastes per week in two digesters of 3,000 m^3 each at 40 °C (Fruteau de Laclos et al., 1997). This corresponds to an OLR of 5 kg VS/m^3.d, a value comparable to the design values of plants relying on wet systems. Optimized 'dry' systems may however sustain much higher OLR such as the Dranco plant in Brecht, Belgium, where OLR values of 15 kg VS/m^3.d were maintained as an average during a one-year period (De Baere, 1999).

When comparing 'dry' and 'wet' one-stage systems in terms of biological performance, OLR_{max} and biogas production need to be considered simultaneously. In the digestion of

OFMSW, the OLR_{max} will be largely determined by the growth rate of the acid producing and hydrolyzing bacteria and the growth rate of the methanogenic bacteria. This is particularly true for the VFG-fraction which generally has a very high biodegradability resulting in high acid production and high biogas yields.

As a whole, higher OLR are being achieved in both bench scale and full scale applications of one-stage 'dry' systems compared with water diluted 'wet' systems. Moreover, slightly higher biogas yields (< 10%) are to be expected in 'dry' systems compared to 'wet' systems since neither heavy inerts nor scum layer need to be removed before or during digestion (De Baere, 1999; Weiland, 1992).

Since inhibitors (mainly ammonia for OFMSW) often limit the OLR_{max} of reactors treating OFMSW, the sensitivity of reactor designs towards inhibition is of particular concern. One-stage 'wet' reactors generally suffer from the disadvantage that the reactor content is fully homogenized. This results on the one hand in the elimination of spatial niches wherein bacteria may be protected from high concentrations of inhibitors. On the other hand, the slurrying of the waste might also lead to an increased solubilization of nitrogen resulting in higher free ammonia levels in the reactor. However, the slurrying of solid waste also results in a dilution of the ammonia concentration. Kayhanian (1999) showed that by adding fresh water to high-solids waste, the ammonia inhibition effect could be mitigated. In general, for solid wastes with a C/N ratio above 20, the ammonia inhibition effect can be compensated by the dilution effect of water which lowers the concentration of potential inhibitors.

Economical and environmental issues

The economical differences between the 'wet' and 'dry' systems are small, both in terms of investment and operational costs. The higher costs for the sturdy waste handling devices required for 'dry' systems are compensated by a cheaper pretreatment and reactor, the latter being several times smaller than for 'wet' systems. The smaller heat requirement of 'dry' systems does not usually translate in financial gain since the excess heat from gas motors is rarely sold to the industry (Baeten and Verstraete, 1993).

Differences between the 'wet' and 'dry' systems are more substantial on environmental issues. While 'wet' systems typically consume one m^3 fresh water per ton OFMSW treated, the water consumption of their 'dry' counterparts is ca. 10-fold less. Moreover, better hygienization can be achieved with 'dry' thermophilic plug flow systems (Baeten and Verstraete, 1993).

TWO-STAGE SYSTEMS

The rationale of two- and multi-stage systems is that the overall conversion process of OFMSW to biogas is mediated by a sequence of biochemical reactions which do not necessarily share the same optimal environmental conditions. Optimizing these reactions separately in different stages or reactors may lead to a larger overall reaction rate and biogas yield (Ghosh et al., 1999). Typically, two stages are used where the first constitutes the liquefaction-acidification compartment, with a rate limited by difficult anaerobically degradable substrates such as the hydrolysis of lignocellulose complexes. The second stage constitutes the acetogenic and methanogenic compartment, with a rate limited by the slow microbial growth rate of the methanogenic bacteria (Liu and Ghosh, 1997; Palmowski and Müller, 1999). With these two steps occurring in distinct reactors, it becomes possible to increase the rate of methanogenesis by designing the second reactor with a biomass retention scheme or other means (Weiland, 1992; Kübler and Wild, 1992). However, the main advantage of a two-stage system is not its higher biogas yield or rate but rather its increased biological stability for wastes which cause unstable performance in one-stage systems (i.e. cellulose-poor wastes with C/N ratios lower than 10).

Without biomass retention

Technical evaluation

The most simple design, used primarily in laboratory investigations, are two completely mixed reactors in series (Pavan et al., 1999; Scherer et al., 1999), where wastes are shredded and diluted with process water to ca. 10 % TS before entering the first digester. Another possible design is the combination in series of two plug-flow reactors, either in the 'wet-wet' or 'dry-dry' mode, as illustrated by the Schwarting-Uhde (Figure 2.13) and BRV processes, respectively. Both fermenters are upwardly through-flowing cylindrical reactors, in which a plug-flow occurs. This is achieved by fitting perforated sheets, which result in a defined residence time. In the first cycle, the tank level in the fermenter is raised within a short time by means of two-way impulse pumps ('in grey', Figure 2.13). This results in a liquid level drop in the equalizing tank. In this way, local intermixing is forced and gas bubbles which have already been formed are ensured. The more heavy particles sink to the bottom of the reactor and are removed (Trösch and Niemann, 1999). A drawback of this technique is the

potential occurrence of methanogenesis in the first reactor when hydrolysis becomes rate-limiting.

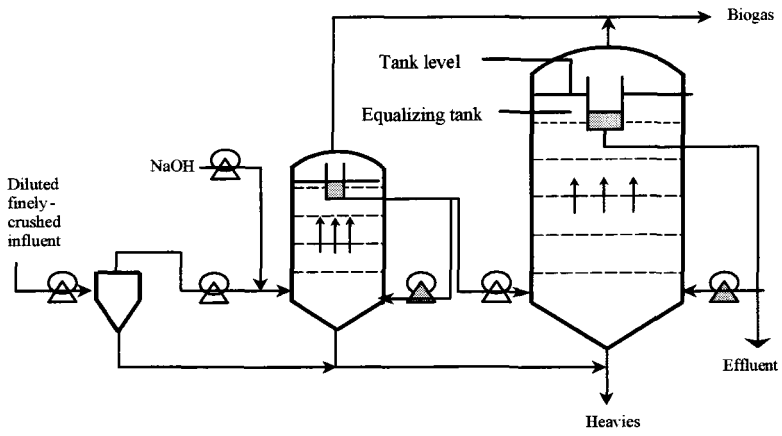

Figure 2.13. The Schwarting-Uhde process, a two-stage 'wet-wet' plug-flow system applicable to source-sorted biowastes, finely-choped (ca. 1 mm) and diluted to 12 % TS

In the BRV process, the source-separated biowastes, adjusted to 34 % TS, pass through an aerobic upstream stage where organics are partially hydrolyzed and ca. 2 % organics are lost through respiration. The reason for conducting the hydrolysis stage under microaerophilic conditions is that the loss of COD due to respiration is more than compensated by a higher extent of liquefaction, which, moreover, proceeds faster than under anaerobic conditions (Wellinger et al., 1999; Capela et al., 1999). After a two-day retention time, the pre-digested wastes are pumped through methanogenic reactors in a horizontal plug flow mode. The digestion is set at 25 days at 55 °C and 22 % TS (after dilution).

Biological performance

As already indicated, the main advantage of the two-stage system is the greater biological stability it affords for very rapidly degradable wastes like fruits and vegetables (Pavan et al., 1999). For instance, short-lived fluctuations of the applied OLR for highly biodegradable kitchen waste will be better buffered with two-stage systems compared to one-stage systems. However, in cases where special care is taken to mix the feed thoroughly and dose it at constant OLR, one-stage 'wet' systems are as reliable as two-stage systems, even for highly degradable organic wastes.

In terms of biogas yields and OLR_{max}, little difference can be noted between one- and two-stage systems, at least for two-stage systems without a biomass retention system. For example, the BRV plant in Heppenheim is designed with an OLR of 8.0 kg VS/m^3.d while the Schwarting-Uhde process can sustain an OLR_{max} up to 6 kg VS/m^3.d (Trösch and Niemann, 1999). The average biogas yields for the BRV-process and the Schwarting-Uhde process are also similar.

With a biomass retention scheme

Technical evaluation

In order to increase rates and resistance to shock loads or inhibiting substances, it is desirable to achieve high cell densities of the slowly-growing methanogenic consortium in the second stage. There are two basic ways to achieve this. The first method to increase the concentration of methanogens in the second stage is to uncouple the hydraulic and solids retention time, thereby raising the solid content in the methanogenic reactor. These accumulated solids represent active biomass only when the wastes do not leave more than 5-15 % of their original solid content as residual suspended solids inside the reactor. One way to uncouple the solid and hydraulic retention times is to use a contact reactor with internal clarifier (Weiland, 1992). Another way is to filter the solid waste of the second stage on a membrane and return the concentrate in the reactor in order to retain the bacteria (Madokoro et al., 1999). A last method to increase the concentration of slowly-growing methanogens in the second stage is to design the latter with support material allowing attached growth, high cell densities and high sludge age.

In the BTA 'wet-wet' process, methanogenic bacteria are enriched by means of a fixed film loop reactor. The 10% TS pulp leaving the pasteurization step is dewatered and the liquor is directly sent to the methanogenic reactor. The major drawback of this system though is its technical complexity as several reactors are necessary to achieve what other systems achieve in a single reactor.

Biological performance

In two-stage designs with attached growth, greater resistance toward inhibiting chemicals is achieved. While the one-stage system failed at OLR of 4 kg VS/m^3.d for those wastes which yielded ca. 5 g NH_4^+/l due to ammonium inhibition, the same wastes could be processed in the two-stage system at OLR of 8 kg VS/m^3.d without impairment of methanogenesis (Weiland,

1992). It was stated that for residues with a C/N-ratio above 15 the one-step process should be used preferably, whereas protein-rich residues with a C/N-ratio below 10 can be treated only in the two-step process. For the different agro-industrial residues (mainly vegetable matter) it was found that about 50-70 % of the organic matter can be degraded within retention times of 10 - 20 days. The biogas production was typically 300 - 500 m^3 per ton of dry organic matter (Weiland, 1992).

Another consequence of two-stage systems with biomass retention is the possibility of applying higher OLR in the methanogenic reactor, with values up to 10 and 15 kg VS/m^3.d reported for the BTA and Biopercolat processes, respectively (Kübler and Wild, 1992; Wellinger et al., 1999).

BATCH SYSTEMS

In batch systems, digesters are filled once with fresh wastes, with or without addition of seed material, and allowed to go through all degradation steps sequentially either in the 'dry' mode, i.e. at 30-40 % TS, or in the 'wet' mode (15% TS or less). Though batch systems may appear as a landfill-in-a-box, they in fact achieve 50- to 100-fold higher biogas production rates than those observed in landfills because of two basic features. The first is that the leachate is continuously recirculated, which allows the dispersion of innoculant, nutrients, and acids, and in fact is the equivalent of partial mixing. The second is that batch systems are run at higher temperatures than those normally observed in landfills.

Technical evaluation

In the single-stage batch design, the leachate is recirculated to the top of the same reactor where it is produced. This is the principle of the Biocel process, which is implemented in a full-scale plant in Lelystad, The Netherlands, treating 35,000 tons/year source-sorted biowaste (ten Brummeler, 1999). The waste is loaded with a shovel in fourteen concrete reactors, each of 480 m^3 effective capacity and run in parallel. The leachates, collected in chambers under the reactors, are sprayed on the top surface of the fermenting wastes. A typical shortcoming of batch systems is the clogging of the perforated floor, resulting in the blockage of the leaching process. This problem can be remediated by limiting the thickness of the fermenting wastes to four meters in order to decrease compaction and by mixing the fresh wastes with bulking material (e.g., wood chips) (ten Brummeler, 1992).

In the sequential batch design, the leachate of a freshly-filled reactor, containing high levels of organic acids, is recirculated to another more mature reactor where methanogenesis takes place (Figure 2.14). The leachate of the latter reactor, free of acids and loaded with pH buffering bicarbonates, is pumped back to the new reactor.

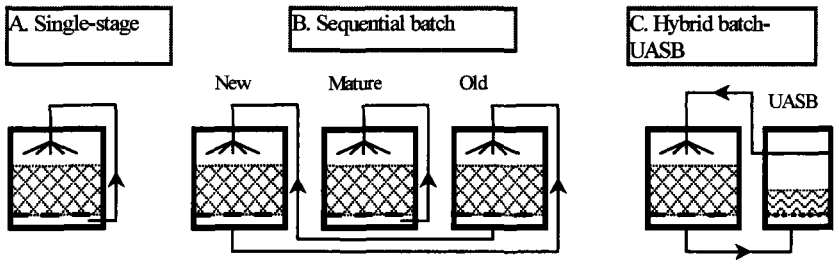

Figure 2.14. Configuration of leachate recycle patterns in different batch systems

Finally, in the hybrid batch-UASB design, the mature reactor where the bulk of the methanogenesis takes place is replaced by an upflow anaerobic sludge blanket (UASB) reactor. The UASB reactor, wherein anaerobic microflora accumulates as granules, is well suited to treat liquid effluents with high levels of organic acids at high loading rates.

Biological performance

The Biocel plant in Lelystad achieves an average yield of 70 kg biogas/ton source-sorted biowaste. This biogas yield is circa 40% smaller than that obtained in continuously-fed one-stage systems treating the same type of waste (De Baere, 1999). This low yield is the result of leachate channeling, i.e. the lack of uniform spreading of the leachate which invariably tends to flow along preferential paths. The design OLR of the Lelystad plant is 3.6 kg VS/m^3.d at 37 °C. Waste peak values of 5.1 kg VS/m^3.d during summer months can be handled (ten Brummeler, 1999).

Economical and environmental issues

Because batch systems are technically simple, the investment costs are significantly (ca. 40 %) lower than those of continuously-fed systems (ten Brummeler, 1992). The land area required by batch processes is however considerably larger than that for continuously-fed 'dry' systems, since the height of batch reactors is about five-fold less and their OLR two-fold less,

resulting in a ten-fold larger required footprint per ton treated wastes. Operational costs, on the other hand, are comparable to those of other systems (ten Brummeler, 1992).

CONCLUSIONS

A remarkable evolution has occurred in the attitude towards in-reactor digestion of solid wastes. The scepticism with respect to the feasibility has changed towards a general acceptance that various digester types are functioning at full scale in a reliable way.
Since most existing full-scale plants were originally designed as one-stage systems, it can be expected that this trend will continue but with improved reactor designs related to specific substrates. However, it is expected that two-stage systems with a high temperature step will start playing a more important role in the near-future to increase sanitation and hydrolysis of certain wastes (e.g., industrial waste to be combined with biowaste).
As a whole, it must be recognized that anaerobic digestion of solid wastes (particularly OFMSW) still has to compete vigorously with aerobic composting. This is in part related to the fact that composting is a long-established technology which generally requires less initial investment. However, current energy prices and targetted reduction of fossil fuel combustion in the coming decades will draw increasingly more attention towards anaerobic digestion.

2.5.4. Pretreatments for enhancement of anaerobic digestion of organic waste[2]

In recent years, considerable efforts have been made to improve the anaerobic conversion of solid wastes, mostly by means of a pretreatment. This is due to the fact that there is an obvious link between the extent of hydrolysis (*solubilization*) and the biodegradation (and hence biogas yield) of solid organic waste. Solid organic waste contains high amounts of lignocellulose, of which the rate and extent of utilization of the embedded polysaccharides is severely limited due to the intense cross-linking of cellulose with hemicellulose and lignin. By enhancing the biodegradation and thus enhancing the expoitation of the biochemical energy contained in solid waste, AD can be made more environmentally sound. However, the economical aspect of such a pretreatment, which is in integrated waste management equally

[2] Redrafted after :
Lissens, G., Ahring B.K. and Verstraete, W. (2003) Pretreatment technologies for enhanced energy and material recovery of agricultural and municipal organic wastes in anaerobic digestion. *European Biogas Workshop 2003*, University of Southern Denmark, Esbjerg, Denmark.

important, is a point that has not been addressed in most of the reported studies (reviewed by Mata-Alvarez et al., 2000 and Delgenès et al., 2003). In this sub-chapter, only the most succesfull biological, mechanical and physicochemical treatments for enhanced biogas and bio-ethanol production from biowaste are highlighted.

2.5.4.1. Biological pretreatments

Several biological pretreatments have been tested recently of which precomposting, pretreatment with digester percolate, hydrolytic enzyme addition and use of thermophilic bacteria are the most important ones (Mata-Alvarez et al., 2000). The number of studies dedicated to the use of commercial cellulases (e.g., from the fungi *Trichoderma resei*) or biomass-grown enzymes (Thygesen et al., 2003) is high (Delgenès et al., 2003). These methods bear the advantage that they are usually straightforward and do not require major capital investments. However, the main drawback of using enzymes is that generally high doses have to be added to achieve a significant increase in biogas or bio-ethanol yield.

Another approach is the application of cellulolytic bacteria from hydrolytic ecosystems such as the rumen of ruminants. This has been successfully shown by Gijzen et al. (1988) with pure cellulose, although it can be expected that the achieved biogas enhancement would be significantly lower with lignocellulosic substrate.

A final promising method is the use of aerobic thermophilic organisms in a pretreatment step, whereby several authors reported significantly higher biogas yield in subsequent methanogenesis. This increase in biogas yield could be attributed to better solubilization of particulate biodegradable solids and bio-oxidation of inhibitory pollutants sorbed onto the solids (Delgenès et al., 2003). However, this method implies high costs due to the large oxygen demand and heat requirement.

2.5.4.2. Mechanical and chemical pretreatments

Mechanical disintegration and maceration has been applied to sewage sludge and to fibers contained in manure (Angelidaki and Ahring, 2000). As a rule of thumb, the smaller the fibers (< 0.35 mm), the higher the gain in methane potential (up to 20% gain) of the macerated manure. This method seems to be one of the most economical and promising to increase the biogas potential of manure and possibly other solid waste streams (Delgenès et al., 2003). Other mechanical treatments are stirred ball milling, ultrasound treatment and high-pressure homogenizing. However, the economic feasibility of the techniques was mostly not addressed and can be questioned, seen the relatively low increase in biogas yield relative to the extra

investment costs made. The same holds true for purely chemical pretreatment methods, which are based on the solubilizing power of acidic or alkaline chemicals (e.g., NaOH or H_2SO_4). These methods generally need high doses and costly and unsustainable neutralization steps afterwards. Moreover, acidic pretreatment methods mostly lead to a considerable oxidation of the organic matter to CO_2, which is undesirable in terms of green energy recovery.

2.5.4.3. Physicochemical pretreatments

Many different physicochemical methods have been explored to enhance the hydrolysis of particulate matter (mostly lignocellulose) as a prior step to the production of biogas, and in particular to the production of bio-ethanol from biomass. These methods can be roughly divided into purely thermal treatments or often referred to as *thermal hydrolysis* and *thermochemical treatments*, the latter involving the use of dilute acid (e.g., H_2SO_4) or alkaline (e.g., NaOH) addition in the presence or absence of a (oxidative) catalyst (e.g., H_2O_2, O_2). Mostly, temperatures equal or below 240°C and pressures varying from 3-40 bar are applied. When biomass is treated with water or steam alone, or with a small amount of acid (0.1-2% typically), the process is also referred to as *prehydrolysis, autohydrolysis*, *steaming* and *steam explosion* (in case a sudden depressurization is applied). When high-pressure oxygen or air is present at elevated temperature and pressure, the process is called *wet oxidation* (Bjerre and Schmidt, 1997).

Hydrothermal processes

Thermal hydrolysis and *steam explosion disruption* are by far the most commonly studied pretreatments prior to biogas and bio-ethanol production (Schieder et al., 2000; Liu et al., 2002). Compared to other thermal treatments, hydrothermal processes bear the advantage that they do not involve the use of chemicals and that heat recovery from steam or water is fairly simple. Beside a solubilization effect, steam processes rely predominantly on a physical disruption of the fibers and higher temperatures (150-230°C typically) are applied than in oxidative thermal treatments, the latter mainly due to the absence of a catalyst. Therefore, these processes lead to significantly higher amounts of fermentation inhibitors such as 2-furfural and 5-hydroxymethyl-2-furfural (Bjerre et al., 1996). These compounds, which are formed by dehydration reactions from respectively pentose and hexose sugars, are together with soluble aromatic lignin derivatives and Maillard compounds known to be potentially inhibitory in subsequent anaerobic conversion (Delgenès et al., 2003).

Mechanistically, hydrothermal processing is based on the *autohydrolysis reaction* that is initially generated during the course of the process by the catalytic action of hydronium ions from water autoionization but mainly by the formation of acetic acid derived from acetylated xylan chains present in hemicellulose. Because the heterocyclic ether bonds of hemicelluloses are most susceptible to autohydrolysis, hydrothermal processing generally results in a high solubilization degree of the hemicellulose fraction whereas the lignin and cellulose fraction remain unaltered in the solids (Garrote et al., 1999; Garrote et al., 2001a). Consequently, this strong species-specific preference limits the applicability of hydrothermolysis for AD of heterogenous mixed waste.

Besides application on lignocellulosic wastes (mostly wood), hydrothermolysis has been extensively studied as a conditioning process for raw or digested sludges and also to improve dewaterability of such wastes (Delgenès et al., 2003). For that particular waste stream, the hydrothermal temperature optimum seemed to be lower (140-180°C) compared to lignocellulosic waste. While several authors found that the most significant enhancement in biogas yield was achieved under alkaline conditions (pH = 11-12), others stated that hydrothermal processing under alkaline conditions severely promotes the formation of toxic lignin derivatives and Maillard compounds (reviewed by Delgenès et al., 2003).

A more exotic category of hydrothermal processes encompass *sub-*, *near-* and *supercritical* thermal treatments relative to the *critical temperature* of water (T = 374°C). The *critical temperature* of a substance is the temperature at and above which vapour of the substance cannot be liquefied, no matter how much pressure is applied. Due to the high pressures (up to 300 bar) and temperatures (up to 450°C) applied, water will act as a solvent and as a catalyst for the acid-mediated hydrolysis reactions of the substrate. One successfull example is the study of Quitain et al. (2002), who applied sub-critical hydrothermal treatment in the presence and absence of H_2O_2 as an oxidant to produce low-molecular-weight carboxylic acids from organic wastes. These authors found high lactic acid production under reductive conditions while mostly acetic acid was formed under oxidative conditions (Quitain et al., 2002).

Wet oxidation and AOP's

Wet oxidation (WO) involves the use of air or oxygen as a catalyst in the liquid phase under elevated pressure and temperature (typically 0.5-150 bar, 150-370°C). Wet oxidation is for semi-solid (2-20% total solids) waste the counter process of what is called *advanced*

oxidation processes (AOP's), which are water treatment processes being based on the generation of hydroxyl radicals (OH·) to initiate destruction of organics at near ambient temperature and pressure. Due to the relatively high costs compared with conventional biological water treatment, AOP's play a role in the abatement of toxic or persistent substances which cannot or only slowly be degraded biologically. The most important AOP's are summarized in Table 2.5 with their reaction mechanism and the chemicals involved from which the OH· are derived.

Table 2.5. Overview of AOP's with the involved oxidants and their reaction mechanisms

Advanced oxidation process	Oxidants	Reaction mechanism
Ozonisation (+UV)	O_3	$O_3 + H_2O \rightarrow O_2 + 2OH\cdot$
Hydrogen peroxide/UV	H_2O_2	$H_2O_2 + h\nu \rightarrow 2\ OH\cdot$
Ozone + hydrogen peroxide	$O_3 + H_2O_2$	$2O_3 + H_2O_2 \rightarrow 2\ OH\cdot + 3O_2$
Fenton's reagent	O_3 and Fe(II)	$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + OH\cdot$
Photooxidation	$h\nu + O_3 + H_2O_2$	$h\nu + 2O_3 + H_2O_2 \rightarrow 2\ OH\cdot + 3O_2$
Photocatalysis	$h\nu + TiO_2 + O_2$	excitation of TiO_2 catalyst $\rightarrow$ OH·
Electrochemical oxidation	H_2O	$H_2O \rightarrow OH\cdot + e^- + H^+$
Electron beam irradiation	e^-	$H_2O + e^- \rightarrow OH\cdot + H\cdot + e^-_{aq}$
Sonolysis	H_2O	H_2O + energy $\rightarrow$ OH· + H·

Electrochemical oxidation or *anodic* oxidation is an AOP whereby electrical power is used to partially or completely decompose organics at the anode. This technology has been reported to have several advantages over other AOP's (Rajeshwar et al., 1994; Kraft et al., 2003):

- No need for the addition and handling of chemicals
- No background losses and no reported toxicity of effluents
- Amenable to automation: only two system variables (current and voltage)
- High energy efficiency due to the development of doped diamond electrodes

➢ *Purposes of the use of wet oxidation and AOP's*

The purpose of applying wet oxidation or AOP's is two-fold: either the total destruction or oxidation of a waste stream to CO_2 is aimed at (~incineration) or WO or AOP is used as a detoxification or modification step of a waste stream before or after final polishing or

biological degradation. In wet oxidation, the main decisive parameter in this regard is the WO temperature with a critical value of 200-250°C (incineration > 250°C versus modification < 250°C), depending on the characteristics of the waste stream employed. In AOP's, the critical parameters are rather the concentration of oxidative hydroxyl radicals derived from the oxidative species employed in relation with the contact or retention time. Furthermore, wet oxidation and AOP's are versatile processes that can provide complete sanitation and disinfection of waste streams.

- *Oxidation reaction mechanism*

The hydroxyl radical is the most powerful, non-selective chemical oxidant known (Table 2.6) and consequently reacts much faster than other oxidative species such as ozone or hydrogen peroxide.

Table 2.6. Relative oxidation power of some oxidizing species (Vogelpohl, 2001)

Oxidant	Molecule	Oxidation power
Hydroxyl radical	$OH\cdot$	2.05
Atomic oxygen	O_2	1.78
Ozone	O_3	1.52
Hydrogen Peroxide	H_2O_2	1.31
Permanganate	MnO_4^-	1.24
Chlorine	Cl_2	1.00

The reactions that take place during **wet oxidation** are still not completely understood. During treatment, *molecular oxygen* is dissolved in the wastewater and reacts with the substrate. The oxidizing power of the system is based on the high solubility of oxygen at the employed reaction conditions. It is proposed that a chain reaction mechanism based on the production of various *radical species* (hydroxyl, hydroperoxyl and organic hydroperoxy free radicals) evolved from oxygen is responsible for the oxidation (Thomsen, 1999). As the reaction progresses, the oxygen and formed radicals also start reacting with oxidation intermediates causing an increased oxidation rate during the course of the process (Kolackzkowski et al., 1999). Thomsen (1999) stated that decarboxylation is an important part of the wet oxidation mechanism, which is highly accelerated in an acidic environment.

The overall reaction oxidation rate in WO is governed by two steps, being 1) the mass transfer of oxygen from the gas to the liquid and 2) the oxidation reaction occurring in the liquid phase. Whereas the first step is relatively easily controllable by the reaction conditions (temperature, pressure and reaction time), the second step largely depends on the nature of the biomass employed. Because an increase in reaction temperature will also increase water vapourisation (and consequently less liquid available for reaction), the total operating pressure also needs to be increased to control oxygen partial pressure (Kolackzkowski et al., 1999).

The hydroxyl racidal mediated reactions that occur in **electrochemical oxidation** are principally the same as the bulk oxidation reactions in wet oxidation but under ambient temperature and pressures. Based on the anode material, the applied potential and the composition of the medium, either direct or indirect oxidation can be the main oxidation mechanism (Figure 2.15).

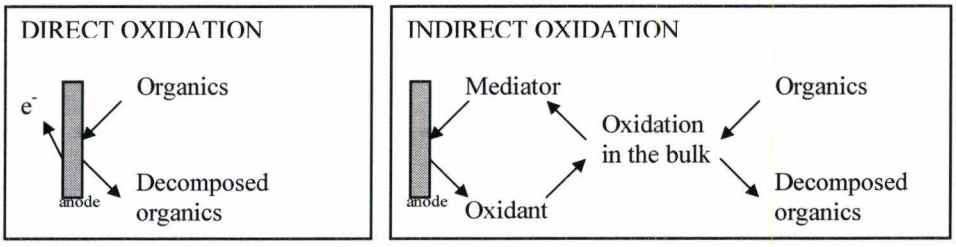

Figure 2.15. Scheme of electrochemical organics decomposition through direct anodic oxidation and indirect bulk oxidation (after Chiang et al., 1995)

In **direct** anodic oxidation, the organics are decomposed at the surface of the anode itself or by free radical species associated with the anode surface (Comninellis, 1994). Distinction can be made between *active* and *non-active* electrodes of which the oxidation mechanism is shown in Figure 2.16.

The oxidation of organics at *non-active* electrodes (e.g., PbO_2, SnO_2, doped diamond electrodes) proceeds directly with physisorbed hydroxyl radicals whereas at *active* electrodes (RuO_2, Pt, IrO_2), the hydroxyl radicals are scavenged away by the formation of an M/MO couple. The MO species then selectively reacts further with substrate (Figure 2.16, a). As a result, *non-active* electrodes have been reported to be ideal electrodes for organics destruction and combustion in wastewater (Comninellis and Pulgarin, 1993). In case Cl^- is present in the

medium, the oxygen transfer at non-active electrodes is mediated by adsorbed hypochlorite species (Figure 2.16., b) (Bonfatti et al., 2000).

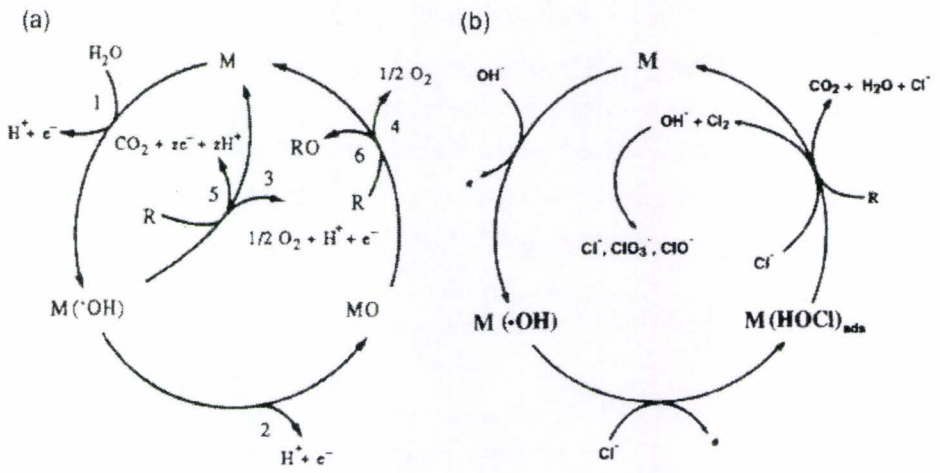

Figure 2.16. **(a)** : direct anodic oxidation of organics (R) at the anode (M) with simultaneous oxygen evolution. Pathway 3 represents the mechanism at non-active electrodes, pathway 2 and 4 represents the mechanism at active electrodes. **(b)** direct anodic oxidation at non-active electrodes in chloride-containing media (Comninellis, 1994 ; Bonfatti et al., 2000)

In **indirect** oxidation, mostly chlorine and hypochlorite have been used as electrochemically generated oxidants from chloride ions (Chiang et al., 1995). The production of these oxidants is highest at *active* electrodes and therefore they can be used for chlorination purposes (Comninellis and Nerini, 1995). However, the possible formation of toxic halogenated compounds bears major concerns for the potential application of this process.

- *Applications of wet oxidation*

The WO process technologies and reactor designs have been thoroughly reviewed by Kolaczkowski et al. (1999). Although the first WO process already dates back to the late 1950s (Zimpro process), wet oxidation has only recently been developed in Europe mostly for the treatment of sewage sludge or toxic wastewaters (Lendormi et al., 2001a; Lendormi et al.,

2001b). Other important WO processes for sludge treatment in Europe are the VerTech, Wetox, Kenox and Oxyjet system (Kolaczkowski et al., 1999). These processes mostly aim at a high COD reduction (> 80%) and further biological treatment of the oxidized products (apart from CO_2 mainly VFA and ammonia) (Lendormi et al., 2001a).

Another emerging and more recent research area is the application of mild WO (< 250°C) to lignocellulosic biomass as a pretreatment for bio-ethanol production (Bjerre et al., 1996; Bjerre and Schmidt, 1997; Klinke et al., 2001; Klinke et al., 2002). The reactor configuration for this purpose most closely resembles the one of the Wetox process (Figure 2.17).

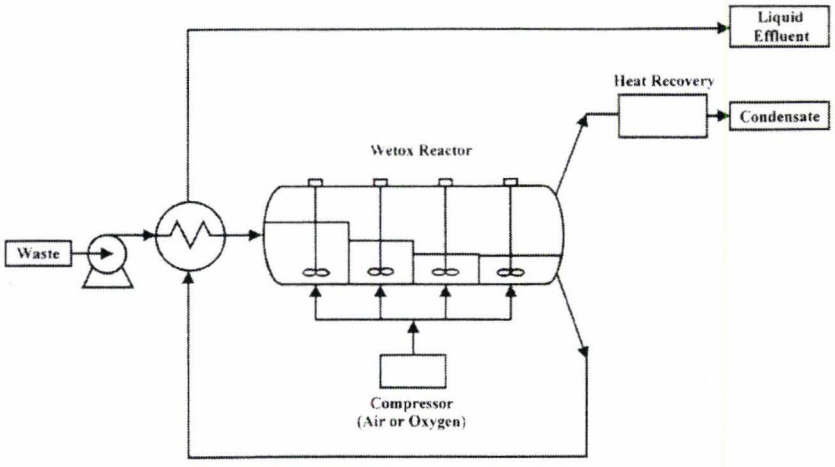

Figure 2.17. Scheme of the Wetox process for sewage sludge processing

The Wetox reactor is a horizontal autoclave which consists of 4-6 compartments that act as a series of continuous stirred tank reactors (CSTR). The reactor can be made *plug flow* in case a higher number of compartments is provided. The main benefits of this design are the improved oxygen transfer (from air or pure oxygen) to the waste. Due to the exothermic character of the WO reaction (13.5 kJ/g COD treated), the temperature progressively increases when the waste further moves in the reactor. The reactor configuration moreover allows for reusing the effluent heat to warm up the influent and for oxygen gas recovery from the vapour phase. It is stated that for concentrated wastes (up to 20% TS), the reactor can be operated in autothermal operation (Kolaczkowski et al., 1999).

At temperatures below 200°C, WO has been successfully applied to pre-treat biomasses (e.g., corn stover, wheat straw) to enhance the biodegradability of the lignocellulose for subsequent

bio-ethanol production (Varga et al., 2003; Bjerre et al., 1996). Due to the presence of oxygen, WO particulary enhances the formation of low molecular weight organic acids that are recalcitrant to further oxidation and CO_2 from liberated sugars and lignin (Garrote et al., 1999). The wet oxidation effect on lignin has been reported to be most pronounced under alkaline conditions (pH ~12) due to promotion of the step-wise one-electron transfer process under these conditions (Verenich and Kallas, 2002; Dorrestijn et al., 2000). Dilute NaOH has already previously been reported to cause a *saponification effect* or breaking of the cross-linkings in lignin and hence to facilitate enzymatic attack and anaerobic bionconversion of lignocellulose (Datta, 1981).

In WO at T > 200°, nutrients are also converted to their highest oxidation state (e.g., sulfur to sulfate, halogens to halides, phosphorous to phosphate) and are predominantly transferred to the aqueous phase forming inorganic salts and acids. At T < 200°C, nitrogen compounds are largely transferred into ammonia while at higher temperatures, more oxidative species can be formed (N_2, NO_3^-, NO) (Kolackzkowski et al., 1999). Besides, the relatively low temperature (< 200°C) does not demand for expensive corrosion-resistant alloys in wet oxidation.

- *Applications of electrochemical oxidation*

The presented electrochemical oxidation process has been extensively studied for a wide variety of organic pollutants and effluents with different anode materials. Examples are the treatment of landfill leachates (Chiang et al., 1995), textile dye solutions (Vlyssides et al., 2000) and olive oil manufacturing wastewaters (Saracco et al., 2001). Electrolysis has also been applied for the removal of inorganic species from water such as nitrite and ammonia (Lin and Wu, 1996) and also for disinfection purposes. With regard to the latter, disinfective chemicals can be produced in situ which have been proven to be effective against virusses, bacteria and protozoa (Venczel et al., 1997). However, the succes of most of these studies has been limited due to low current efficiencies (and hence high operational costs), low electrode stability or the formation of toxic compounds.

Recently, doped diamond electrodes have been developed which have unique properties for the decomposition of a variety of organics. The material has shown very high current efficiencies (> 90%) in the electrochemical mineralisation for many target compounds such as phenol, benzoic acid, pyridine, polyacrylates and dyes (reviewed by Kraft et al., 2003). These authors concluded that diamond anodes can very efficiently produce hydroxyl radicals,

resulting in much higher current efficiencies compared to other materials. These efficiencies are high as long as mass transport of organic compounds to the anode is not a limiting factor (Kraft et al., 2003). Doped diamond electrodes have much higher overvoltages for oxygen evolution (~ 2.8 V) compared to other materials and hence much higher efficiencies for hydroxyl radical production can be reached. Besides, diamond is very resistant to corrosion, heat and radiation, optically transparent and thermally conductive. In order to make diamond electrically conductive, these anodes are usually doped with boron by a hot-filament vapour deposition process (Tröster et al., 2002). These unique characteristics of boron-doped diamond electrodes can render electrochemical oxidation one of the most interesting AOP's for the future (Kraft et al., 2003). Diamond doped electrodes have recently found their way into commercial applications for the disinfection and final polishing of process water and drinking water (DiaCell™ technology).

2.6. EUROPEAN POLICY ON RENEWABLE ENERGY FROM BIOMASS

2.6.1. Biomass as a source for renewable energy production

Renewable energy includes the separate or combined production of electricity and heat from renewable energy sources. Defined renewable energy sources are solar, wind, biomass and waste, hydropower (large and small schemes) and geothermal. Biomass has several important advantages over other renewable sources such as its whidespread availability and its versatility (e.g., high diversity of plant species and wastes) (Nath and Das, 2003). Hence, biomass is considered to be one of the most emerging renewable sources on a global scale.

2.6.2. Renewable electricity policy in Europe

In 2001, about 6% of the energy use was renewable while the EU's indicative target is set at 12% renewable energy use by the year 2010, corresponding to raising renewables' share of EU electricity consumption to 22.1% (de Vries et al., 2003). This directive, which is obligatory to all EU member states, implies that the EU annual rate of growth in renewable energy needs to more than double (to 7%) from 2000 to 2010 compared to the growth rate before 2000.

To meet this directive, a number of policy instruments are in place to promote renewable energy, either affecting the *supply* or *demand* of renewable electricity (Figure 2.18). The three

main instruments are feed-in tariffs for supply of renewable electricity to the grid, quota obligations in combination with a green certificate system, and tendering/bidding schemes. Besides, investment subsidies and fiscal measures can be taken.

One of the most important instruments for the promotion of electricity generated from biogas is the provision of feed-in tariffs to the electricity supplier. A feed-in tariff is used for a minimum guaranteed price per unit (kWh) of produced electricity to be paid to the producer (including a premium in addition to market electricity prices). The feed-in tariffs for renewable energy from biomass (and hence biogas) vary between the EU member states with a factor of 7 with the lowest tariff for Belgium (7.3 €ct/kWh) and the highest for Austria and Germany (10-16.5 €ct/kWh) (de Vries et al., 2003).

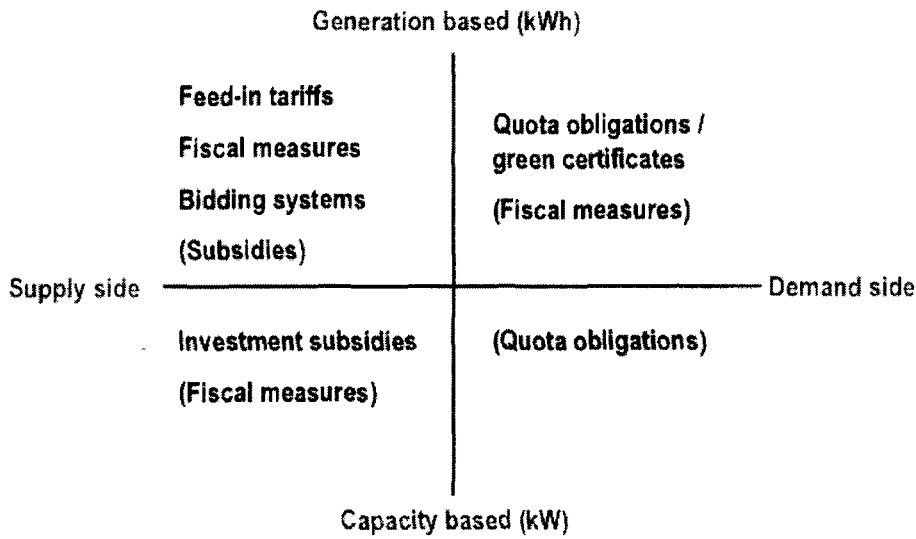

Figure 2.18. Scheme of policy instruments to promote renewable energy

2.7. IMPORTANT RESEARCH QUESTIONS

Anaerobic digestion of organic waste is a technology being applied for a few decades on industrial scale. Despite its maturity, its applicability on a large scale has only recently started as proven by a 10-fold increase in digestion capacity from 1990 to 2000 (Mata-Alvarez et al., 2000). The reasons for this delay in expansion are inherently connected to the knowledge

gained or still missing in both the management and performance of the AD process. In order to further promote AD as a key technology in sustainable waste management, a few important research questions can be formulated:

- Knowledge with regard to the controlled degradation of xenobiotic compounds under anaerobic conditions is still lacking, contrary to aerobic degradation which is often better studied. An example here-of is the biological degradation of chelating agents.
- Studies on the development of (biological or physicochemical) technologies that can enhance the digestion of organic waste are only limited or uncomplete. For the reported technologies, mostly the economical aspect is not considered and thus the usefulness of the work is considerably impaired.
- The recent EU directives on landfilling as well as the Kyoto agreements can possibly provoke an enormous growth market for AD. However, the current AD management practice largely impairs this expansion due to the low value of the solid end-product (compost). Further research should be dedicated to develop technologies in conjunction with AD that allow the separation of the digested waste in better defined recycable fractions (biogas, liquid and solids). These recyclable fractions should then have a higher purity degree than compost and hence more marketing value.

Chapter 3

ADVANCED ELECTROCHEMICAL OXIDATION AND DEACTIVATION OF XENOBIOTIC ORGANIC POLLUTANTS IN WASTEWATER

3.1. ELECTROCHEMICAL DEGRADATION OF COMMON SURFACTANTS IN MUNICIPAL WASTEWATER[1]

ABSTRACT

The electrochemical oxidation of anionic (sodium dodecylbenzenesulfonate) and cationic (hexadecyltrimethyl ammonium chloride) aqueous dilute surfactant solutions at a BDD (boron-doped diamond) electrode has been studied by batch electrolysis experiments and potentiodynamic measurements. In the potential region of water decomposition (E > 2.3 V vs. SHE), surfactants could be deactivated and oxidized with TOC (Total Organic Carbon) removals up to 82% by the action of intermediates of water discharge (e.g., hydroxyl radicals). Of the investigated process parameters, the initial electrolyte pH had the highest impact on surfactant oxidation. An initial pH of 10 significantly enhanced the electrochemical oxidation of both surfactants. The process was not diffusion-controlled and instantaneous current efficiencies (ICE) for TOC removal were in all cases low, varying from 5-12% on average.

The surfactant deactivation and oxidation potential of the BDD was compared with other carbon-based electrodes. Applying an equal electrode surface, the BDD electrode showed much higher surfactant removals compared to plane graphite. Graphite granules and carbon felt suffered from abrasion, leading to additional carbon loading of the surfactant solutions.

Based on the current electrolysis configuration, the specific energy requirement with the BDD electrode for the electrochemical oxidation of surfactants was estimated at 10-20 kWh m^{-3} effective wastewater.

Keywords: *household surfactant; boron-doped diamond electrode; carbon electrode; electrochemical combustion of organics; surfactant deactivation*

[1] Redrafted after :
Lissens, G., Pieters, J., Verhaege, M., Pinoy, L. and Verstraete, W. (2002). Electrochemical degradation of surfactants by intermediates of water discharge at carbon-based electrodes. *Electrochimica Acta* 48(12) : 1655-1663.

INTRODUCTION

Recent studies have shown that the electrochemical abatement of xenobiotic organic compounds (XOC's) present in wastewaters is a promising alternative in addition to conventional wastewater treatment techniques (Panizza et al., 2000; Chiang et al., 1997; Wang et al., 1996). So far, electrochemical treatment has been applied successfully for the partial or complete oxidation of various organic pollutants, particularly for concentrated electrolytes (Pakalapati et al., 1996; Fóti et al., 1999; Kirk et al., 1985; Comninellis and Pulgarin, 1993; Oturan, 2000; Rodrigo et al., 2001). In some studies, the oxidation of organic pollutants with various anode materials was compared (Johnson et al., 2000). A wide variety of electrode materials have been suggested: dimensionally stable anodes (DSA®) (e.g., RuO_2 or ZrO_2 coated Ti), thin film oxide anodes (PbO_2, SnO_2), noble metals (e.g., platina) and carbon-based anodes. The latter encompass, besides the traditional graphite electrodes (e.g., carbon felt, graphite granules and glassy carbon), also the recently developed synthetic boron-doped diamond (BDD) thin film electrodes. Particularly the BDD electrodes received great attention recently due to their high efficiency to combust organic pollutants partially or completely (Panizza et al., 2001a; Panizza et al., 2001b; Iniesta et al., 2001a; Iniesta et al., 2001b; Gandini et al., 2000) .

Household surfactants account for the majority of the chemical oxygen demand (COD) present in washing wastewater (e.g., laundry water). The major compounds are surfactants used in detergents, dishwashing liquids and hygienic products such as shampoos and soaps (Eriksson et al., 2003). The most common surfactants present in household water are the negatively charged linear alkyl sulfonates (LAS). As a result, their fate in the environment has been studied widely (Beltran et al., 2000a; Beltran et al., 2000b; Leu et al., 1998). Other frequently used surfactants with low biodegradability are cationic (e.g., hexadecyltrimethyl ammonium chloride) and non-ionic (e.g., alkylphenol ethoxylates) species. In wastewater treatment plants, persistent surfactants or intermediate products thereof (e.g., aromatics) can give rise to foaming, adsorption onto microbial sludge and loading of the purified effluents in concentrations up to the ppm-range (Eriksson et al., 2003).

Although the electrochemical oxidation of organic species is relatively well documented, less attention has been paid to the electrochemical oxidation of surfactants. In the study of Leu *et al.* (1998), the complete indirect oxidation of linear alkyl sulfonates (LAS) and alkylbenzene sulfonates (ABS) at conventional bipolar DSA® anodes was investigated. These authors could achieve a complete surfactant removal with an electrolyte addition of 0.05 M NaCl at a

current density of 16.8 mA cm^{-2} applying an electrochemical oxidation process in conjunction with chemical coagulation. Ciorba *et al.* (2000) also performed an electro-coagulation process with an aluminium electrode and achieved a 40 to 60% surfactant removal on COD basis.
In this work, both the electrochemical deactivation and oxidation of two common household surfactants was investigated in dilute aqueous electrolytes at a BDD electrode and to a lesser extent at other carbon-based electrodes. Most of the attention has been paid to the behaviour of the BDD electrode as this material is frequently mentioned as a stable, chemically inert and electrochemically very efficient material for the combustion of organics. The influence of several process parameters such as initial pH, bulk amount of surfactant, electrolyte conductivity, flow rate and current density on surfactant removal for this material has been evaluated.

MATERIALS AND METHODS

Reagents

Two aqueous surfactant solutions (20 mg dm^{-3}) were prepared with tap water (pH = 7.1): a 0.07 mM hexadecyltrimethyl ammonium chloride solution (Fluka) (cationic surfactant, molar weight (M) = 284) and a 0.0615 mM sodium dodecyl benzenesulfonate solution (Riedel-de Haën) (anionic surfactant, M = 325). All chemical reagents used were analytical grade. The anionic surfactant was chosen as a common representative of the linear alkyl sulfonates (LAS) surfactants. The cationic surfactant, also a common household surfactant, was selected because of its poor biodegradability (Eriksson et al., 2003).
Surfactant solutions were made alkaline (pH = 10) or acid (pH = 4) by means of sodium hydroxide and sulfuric acid addition respectively.

Electrolysis and electrode materials

The boron-doped diamond electrode was prepared by hot filament chemical vapour deposition (HF CVD) on Niobium sheet and was kindly supplied by Magneto Special Anodes (Netherlands). The graphite granules had an average diameter of 0.4 cm and filled up the anode compartment (V = 0.080 dm^3) completely. The open-cell glassy carbon foams with a total porosity of more than 90% (reticulated vitreous carbon) were tested in two grades (100 pores per inch (ppi) and 500 ppi, V = 0.080 dm^3) and were received from Destech Corporation

(U.S.). Optional high-temperature firing yielded electrically conductive glassy carbon foam. Woven carbon felt (GFA10- SGL Carbon, Germany) with a thickness of 0.8 cm was also tested. All flat electrode materials had a visual surface area of 0.50 dm^2 (1 dm x 0.5 dm) unless otherwise stated. A few experiments were performed with a BDD anode and a plane flat graphite anode with a higher visual surface (70 cm^2) for both electrodes. In all experiments, a stainless steel (316 L) sheet was used as cathode (50 cm^2 unless otherwise stated).

Batch oxidation of surfactants was performed in an undivided electrolytic cell under galvanostatic conditions (0.2 A) (Figure 3.1). The inter-electrode spacing was 0.10 dm and the total cell volume was 0.165 dm^3. Batch experiments were performed with different electrolyte volumes (0.150 dm^3 to 1 dm^3).

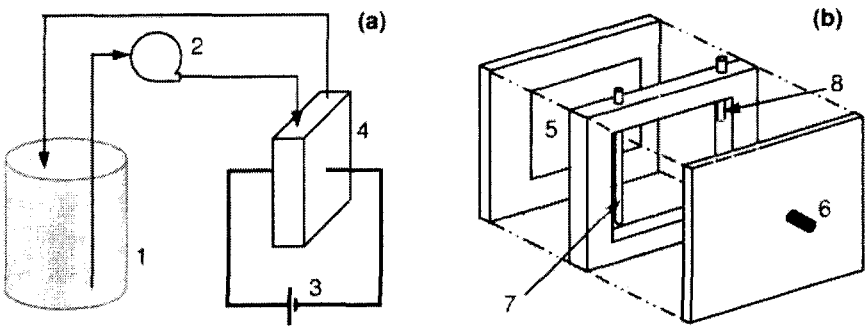

Figure 3.1. Scheme of the electrolysis equipment used. **(a)** experimental set-up: (1) stirred vessel, (2) peristaltic pump, (3) power supply, (4) electrochemical cell. **(b)** Electrochemical cell: (5) anode, (6) cathode electrical connection, (7) electrolyte inlet, (8) electrolyte outlet

Two types of batch experiments were performed: low volume batch tests operated by just filling the electrolytic cell and batch experiments with higher electrolyte volumes of up to 1 dm^3, where the electrolyte was recycled from a holding vessel at a pump rate of 0.25 dm^3 min^{-1}. The former will be denoted as "static test", the latter as "recycling test".

Analytical procedures and calculations

The COD content and pH of all solutions and samples was determined according to Standard Methods for the examination of water and wastewater (Greenberg et al., 1992). TOC (Total

Organic Carbon) analysis was carried out by means of a Shimadzu TOC-5000A Total Organic Carbon Analyser. Surfactant activity was monitored spectrophotometrically by means of Dr. Lange cuvette tests (Germany) for both anionic (MBAS or methylene blue-active substances) and cationic surfactants (bromophenol blue-active substances).

Potentiodynamic measurements were performed in a conventional three-electrode cell (T = 20°C, stirred 0.150 dm^3 reactor) with a Princeton Applied Research 263A Potentiostat at a scan rate of 10 mV s^{-1}. The working electrode was tested with an exposed apparent area of 0.01 dm^2 with a Ag/AgCl reference electrode and a Pt counter electrode.

The instantaneous current efficiency (ICE) was calculated according to the definition of Panizza *et al.* (2001a):

$$ICE = \frac{(\text{COD decrease})(\text{Volume of solution})}{(\text{Mass of oxygen equivalent to electricity})} = \frac{F\,V(\text{COD}_t - \text{COD}_{t+\Delta t})}{8I\Delta t} \quad (1)$$

where COD_t and $COD_{t+\Delta t}$ are the COD values at times t and $t+\Delta t$ (g O_2 dm^{-3}), respectively, I is the applied current (A), F is the Faraday constant (96 487 C mol^{-1}) and V is the volume of electrolyte (dm^3). The average current efficiency was then calculated as the average of the ICE-values. The current efficiency for the anodic combustion of both surfactants was also calculated using Faraday's law (2) and after defining the current efficiency (3):

$$i = \frac{m\,n\;96500}{M\;t} \quad (2) \qquad\qquad \rho_{i(\%)} = \frac{i}{I_{cell}} 100 \quad (3)$$

Equation (2) shows the theoretical current i (A) required to oxidize m gram of the compound. M is the molar mass (g) of the compound, n the number of electrons involved and t the applied electrolysis time (s). Equation (3) represents the current efficiency $\rho_{i(\%)}$ defined as the ratio of the theoretical amount of current i required to oxidize one mole of the compound (g) over the applied current I_{cell}.

The specific energy consumption SEC (kWh kg^{-1} oxidized compound) was then estimated:

$$SEC = \frac{V_i \;\; 26.8}{\frac{M}{n}\; 0.01\; \rho_{i(\%)}} \quad (4)$$

with V_i the applied cell voltage (V), M the molecular mass (g) of the oxidized compound, n the number of electrons involved and $\rho_{k(\%)}$ the current efficiency.

The required electrode area to combust organics at the surface of a BDD electrode was calculated according to

$$A = 4F\frac{X\,P}{I_{cell}\eta} \qquad (5)$$

with A the required electrode area (cm^2), F the Faraday constant, X the target COD conversion, P the given organic loading (mol COD s^{-1}), I_{cell} the applied current density (A cm^{-2}) and η the average current efficiency during electrochemical combustion (Panizza et al., 2001a).

RESULTS AND DISCUSSION

Anodic degradation of surfactants at a BDD electrode

The electrochemical oxidation of both the anionic and cationic surfactant to carbon dioxide was followed as a function of time by means of TOC-analysis (Total Organic Carbon) (Figure 3.2). In the batch tests, both surfactants could be oxidized to a large extent, with 83% TOC removal for the anionic surfactant and 68% TOC removal for the cationic surfactant after an applied charge of 2.7 Ah dm^{-3} solution. For both solutions, a sharper decrease of both the TOC and TIC (Total Inorganic Carbon) was obtained in the initial phase of electrolysis. Simultaneously, it was visually observed that a white-grey layer was formed on the stainless steel cathode. This layer was most probably the result of the precipitation of (bi)carbonates causing a decrease of the TIC.

In Figure 3.3, the ICE values (Instantaneous Current Efficiencies) for the electrochemical combustion of both surfactants are shown. COD contents were 2.5 times and 3.2 times higher then the TOC content for the anionic and cationic surfactant, respectively. ICE values were found to be low with an average current efficiency of 6% for the anionic surfactant and 12% for the cationic surfactant during the first period (1 Ah) of electrolysis.

From Figure 3.2 and Figure 3.3, it can be derived that the electrochemical combustion (expressed in TOC) and the ICE values of the cationic surfactant showed a rather sharp decrease in the first phase of electrolysis (1 Ah) whereas this trend was less pronounced for the anionic surfactant. Other studies, in which the electrochemical combustion of various organic pollutants (e.g., 2-naphtol (Panizza et al., 2001b), 3-methylpyridine (Iniesta et al.,

2001b)) was studied on BDD electrodes, also showed a higher electrochemical degradation rate during the initial phase of electrolysis.

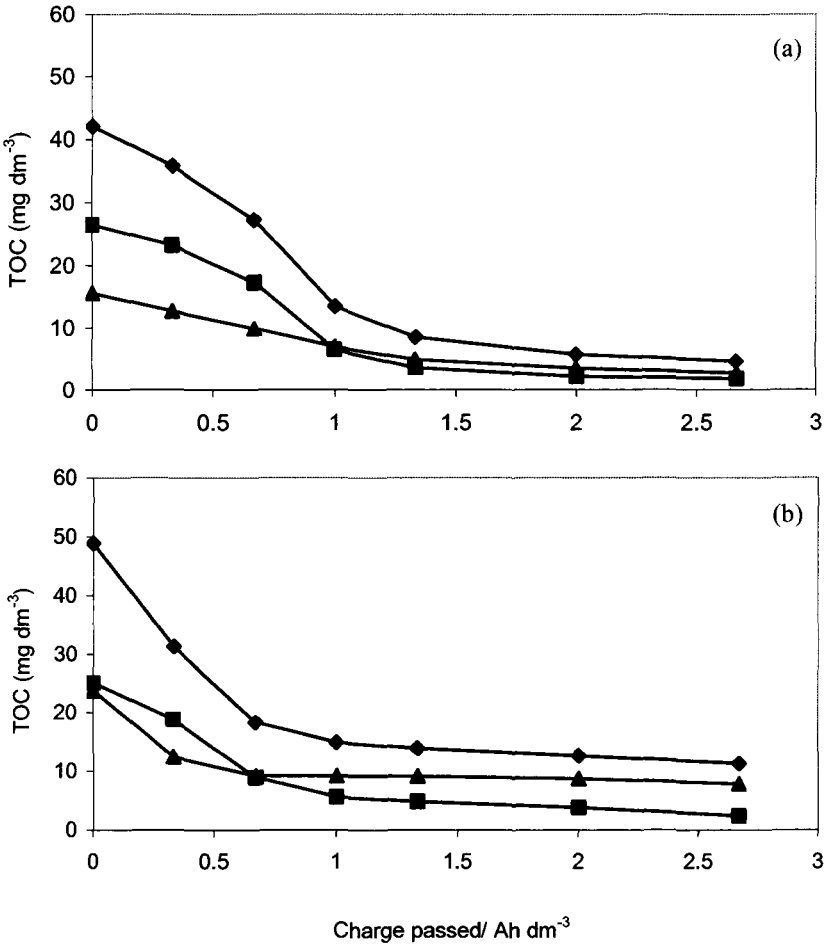

Figure 3.2. TOC removal of anionic (a) and cationic (b) surfactant solution during electrolysis at a BDD electrode. Key: Total Carbon (TC) (♦), Total Inorganic Carbon (TIC) (■), Total Organic Carbon (TOC) (▲). Electrolyte: 0.0615 mM sodium dodecylbenzene sulfonate solution, 0.07 mM hexadecyltrimethyl ammonium chloride solution, i = 4 mA cm^{-2}

Surfactant activity measurements largely showed a similar trend as the TOC results (Figure 3.4). In the recycling experiments, up to 80% of the surfactant activity could be removed for

both surfactants at an applied charge of 2.5 Ah. Similar to the TOC results, the decrease of the cationic surfactant activity showed a higher initial decrease rate compared to the anionic surfactant.

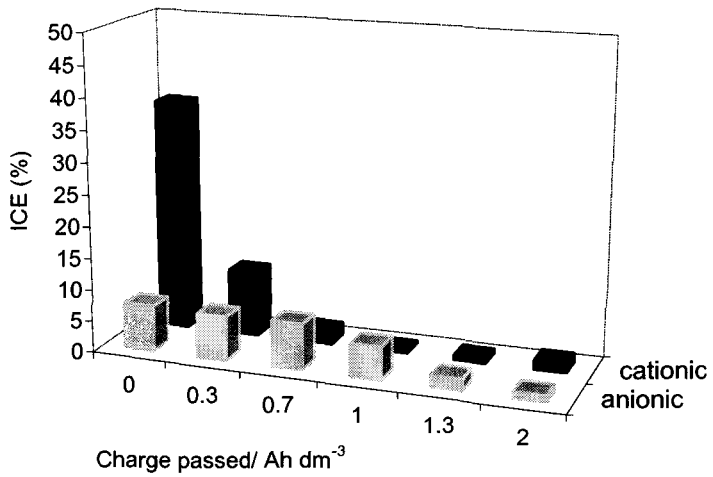

Figure 3.3. ICE values during the electrolysis at a BDD electrode of anionic and cationic surfactant solution. Electrolyte: 0.0615 mM sodium dodecylbenzenesulfonate solution; 0.07 mM hexadecyltrimethyl ammonium chloride solution, i = 4 mA cm^{-2}

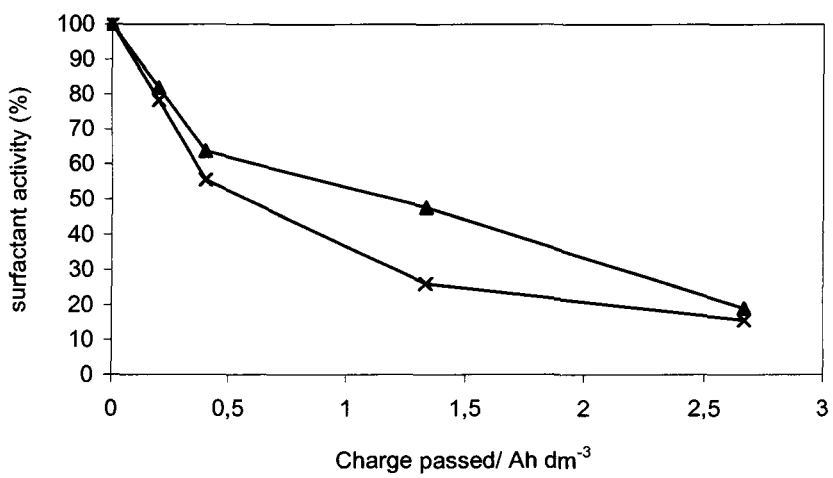

Figure 3.4. Surfactant deactivation during electrolysis at a BDD electrode. Key: anionic surfactant solution (▲), cationic surfactant solution (x), i = 4 mA cm^{-2}

The electrochemical oxidation of the cationic surfactant clearly proceeded at the highest rate during the initial electrolysis period 0-0.5 Ah (Figure 3.2) at ICE-values as high as 35-40% (Figure 3.3). The percentage TOC removal in the next period 0.5-2.5 Ah for the cationic surfactant, however, was low (1-2%), whereas the percentage TOC removal for the anionic surfactant was still high (50-55%) (Figure 3.2).

Due to their different chemical nature, the electrochemical oxidation of the surfactants can be assumed to be strongly dependent on their interaction with specific electro-oxidative species which are formed in the tap water medium throughout electrolysis. The formation of hydroxyl radicals and other oxidative species such as active chlorine substances in combination with the electrolyte pH (see 3.3) probably play an important role (Rodrigo et al., 2001). As a matter of fact, various dissolved and electroactive chlorine species (chlorine, hypochlorous acid, hypochlorite) can be formed at BDD electrodes in dilute chloride media at a neutral-weakly alkaline pH, even with high selectivity and high faradaic yields (Ferro et al., 2000). In this respect, it is assumed that the higher rate of TOC removal for the cationic surfactant is due to the extra input of chlorides, causing two effects. The first effect is to be situated on the level of bulk oxidation. The electronegative chlorine substances evolving from chloride will most probably react instantaneously with the cationic surfactant, causing an initially higher oxidation and surfactant deactivation rate compared to the anionic surfactant (Figure 3.2a vs. Figure 3.2b). Secondly, the lower water solubility of the formed chlorinated compounds and the lower molecular weight of the cationic surfactant are factors which are known to enhance the adsorption on hydrophobic carbon surfaces (e.g., on a BDD electrode) (Polcaro and Palmas, 1997). Both effects might explain the higher initial oxidation rate and surfactant deactivation rate of the alkyl ammonium chloride (cationic) compared to the alkyl sulfonate (anionic).

Influence of initial surfactant amount and surfactant concentration

A series of batch experiments and recycling experiments with varying electrolyte volumes and initial surfactant concentrations at constant current density were performed to derive the influence on the absolute TOC removal and the reaction rate.

The initial absolute amount of surfactant (expressed as mg) varied with a factor 6.6 for the small static experiment (0.15 dm^3 electrolyte) compared to the recycling experiments (1 dm^3 electrolyte). Despite the lower applied charge per unit electrolyte volume in recycling mode, the absolute surfactant oxidation was higher at initially higher electrolyte volumes and

consequently also at higher initial surfactant amounts (Figure 3.5). Moreover, it was found that a decrease of the initial surfactant concentration gave rise to a decrease in reaction rate and absolute surfactant removal. As a matter of fact, the absolute surfactant removal for a given applied charge of a 20 mg dm^{-3} solution was 3-4 fold lower compared to a 200 mg dm^{-3} concentrated solution with the same electrolyte volume and current density (not shown).

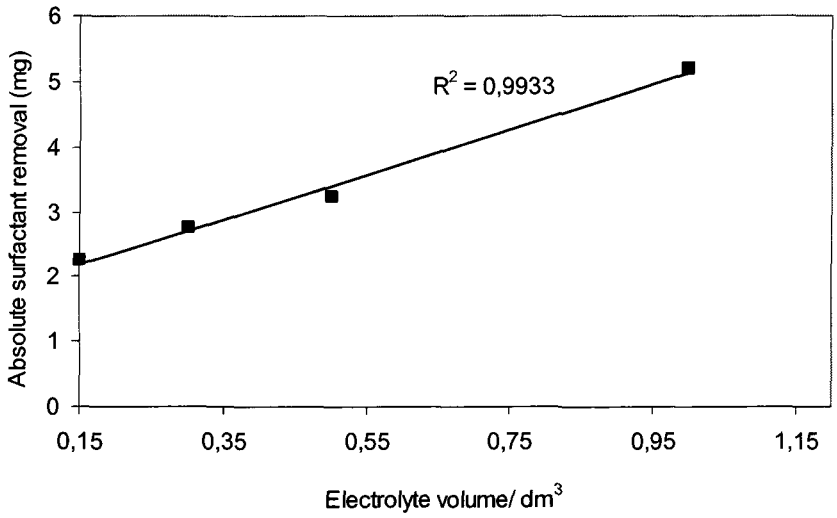

Figure 3.5. Influence of electrolyte volume on the absolute surfactant removal of cationic surfactant solution at a BDD electrode for an applied charge of 0.4 Ah (■) in recycling mode (20 mg dm^{-3} initial surfactant). Electrolyte: 0.07 mM hexadecyltrimethyl ammonium chloride solution, i = 4 mA cm^{-2}

In another study on the electrochemical decomplexing of common chelating agents at a BDD electrode, the initial chelator amount also played an important role (Lissens et al., 2003). In that particular study, high decomplexing and COD removal yields could be achieved simultaneously in static mode (0.15 dm^3 electrolyte) while in recycling mode (1 dm^3 electrolyte), a high decomplexing yield was still observed despite poor COD removal.

Influence of the electrolyte pH on surfactant oxidation yield

A significant difference in surfactant degradation was noted between electrolysis with an electrolyte under initially neutral, acid (pH = 4) or alkaline (pH = 10) conditions (Figure 3.6).

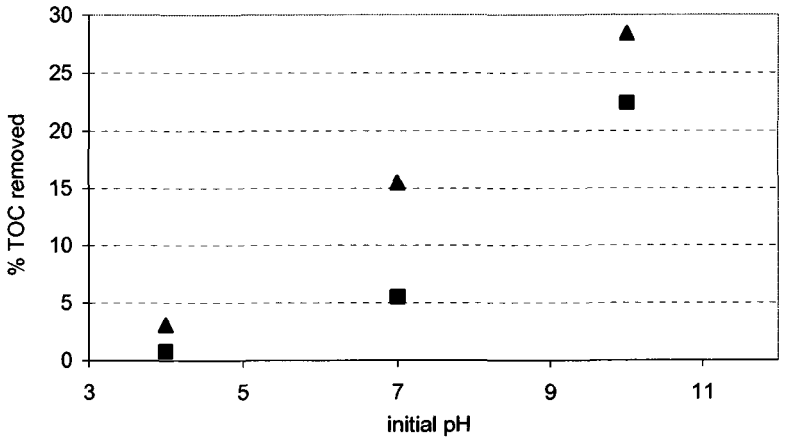

Figure 3.6. Influence of initial pH on the electrochemical TOC removal of the anionic surfactant solution in recycling mode. Key: 0.2 Ah (■) and 0.4 Ah (▲). Electrolyte: 0.0615 mM sodium dodecylbenzenesulfonate, i = 4 mA cm^{-2}

While almost no degradation took place at an initial pH of 4, alkaline conditions clearly promoted the electrochemical combustion of surfactants at the BDD electrode. Leu *et al.* (1998) also concluded that an initial pH of 7 or higher is optimal for the electro-coagulation of surfactants with addition of H_2O_2. Beltrán *et al.* (2000a) found that the removal of sodium dodecylbenzenesulfonate by ozonation, also involving the production of hydroxyl radicals, proceeds especially fast at pH 10.

The influence of the pH mainly acts on the level of the oxidation mechanism. Rodrigo *et al.* (2001) suggested that the oxidation of organics at BDD electrodes in the potential region of water decomposition is due to the action of physisorbed hydroxyl radicals. In this way, the oxidation of sodium dodecylbenzenesulfonate and hexadecyltrimethyl ammonium chloride is promoted by an alkaline pH and can be written as follows, respectively:

$$(C_{12}H_{25})(C_6H_4)SO_3^- + 137\ OH^- \rightarrow 18\ CO_3^{2-} + SO_3^{2-} + 83\ H_2O + 100\ e^- \quad (6)$$

$$(C_{16}H_{33})N^+(CH_3)_3 + 153\ OH^- \rightarrow 19\ CO_3^{2-} + NH_3 + 96\ H_2O + 114\ e^- \quad (7)$$

Both in the static experiments (0.15 dm^3 electrolyte) and recycling experiments (1 dm^3 electrolyte), the pH during electrolysis gradually decreased from a value of 8 to a value of 3 and 6, respectively. This pH drop can to a major extent be explained by the precipitation of (bi)carbonates from the solution as measured by TIC analysis (Figure 3.2). Moreover, the

electrochemical oxidation of organics also resulted in an acidification of the surfactant solutions (equations 6 and 7).

Influence of other process parameters and process optimisation

Additional parameters investigated were flow rate, conductivity of the electrolyte (Na_2SO_4 addition), and current density.

Firstly, the flow rate (0.05 dm^3 min^{-1} vs. 0.250 dm^3 min^{-1}) had no significant effect on electrochemical surfactant removal indicating that in the examined range of flow rates for the recycling experiments, the reaction was not under diffusion control. Without diffusion limitation, the organic compounds are first transformed into organic intermediates before being combusted to CO_2 (Panizza et al., 2001a). This effect is caused by a stabilising adsorption reaction between adsorbed hydroxyls due to water oxidation and the electrode surface (Ferro et al., 2000). Therefore, a theoretical consideration can be made by applying Langmuir adsorption kinetics. The results presented in this study support the idea that the rate of adsorption, being dependent on 1) the rate of arrival of molecules at the electrode surface and 2) the proportion of incident molecules which undergo adsorption, is limiting for the surfactant oxidation rate. The rate of adsorption R_{ads} (expressed as molecules m^{-2} s^{-1}) can then be expressed as (Jung and Campbell, 2000):

$$R_{ads} = S.J_s \qquad (8)$$

with S the sticking probability and J_s the incident molecular flux or collision frequency (molecules m^{-2} s^{-1}). While the sticking probability S is mainly dependent on the concentration of adsorbed species (n) and the presence of any activation barrier to adsorption, the incident molecular flux J_s can be expressed as (Jung and Campbell, 2000):

$$J_s = C_s\left[k_B T/(2\pi m)\right]^{1/2} \qquad (9)$$

with C_s the concentration of the solute in the liquid nearest to the surface, k_B the Boltzmann's constant, T the electrolyte temperature and m the mass of the adsorbate molecule.
Equations 8 and 9 explain why higher reaction rates and higher current efficiencies are found at higher electrolyte volumes (recycling mode) and higher surfactant concentrations (Figure 3.5). In the presence of higher amounts of surfactant, both the sticking probability S and

collision frequency J_s are affected, subsequently leading to a higher adsorption rate R_{ads}. At lower electrolyte volumes (static mode) and lower surfactant concentrations, the adsorption rate is lower and side-reactions (e.g., due to recombination of hydroxyl radicals) become more pronounced resulting in lower current efficiencies.

Secondly, an increase of the conductivity (addition of 1 g dm^{-3} Na_2SO_4) had only a minor effect on TOC removal (7% increase) of both surfactants (not shown) but the required voltage dropped 3-fold compared to the experiments without electrolyte addition. These conditions were considered to be suitable for an estimation of the *SEC* (specific energy consumption) for electrochemical treatment of a surfactant solution because of its representative conductivity for effective household sewage. Taking into account an overall current efficiency of 6 to 12% for both surfactants, an energy demand of 10-20 kWh m^{-3} surfactant solution was needed in the present configuration to electrochemically combust 70-80% of the TOC of a wastewater containing 20 mg dm^{-3} surfactants and 1 g dm^{-3} Na_2SO_4. Alternatively, 3 times more energy would be required for an aqueous surfactant solution with only 20 mg dm^{-3} surfactant. These values were found to be competitive with other oxidation techniques such as ozonisation (Gattrell and Kirk, 1990).

Finally, the current density was investigated as a parameter in a range from 4 mA cm^{-2} to 20 mA cm^{-2}. The TOC removal at the 5-fold higher current density only increased with 7-10% for both surfactants.

As a whole, several measures can be taken at the level of cell design (e.g., inter electrode distance) or electrolysis parameters to optimise an electrolytic process. Important electrolysis parameters with regard to oxidation efficiencies are the current density and the exposed electrode area. With regard to the latter, the equation of Panizza et al. (2001a) can be applied to calculate the required electrode area (eq. 5). It can be derived that the required electrode area A in the recycling mode would need to be 3 to 4-fold higher compared to the batch experiments to achieve the same % TOC removal for a given applied charge. In fact, only the organic loading P and to a lesser extent the average current efficiency η differs for both experiments. A higher current density could make an increase of the electrode surface area largely superfluous but would result in higher energy consumption due to increased water decomposition. As a result, it might be more convenient for larger electrolyte volumes to increase the electrode area A at constant current density I instead of increasing the current density at constant electrode area. This way, more adsorption sites will be available for a given amount of surfactant molecules and higher oxidation yields could be achieved.

Surfactant removal at graphite-based electrodes

Figure 3.7 shows the TOC removal of both surfactants for graphite granules, carbon felt and the BDD anode during the first phase (0-0.5 Ah). Glassy carbon foam (100 ppi and 500 ppi) became available during the course of the testing period and was also tested. The TOC-removal was clearly higher for the graphite-based materials compared to the BDD electrode for both surfactants. The current density obtained for the porous graphite electrodes could not be calculated but was obviously much lower than the one of the BDD electrode (4 mA cm^{-2}) due to its high porosity and 3-dimensional structure. While the BDD electrode was a flat rectangular plate, the graphite granules and the glassy carbon foam completely filled up the anode compartment assuring a much higher contact surface with the liquid.

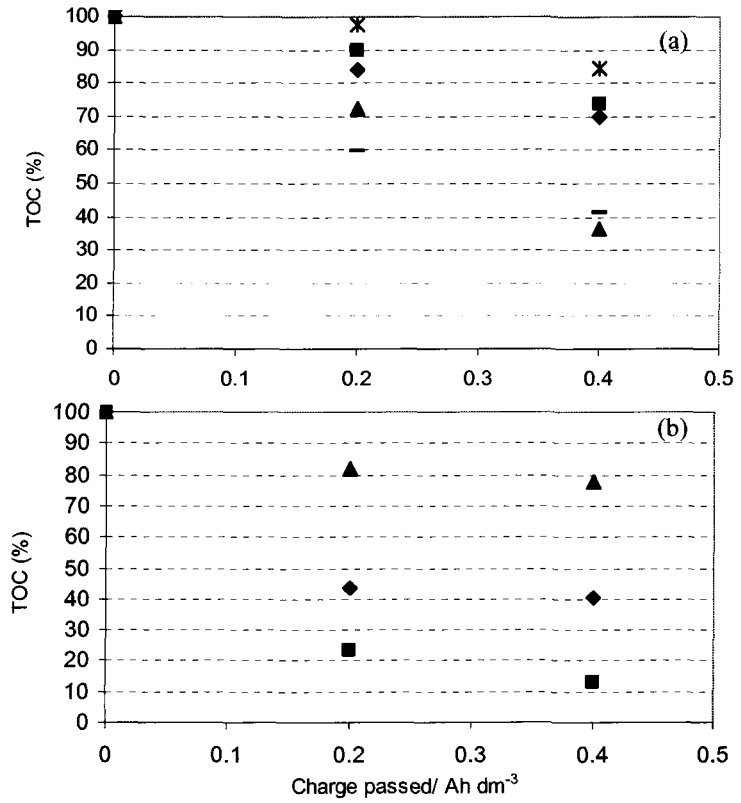

Figure 3.7. TOC decrease with increasing charge during electrolysis of anionic (a) and cationic (b) surfactant solution at carbon-based electrodes in recycling mode. **(a)** glassy carbon 500 ppi (♦), glassy carbon 100 ppi (■), graphite granules (—), BDD electrode (x), carbon felt (▲). **(b)** BDD electrode (▲), graphite granules (♦), carbon felt (■)

Figure 3.8 shows the importance of the exposed electrode area on the TOC removal yields. From Figure 3.8, it can be deducted that the BDD electrode had a much higher oxidation power towards both surfactants compared to a plane graphite electrode with the same exposed surface area. In fact, the superior TOC removal of the 3-dimensional graphite-based electrodes is largely related to the decreased electrolyte volume to electrode surface ratio for these materials.

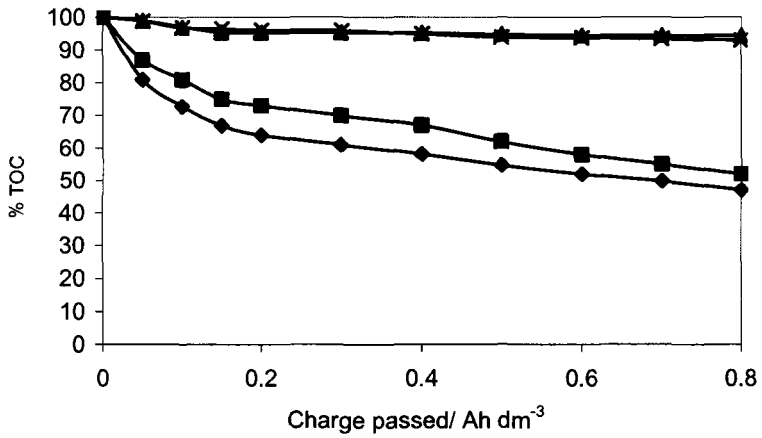

Figure 3.8. % TOC decrease with increasing charge during electrolysis of cationic and anionic surfactant (20 mg dm^{-3}) with plane graphite and BDD anode (equal electrode surface of 70 cm^2) in recycling mode. Key: anionic surfactant with BDD anode (■), cationic surfactant with BDD cathode (♦), anionic surfactant with graphite anode (x), cationic surfactant with graphite anode (▲)

A minor adsorption effect (2%) of the surfactants to the graphite surface could be noticed in the absence of electrical current. This physicochemical adsorption effect was most pronounced with the carbon felt material, probably due to its high porosity and rough surface (not shown). Other authors also stated fouling and adsorption of various carbon electrodes during electrolysis (Gattrell et al., 1990). Kuramitz *et al.* (2002) recently reported a novel electrochemical polymerisation treatment with a carbon fibre anode for the removal of p-nonylphenol, a common endocrine disruptor frequently encountered in non-ionic surfactants. It could be shown that in dilute solutions, the formation of the adsorbed film on the carbon fibre electrode was the result of the electrochemical oxidation of p-nonylphenol at low current density and was the cause for the high removal efficiency (Kuramitz et al., 2002). It is therefore assumed that, considering the low current densities and high contact surface area

applied, the high surfactant removal on the graphite-based electrodes in this study might have been not only the result of electrochemical oxidation as such but also due to electrochemical adsorption. Therefore, a strict comparison in terms of electro-oxidative TOC removal between the BDD anode and the 3-dimensional carbon electrodes could not be made.
Finally, the carbon felt and graphite granules clearly showed abrasion, leading to additional TOC loading of the surfactants solutions. This effect was taken into account when calculating TOC removals by performing electrolysis in the absence of surfactants.

Potentiodynamic measurements

Potentiodynamic measurements were performed to determine the activity of a conventional planar graphite anode and a BDD anode in both aqueous surfactant solutions (Figure 3.9).

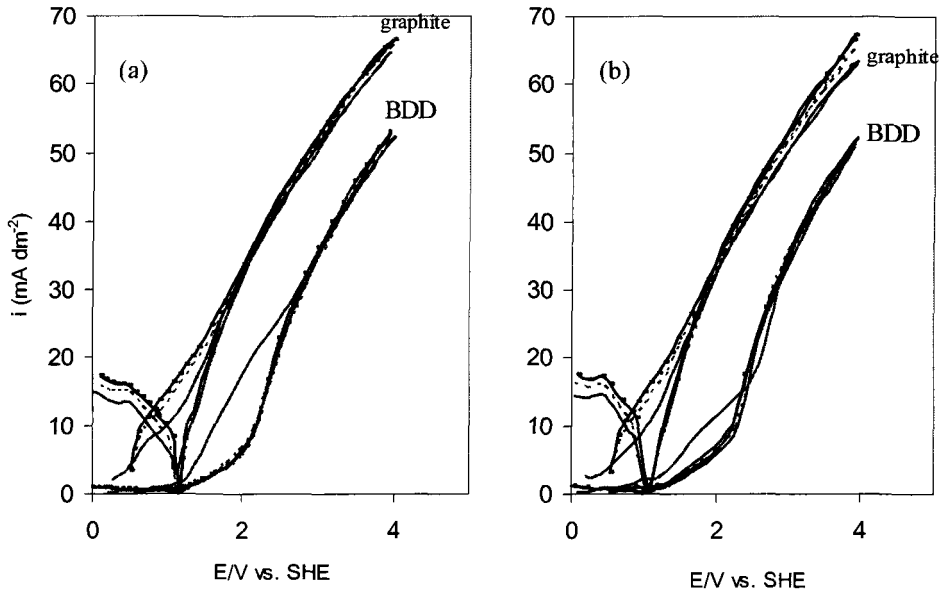

Figure 3.9. Anodic polarisation curves for plane graphite and BDD electrode in anionic (a) and cationic (b) surfactant solution. Key (for each material): *full line*; cycle 1, *dotted line*; cycle 2, *marked full line*; cycle 3. Scan rate 2,5 mV s-1, T = 20°C

The polarisation curves obtained for the anionic surfactant solution (Figure 3.9a) were very similar to the ones observed for the cationic surfactant solution (Figure 3.9b) for both materials. The BDD electrode shows a stable electrode activity: cycle 2 and cycle 3 even

show a very high similarity for the BDD electrode, indicating no electrode activity loss at all. For the graphite electrode, cycle 2 and cycle 3 showed a relatively high similarity, indicating little loss in electrode activity in the potential region of water stability.

Both the graphite and BDD electrode show a consistent electrode activity in the lower region of water discharge (E > 2.3 V vs. SHE). Given the noticed current densities, the rate of oxygen evolution on the BDD electrode in the region of water discharge is lower than on a plane graphite electrode, and occurs at higher electrode potentials. This is consistent with the experience that a BBD electrode has indeed a broader electrochemical operating window. The decrease of BDD electrode activity around 2 V (vs. SHE) for the BDD anode (Figure 3.9) might also indicate the formation of polymeric adhesive products at lower voltages. However, in the region of water discharge (E > 2.3 V vs. SHE), these polymeric substances can be removed again involving besides oxygen evolution also the production of hydroxyl radicals (Comninellis and Pulgarin, 1991; Rodrigo et al., 2001; Iniesta et al., 2001b). In fact, the diamond electrodes have been observed to be chemically inert and microstructurally stable in a wide variety of acidic and alkaline electrolytes in the potential window of water decomposition (Fryda et al., 1999a; Fryda et al., 1999b).

CONCLUSIONS

The electrochemical stability of a BDD electrode and its ability to oxidize and deactivate cationic and anionic surfactants were the focus of this study. At a given charge of 2.7 Ah, TOC removals as high as 83% and 68% could be reached in the potential region of water decomposition for a dilute aqueous sodium dodecylbenzenesulfonate- and hexadecyltrimethyl ammonium chloride solution (20 mg dm^{-3}), respectively. The initial electrolyte pH and initial surfactant amount were found to be major influencing parameters for electrochemical surfactant degradation.

The BDD electrode showed the highest electrochemical surfactant removal compared to a plane graphite anode with equal electrode surface. However, 3-dimensional graphite-based electrodes with very high contact surface showed highest TOC removal towards the tested surfactants, which is presumably the result of combined electrochemical oxidation and electrochemical adsorption. The use of the graphite-based electrodes is limited due to the additional loading of the solutions as a result of abrasion.

Results presented in this study also show that the process is rate-limited by adsorption at molecular level and that the process is not under diffusion control. Attention should be given

to the optimisation of the required electrode area of the BDD electrode at relatively low current density (4-20 mA cm^{-2}) for the surfactant deactivation and/or complete surfactant combustion of larger electrolyte volumes.

This study shows that the electrochemical oxidation of surfactants with BDD electrodes has potential to be competitive with other oxidation processes such as ozonisation (e.g., as a pretreatment) and that the process can be used as an alternative for the treatment of non-biodegradable molecules such as surfactants present in recalcitrant wastewaters.

ACKNOWLEDGEMENTS

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3.2. ELECTROCHEMICAL DECOMPLEXING AND OXIDATION OF COMMON CHELATING AGENTS IN MUNICIPAL AND INDUSTRIAL WASTEWATER[2]

ABSTRACT

The electrochemical decomplexing and oxidation of two frequently used complexing agents in surface treatment and metal finishing - EDTA (ethylene-diamine-tetra-acetic acid) and NTA (nitrilo-tri-acetic acid) - and of organic non-complexing additives used in nickel-plating baths was the subject of this study. By means of a Ti-RuO_2 electrode, a partial indirect oxidation by in-situ electrochemical generation of chlorine compounds could be achieved for EDTA and NTA. However, at a boron-doped diamond (BDD) electrode, complete decomplexing and high COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) (up to 95%) removal occurred at an average current density of 2 A dm^{-2}. It is shown that direct electrochemical oxidation at a BDD electrode resulted in lower energy consumption and higher treatment rates than indirect oxidation at a Ti-RuO_2 electrode. Decomplexing at the BDD electrode occurred at high current efficiencies ranging from 71% to 95% with decomplexing rates in the order of 3.13 mmol $(Ah)^{-1}$ and 5.13 mmol $(Ah)^{-1}$ for EDTA and NTA respectively. COD removal rates obtained were 0.090 g $(Ah)^{-1}$ for EDTA, 0.100 g $(Ah)^{-1}$ for NTA and 0.205 g $(Ah)^{-1}$ for the nickel-plating additives.

Electrochemical decomplexing and oxidation of common chelating agents can render the subsequent metal precipitation and biological waste water treatment of surface treatment and metal finishing effluents more efficient.

Keywords: *electrochemical decomplexing, electrochemical oxidation, chelating agents, BDD electrode*

[2] Redrafted after :
Lissens, G., Verhaege, M., Pinoy, L. and Verstraete, W. (2003). Electrochemical decomplexing and oxidation of organic (chelating) additives in effluents from surface treatment and metal finishing. *Journal of Chemical Technology and Biotechnology* 78(10) : 1054-1060.

INTRODUCTION

Chelating additives such as EDTA and NTA are widely used in the plating industry for various goals. By means of strong complexing agents, a high metal content in the plating bath can be achieved which leads to more energy efficient plating and/or to higher plating rates. They also have a beneficial effect on the throwing power (coating distribution) of the plating bath (Murphy, 1997). Other additives are used to achieve defined mechanical or visual characteristics (brightheners, levelling agents) of the plated surface. Plating baths and effluents (rinse solutions) containing these complexing agents need to be carefully monitored and their entering into the final waste water treatment unit needs to be prevented. This is necessary as these complexing molecules inhibit metal precipitation, leading to exceedingly high metal loadings of the final waste water effluent.

Special means and practices are currently employed to pretreat metal effluents, varying with the type and strength of the complexing agent. The use of suitable chemical precipitants, metered into the complexed waste stream or into the neutralisation tank is effective. Applied chemical precipitants include dithiocarbamates, dithiocarbonates, starch and cellulose-xanthates, poly-quaternary amines and ozone/hydrosulfite (Murphy, 1997). However, precipitation chemicals are generally difficult to dose, show relatively low settling rates and both the chemical itself and its by-products are highly toxic (Craig, 2001). Moreover, the EPA recommends no detectable residuals of chemical precipitants in the effluent, impeding additional post-treatments such as chlorination or peroxide treatment.

Many chelating agents and non-complexing organic additives (e.g., nickel-plating additives) are inert to biological degradation. In the study of Hinck *et al.* (1997) it was shown that none of the four tested enriched microbial inoculants were able to degrade EDTA or DTPA (diethylene-triamine-penta-acetic acid) aerobically. Only at higher concentrations (e.g., for EDTA > 0.5 g dm^{-3}), rapid biological degradation could be achieved. Since effluent concentrations are mostly in the lower ppm-range, biological degradation of complexing species is insignificant, leading to considerable pollution of surface waters (Nowack et al., 1996). Complexing agents such as EDTA for instance can redissolve toxic heavy metals trapped in underwater sediments, allowing them to re-enter in the food chain (Sillanpää and Ramo, 2001).

In recent years, the electrochemical destruction of dissolved organic molecules in aqueous effluents has been studied intensively. The attention has mainly been focussed on the treatment of discharge wastewater from the textile industry, tannery industry and from landfill

leachates (Rao et al., 2001; Vlyssides and Israilides, 1998). These effluents carry a large amount of non- or poorly biodegradable organic pollutants and consequently have a high COD/BOD ratio (Chiang et al., 1997; Wang et al., 2001). Intense research on the electrochemical oxidation of specific organic molecules (e.g aniline, phenol, EDTA, 3-methyl pyridine) has been carried out recently (Kirk et al., 1985; Comninellis and Pulgarin, 1991; Pakalapati et al., 1996; Iniesta et al., 2001a).

For indirect oxidation with in situ generated oxidants such as chlorine or ozone, precious metal coated electrodes (e.g., Pt-Ti) and titanium coated with RuO_2 (RuO_2-Ti) have been proposed. For direct oxidation of organic pollutants, a broad range of anode materials has been tested. However, some of them presented a rapid loss of activity due to surface fouling (glassy carbon), release of toxic ions (PbO_2 anodes) or limited service life (SnO_2 anodes) (Gattrell and Kirk, 1999; Tahar and Savall, 1998; Correa-Lozano et al., 1997). In the study of Kusakabe *et al.* (1986), EDTA and NTA could be electrochemically oxidized at platinum-plated titanium pellets but only moderate COD removals (25-41%) could be reached.

One of the most promising materials developed recently is the boron-doped diamond (BDD) coating. This coating offers exciting new possibilities as electrode material for electrochemical systems. The unique properties of this material being its (1) extreme hardness, (2) corrosion resistance, (3) optical transparency, (4) heat and radiation resistance, and (5) high thermal conductivity make this an attractive electrode material for the electrochemical oxidation of organic pollutants in wastewater (Panizza et al., 2001a; Rodrigo et al., 2001).

In this work, an electrochemical oxidation method is proposed for decomplexing and oxidation (TOC/COD) of three commonly used (chelating) organic additives in an undivided electrolytic cell containing a Ti and a BDD electrode. An electrochemical pretreatment of the complexing agents as proposed in this contribution could result in easier final treatment practice, as additional chemicals to decrease the complexing power of the chelating chemicals are superfluous.

EXPERIMENTAL

Reagents

In this work three types of synthetic solutions have been investigated. The first two contained commonly used complexing agents: EDTA (ethylene-diamine-tetra-acetic acid) and NTA

(nitrilo-tri-acetic acid); the third solution contained a mixture of additives industrially used in nickel-plating baths.

EDTA and NTA solutions were made up by dissolving appropriate amounts of Kestranal 2S (di-sodium salt of EDTA) and Kestranal I (VEL, Belgium) in demineralised water. Based on effective industrial applications, their initial concentrations were ~ 0.01 M for EDTA and ~ 0.02 M for NTA. The solution containing additives for nickel-plating was made up according to the technical information provided by Atotech (the Netherlands). The composition was as follows: Suprème BE (brightener - 2 cm^3 dm^{-3}), NPA (wetting agent - 2 cm^3 dm^{-3}), NLC (brightness carrier – 20 cm^3 dm^{-3}) and ZDA (secondary additive - 6 cm^3 dm^{-3}). The Suprème BE solution contained heterocyclic sulfabetain derivatives and unsaturated ethoxylated alcohols. For proprietary reasons, no further information is available about the chemical structure of these products. This solution will be denoted as SUP. The SUP solution had no complexing power towards metals.

Electrolysis and electrode materials

Electrolysis was performed in a one-compartment electrolytic cell in galvanostatic mode (1 Ampère). A boron-doped diamond coated Nb-electrode (BDD electrode) and a Ti-RuO_2 electrode were used similar to the ones described in section 3.1 of this chapter. The cathode was a plain titanium sheet (Good Fellow, U.K.).

All electrolysis experiments were carried out similarly to the procedure described in section 2.1 of this chapter (*static* and *recycling* experiments). *Static* mode resulted in a lowering of the liquid level with 3 mm in the electrolysis cell and consequently decreased the contact surface area by 6 % per sampling action. Clearly, since the cell current was maintained throughout the experiments at 1 A, the current density increased by the same amount after each sampling action. Small batch electrolysis with the Ti-RuO_2 anode was performed: once with pure chelating solutions and once with solutions to which 1 g dm^{-3} of NaCl had been added. In all other experiments, no additions were made.

Analytical procedures and calculations

All chemical analyses were carried out as described in section 2.1 of this chapter. The concentrations of EDTA and NTA were determined by titration in a buffered solution (pH 10) against $ZnSO_4$ (0.01 M). The equivalence point was detected potentiometrically (Hg drop-

$Hg/Hg_2SO_4/K_2SO_4$ sat.) by means of a Metrohm Titrino DMP785 titrator. As the concentration of EDTA and NTA is directly related to the metal complexing power of the solution, the decrease of the EDTA and NTA content as a function of the electrical power input (Ah), has been defined as the *decomplexing rate*.

The electrochemical decomplexing and oxidation efficiencies were determined by the equations given in *Materials and Methods* under point 3.1 of this chapter.

RESULTS

Electrochemical oxidation at a Ti-RuO_2 anode

A Ti-RuO_2 electrode (DSA®) was first tested in the batch static mode with respect to its oxidation behaviour (TOC removal) towards EDTA, NTA and SUP. A TOC-removal of about 60% was achieved for EDTA (0.01 M) and NTA (0.02 M) after passing an electrical charge of 2.8 Ah. Under the same conditions, no TOC-removal was obtained for the SUP solution. On average, EDTA and NTA were oxidized with an overall oxidation rate of 0.0063 g $(Ah)^{-1}$ dm^{-3} electrolyte.

It is known that Ti-RuO_2 is very efficient for the "in situ" production of chlorine compounds in chloride containing electrolytes. These compounds can subsequently oxidize organic species in the solution (Fryda et al., 1999a). Addition of 1 g dm^{-3} sodium chloride resulted in 10-20% higher TOC removals after passing 2.8 Ah of electrical charge for all species that were studied. Indirect oxidation of these species by in situ generation of chlorine compounds as already described for other organic compounds (Fóti et al., 1999; Ferro et al., 2000) can thus be considered, especially if chloride is present in the electrolyte. However, direct oxidation at a BDD electrode is far more effective as will be shown.

Electrochemical decomplexing and oxidation at a BDD anode

Batch static experiments

Similar experiments as with the RuO_2-Ti electrode have been performed with a BDD electrode. In this case, however, no additions were done in any of the solutions. For all investigated electrolytes, TOC gradually decreased with increasing charge input (Figure 3.10). At a constant current density of 2 A dm^{-2}, the TOC included in the chelating solutions of EDTA and NTA could be completely removed when exceeding a cumulative charge of 1.6-

2 Ah (Figure 3.10). Similar observations were made with regard to the COD decrease of the tested solutions. COD-removal rates were calculated taking into account the change in volume caused by the successive sample withdrawals. EDTA could be oxidized at a rate of 0.097 g $(Ah)^{-1}$ while NTA was removed at 0.163 g $(Ah)^{-1}$. The average ICE-values for COD-removal were 38.4 % for EDTA and 54.5 % for NTA. An energy supply of 164 kWh kg^{-1} EDTA and 94 kWh kg^{-1} NTA was needed to completely remove the COD from the respective electrolytes.

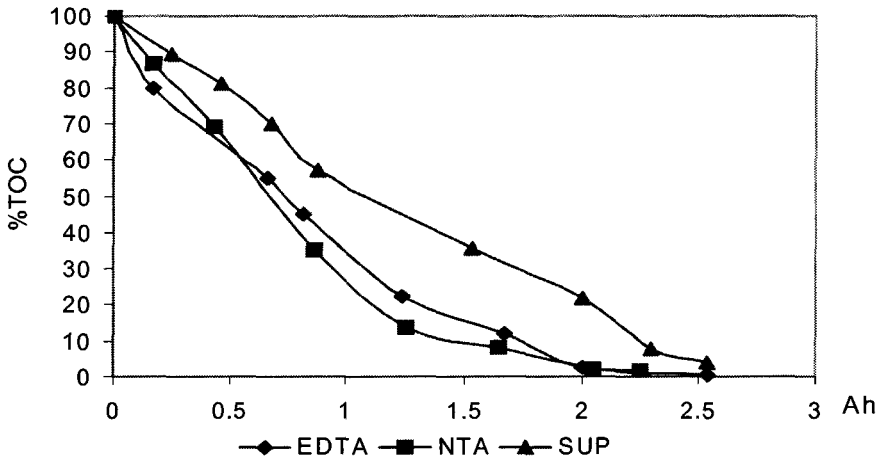

Figure 3.10. % TOC removal as a function of cumulative electrical charge input for EDTA, NTA and SUP with a BDD anode (batch *static* experiment; 0.15 dm^3 electrolyte)

The TOC removal rate was clearly lower for the solution containing the nickel-plating bath additives (SUP) compared to EDTA and NTA (Figure 3.10). COD removal as a function of electrical charge input for the SUP solution is shown in Figure 3.11. The overall COD-removal rate was 0.199 g $(Ah)^{-1}$ and the ICE-value reached was 83.6 %. While the Ti-RuO_2 electrode showed no affinity for the SUP-solution, a total COD removal of 98.7 % could be achieved with the BDD electrode after passing a charge of 2.5 Ah (Figure 3.11).

The change of the complexing power of EDTA and NTA was determined and compared to the COD decrease of both solutions. For both EDTA and NTA, decomplexing initially proceeded at high rates but gradually slowed down after a charge input of 0.5 Ah. The overall decomplexing rate amounted to 9.3 mmol $(Ah)^{-1}$ for EDTA (0.01 M) and 14.2 mmol $(Ah)^{-1}$ for NTA (0.02 M). The electrical energy required for complete destruction of the complexing

power was 42.5 kWh kg^{-1} for EDTA (average ICE of 35.8% for 50 min) and 33.9 kWh kg^{-1} for NTA (average ICE of 40% for 50 min) for a noticed cell voltage of 20 V in both cases.

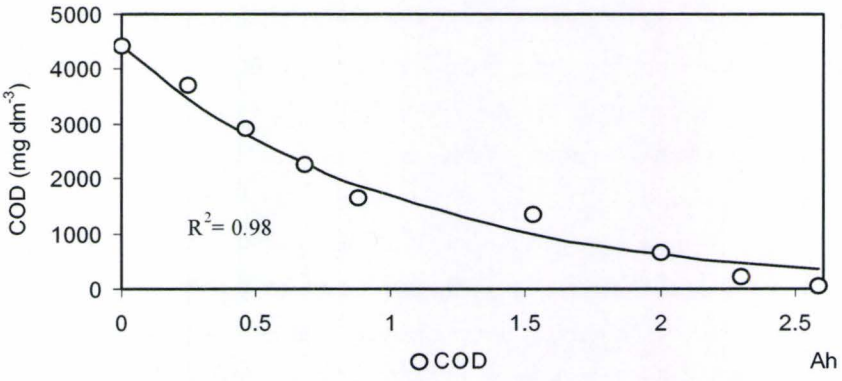

Figure 3.11. Evolution of the COD content as a function of charge of a solution containing nickel plating bath additives (SUP) with a BDD anode (batch static experiment)

The current efficiencies were the highest during the first period of decomplexing for both EDTA (98%) and NTA (82%). Decomplexing efficiencies for both chelating agents however rapidly dropped after passing 0.5 Ah to average values of 7-10%. During the first phase of electrolysis (0-0.5 Ah), also high differences in decomplexing efficiency could be noticed for EDTA (28%) compared to NTA (80%). This difference is probably mainly to be attributed to the different initial concentrations of the species (0.01 M for EDTA versus 0.02 M for NTA).
In all static batch experiments, a gradual increase of the temperature and a decrease of the pH could be noticed. The temperature increase (from room temperature to 40 °C for NTA and 60°C for EDTA at the end of each experiment) was a result of the ohmic resistance of the solution. The electrochemical decomposition of water and the consumption of OH^- by the eletrochemical oxidation reaction of the organics caused a 1-3 units decrease of the pH.

Batch recycling experiments

By continuously recycling 1 dm^3 of electrolyte through the electrolysis cell, complete decomplexing by electrochemical treatment without any chloride addition was possible after passing a charge of 3 Ah for EDTA (0.01 M) and 4 Ah for NTA (0.02 M). The overall decomplexing rate was found to be 3.13 mmol $(Ah)^{-1}$ dm^{-3} EDTA solution and 5.02 mmol $(Ah)^{-1}$ dm^{-3} NTA solution. Both EDTA and NTA solutions could be decomplexed with high

current efficiencies. The average ICE-value for complete decomplexing was 71% for EDTA and 95% for NTA. Assuming the need of 8 e^- per molecule of EDTA and 6 e^- per molecule of NTA to achieve complete decomplexing (Pakalapati *et al.*, 1996), the estimated energy requirement was calculated: 20.9 kWh kg^{-1} for EDTA and 18 kWh kg^{-1} for NTA at a cell voltage of 20 V and a current density of 2 A dm^{-2}. Assuming realistic industrial wastewater concentrations of 2.88 g dm^{-3} (0.01 M) and 3.76 g dm^{-3} (0.02 M) for EDTA and NTA respectively, this corresponds to an average energy requirement of 60 kWh m^{-3} and 67 kWh m^{-3} for complete decomplexing of EDTA and NTA solution, respectively.

The change of COD in these experiments showed a gradual linear decrease. The COD-removal rate was 0.090 g $(Ah)^{-1}$ dm^{-3}, 0.100 g $(Ah)^{-1}$ dm^{-3} and 0.205 g $(Ah)^{-1}$ dm^{-3} for EDTA, NTA and SUP respectively. The average current efficiencies for COD-removal were 30.2 %, 33.5 % and 73% during the first 3 hours of electrolysis for EDTA, NTA and SUP, respectively. The ICE-values were in good correspondence with the Faraday current efficiency (27.4% for EDTA and 30.3% for NTA). The pH of all three chelating solutions remained practically constant within the course of the recycling experiments.

Characterisation and activity of the electrodes

Scanning Electron Microscopy (SEM) analysis of the surface of the BDD electrode and the Ti-RuO_2 electrode revealed clear visual differences in structure (Figure 3.12). While the Ti-RuO_2 electrode showed a rather smooth surface with microscopic cracks, the BDD electrode surface had an amorphous and rather rough structure (Figure 3.12).

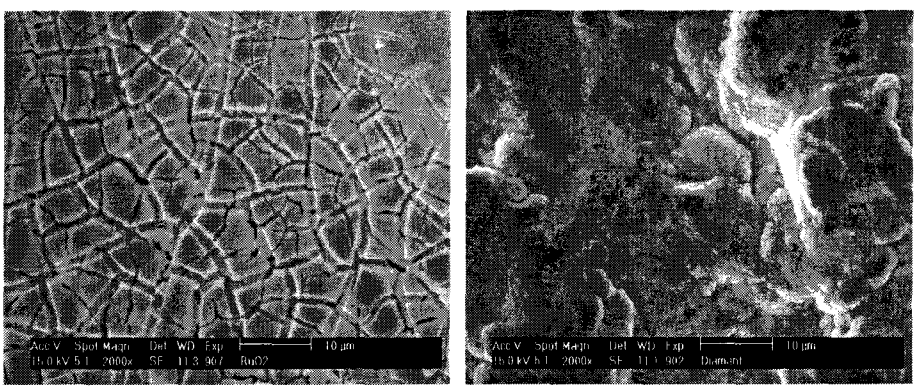

Figure 3.12. SEM of the surface of a Ti-RuO2 electrode (left) and a BDD electrode (right)

By means of anodic polarisation, the electrochemical activity of the BDD electrode was studied in the potential range of 0-4 V (vs. the SHE). For both EDTA and SUP, a small loss in electrode activity around 1.5 V was noticed in the second cycle. This observation can be explained as a result of modification of the electrode surface due to the formation of less conductive oxygen containing functional groups (Van Hege et al., 2002) and indicates that electrode fouling occurs during the 1st cycle. The fouling layer can be removed by further anodic polarisation in the potential region of electrochemical water decomposition at the BDD electrode, resulting in a higher activity in the 2nd cycle. Other authors also stated that in the region of electrolyte decomposition, electrode fouling at the BDD electrode is inhibited (Rodrigo et al., 2001; Panizza et al., 2001b).

DISCUSSION

COD removal rates obtained in the batch recycling experiments were 0.090 g $(Ah)^{-1}$ dm^{-3}, 0.100 g $(Ah)^{-1}$ dm^{-3} and 0.205 g $(Ah)^{-1}$ dm^{-3} for EDTA, NTA and SUP, respectively. Chiang *et al.* (1997) found a COD removal rate of 0.100 g $(Ah)^{-1}$ dm^{-3} in their study of EDTA destruction in a one-compartment cell containing a PbO_2/Ti anode. The removal rate of EDTA calculated from our data corroborate well with this value. PbO_2 electrodes, however, suffer from slight release of Pb, indicating lack of stability (Tahar and Savall, 1998). Kusakabe *et al.* (1986) obtained COD removal rates which are quite higher: 0.263 g $(Ah)^{-1}$ dm^{-3} and 0.194 g $(Ah)^{-1}$ dm^{-3} for EDTA and NTA, respectively. These results were obtained by feeding the electrolyte in the anode compartment (filled up with Pt-plated Ti pellets) in a packed-bed membrane reactor and using Na_2SO_4 as a background electrolyte. No information is available on the long term performance of this membrane cell. From our results and the information available from other authors, long term stable operation with BDD electrodes can be guaranteed (Fryda et al., 1999a; Panizza et al., 2001b).

We have shown that more than 80% of TOC removal can be achieved after passing ~10 Ah dm^{-3} for the EDTA and NTA solutions while 13 Ah dm^{-3} were needed for the SUP solution (Figure 3.10). The nickel-plating additive mixture (SUP) could be readily oxidized on diamond electrodes as a COD removal of 98.7% and an average current efficiency of 84 % was obtained (Figure 3.11). This corresponds to an average specific energy consumption of 97 kWh kg^{-1} COD for the SUP solution. These results confirm the earlier findings that electrochemical destruction at BDD electrodes is worth to be considered for industrial application when organic pollutants have to be eliminated.

From the static batch experiments, it was shown that the difference in energy requirement between complete COD destruction and decomplexing is about four times and two times higher for EDTA and NTA, respectively. This is worth to be kept in mind when dealing with metal containing effluents. Indeed, when electrochemical oxidation is considered a pretreatment operation for more efficient metal precipitation, only decomplexing by breaking down the carboxylic acid groups of EDTA and NTA is necessary and a lot of energy can be saved if there is no requirement for further COD removal.

From the results of the batch static experiments and the batch recycling experiments, it is also obvious that applying high current densities have a detrimental effect on current efficiency and consequently on energy consumption. This is clearly illustrated in Table 3.1, which contains a compilation of the most important results of both types of experiments.

Table 3.1. Compilation of the most important results obtained for electrochemical oxidation of organic chelating additives EDTA and NTA. Cathode Ti; anode BDD

	Batch static experiments		Batch recycling experiments	
	EDTA	NTA	EDTA	NTA
COD removal rate g $(Ah)^{-1}$	0.097	0.163	0.090	0.100
Decomplexing rate mmol $(Ah)^{-1}$	9.3	14.2	3.13	5.02
ICE (decomplexing) %	35.8	40	71	95
Energy requirement kWh kg^{-1}	42.5	33.9	20.9	18.9

Considering decomplexing, it was shown from the batch recycling experiments that complete decomplexing could be achieved at an energy input of 18-20 kWh kg^{-1}, which is similar to the values obtained by Kusakabe *et al.* (1986). Due to the high oxygen overpotential of the BDD electrode compared to a DSA® electrode (e.g., Ti- RuO_2 electrode), decomplexing and electrochemical mineralisation is more efficient with the former.

In this paper the attention has been focussed on the electrolytic anodic destruction of the organic species. Industrial effluents containing these chemicals usually also contain metal

ions and salts. The presence of metals (forming metal chelates) seems to have no effect on the electrochemical destruction of complexing agents such as EDTA (Kusakabe *et al.*, 1986). Salt content lowers the ohmic resistance of the solution and consequently should lower energy consumption.

CONCLUSIONS

It was shown that, using a simple one-compartment electrolysis cell with a Ti cathode and a BDD anode, complete decomplexing and substantial COD removal of NTA and EDTA was possible without addition of chemicals. Decomplexing of EDTA and NTA could be achieved with high current efficiency (up to 95%) and COD/TOC removal with moderate efficiency (38-55%) at a current density of 2 A dm^{-2}. Complete electrochemical mineralisation of a typical solution containing nickel-plating additives has also been demonstrated.

From the results presented in this study, it can be concluded that electrochemical decomplexing and oxidation of common recalcitrant chelating agents and organic additives at a BDD electrode is feasible. Furthermore, it is shown in Chapter 7 that the electrochemical oxidation process for this type of application involves lower operational costs compared to other advanced oxidation processes (AOP's). This study shows that the technology is highly suited as a pretreatment operation for metal precipitation and has the potential to enhance the biological degradation of industrial effluents (e.g., from the metal plating industry).

ACKNOWLEDGEMENTS

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Chapter 4

ADVANCED ANAEROBIC BIOCONVERSION OF LIGNOCELLULOSIC WASTE INTO BIOGAS FOR BIOREGENERATIVE LIFE SUPPORT

4.1. MELiSSA: A BIOREGENERATIVE LIFE SUPPORT SYSTEM FOR ORGANIC WASTE RECOVERY

MELiSSA (Micro-Ecological Life Support System Alternative), developed by the ESA (European Space Agency), has been conceived as a micro-organism and higher plants based artificial system intended as a tool to mimic the earth's natural ecosystem. MELiSSA functions as a frame for the development of technologies for future regenerative life support for long term manned space missions. The driving element of MELiSSA is the maximum recovery of the generated organic waste and its complete biosafe conversion into edible biomass and other renewables (e.g., clean water, oxygen and minerals).

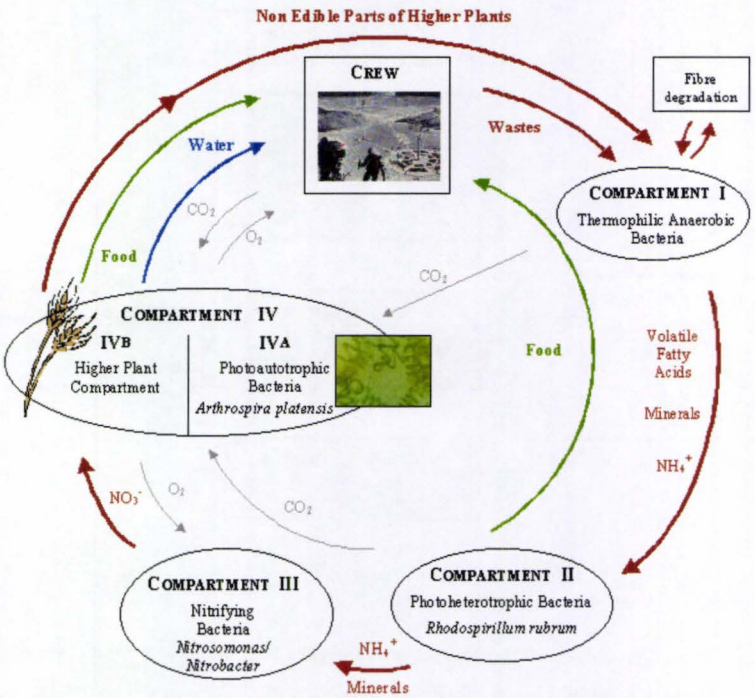

Figure 4.1. The four essential compartments of MELiSSA

MELiSSA comprises 4 compartments with each their specific organisms (Figure 4.1).The first compartment of the loop is responsible for the anaerobic biodegradation of the waste (generated by the crew) and thus its performance largely determines the conversion efficiency of the total MELiSSA cycle. In the compartment as presented in Figure 4.1, the waste is converted (or liquefied) into dominantly volatile fatty acids, ammonia and salts which are further transported to the next compartment. However, with this compartment, only moderate liquefaction yields in the range of 60-65% could be reached with only 55% liquefaction efficiency for sugars and fibrous material (Lasseur and Paillé, 2001). In addition, due to the lack of sanitation steps in the loop, absolute biosafety for the crew cannot be guaranteed.

To improve the performance of the first compartment, a European project was carried out whereby a series of biological and physicochemical treatments were tested for maximum (C, N, P...) recycling and bioconversion of the waste in closed cycle perspective (treatments summarized in Figure 4.2). Secondly, the project also aimed at providing maximum biosafety in terms of exclusion of possible contamination of the recycled products by potentially dangerous propagates such as pathogenic micro-organisms. The results of this project are described in section 4.2.

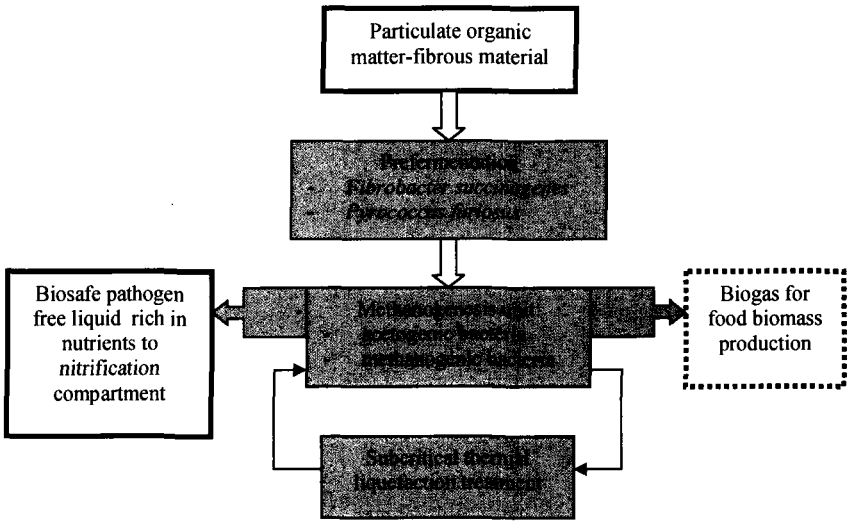

Figure 4.2. Possible configuration of novel pre- and post-treatments in conjunction with anaerobic digestion for maximum bioconversion of organic waste in a life support context

4.2. A TOTAL CONVERTING AND BIOSAFE LIQUEFACTION COMPARTMENT FOR THE RECOVERY OF WASTE IN A LIFE SUPPORT CONTEXT[1]

ABSTRACT

The feasibility of nearly-complete conversion of lignocellulosic waste (70% food crops, 20% faecal matter and 10% green algae) into biogas was investigated in the context of a life support project. The treatment comprised a series of processes, i.e. a mesophilic laboratory scale CSTR (continuously stirred tank reactor), an upflow biofilm reactor, a fiber liquefaction reactor employing the rumen bacterium Fibrobacter succinogenes and a hydrothermolysis system in near-critical water.

By the one-stage CSTR, a biogas yield of 75% with a specific biogas production of 0.37 l biogas g^{-1} of VSS (volatile suspended solids) added at a RT (hydraulic retention time) of 20-25 d was obtained. Biogas yields could not be increased considerably at higher RT, indicating the depletion of readily available substrate after 25 d. The solids present in the CSTR-effluent were subsequently treated in two ways.

Hydrothermal treatment (T ~ 310-350°C, p ~ 240 bar) resulted in effective carbon liquefaction (50-60% without and 83% with carbon dioxide saturation) and complete sanitation of the residue. Application of the cellulolytic Fibrobacter succinogenes converted remaining cellulose contained in the CSTR-effluent into acetate and propionate mainly.

Subsequent anaerobic digestion of the hydrothermolysis and the Fibrobacter hydrolyzates allowed conversion of 48-60% and 30%, respectively. Thus, the total process yielded biogas corresponding with conversions up to 90% of the original organic matter.

It appears that particularly mesophilic digestion in conjunction with hydrothermolysis at near-critical conditions offers interesting features for (nearly) complete and hygienic carbon and energy recovery from human waste in a bioregenerative life support context.

Keywords: *biogas, biosolids, carbon cycling, food waste, hydrothermolysis*

[1] Redrafted after :
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INTRODUCTION

In bioregenerative LSS (life support systems), lignocellulosic crop residues and biosolids (e.g., faeces) represent an important source of biochemical energy both for energy recovery and for the subsequent production of foods in space (Kohlmann et al. 1995; Strayer and Atkinson 1997; Fulget et al. 1999; Kudenko et al. 2000). Microbial cellulose utilization in natural environments is responsible for one of the largest material flows in the biosphere and is of great interest in relation to carbon cycling at global and local scales (e.g., life support) (Lynd et al. 2002).

On earth, anaerobic digestion of various organic wastes is a well-established technology in which part of the energy can be recovered in the form of biogas (Schober et al. 1999; Zhang & Zhang 1999; Stroot et al. 2001; Liu et al. 2002). The anaerobic decomposition process can be divided in four steps of which the first step, the hydrolysis of particulate biopolymers (e.g., cellulose, hemicellulose), is considered the rate-limiting step for the overall process (Schieder et al. 2000; Sanders et al. 2000). Because certain cellulosic polymers are shielded by lignin in a solid and water-insoluble structure, these polymers have little bioavailability for many fermenting microorganisms (Ahring et al. 1999; Liu et al. 2002).

Various (thermo) chemical and biochemical hydrolysis methods that split plant biopolymers into water-soluble and biodegradable short-chain compounds have been the subject of investigation in recent years (Delgenes et al. 2000; Schieder et al. 2000; Kim & Hong 2001; Liu et al. 2002). By employing pretreatments, biogas yields and conversion rates from organic waste can be enhanced and retention times can be lowered, allowing for more compact digester systems.

Thermal hydrolysis technologies have been explored as pre-and post-treatment for the anaerobic digestion of lignocellulose. These technologies can be divided into wet oxidation (Schmidt et al. 2002), steam explosion (Saddler et al. 1993) and hydrothermolysis (Schieder et al. 2000). During treatment, lignocellulose is (partially) degraded into smaller fragments (cellulose, hemicellulose, lignin and sugar derivatives) by the action of hot water or steam under moderate pressures (e.g., 5-50 bar) and temperatures (180-325°C), either in the absence or presence of a catalyst (e.g., pressurised oxygen) (Schmidt & Thomsen 1998; Lendormi et al. 2001a; Lendormi et al. 2001b; Bonmati et al. 2001). The thermal prehydrolysis step also offers other advantages such as complete sanitation of the waste and a decrease of the methane reactor volume (Schieder et al. 2000).

In biochemical hydrolysis processes, enzymes (e.g., cellulases) or (metabolically engineered) fermenting microorganisms are used to convert cellulosic compounds into monomeric sugars and/or organic acids at ambient temperatures and pressures. In this respect, ruminant cellulolytic bacteria are able to digest cellulose and produce organic acids such as succinate and acetate at high rates (Fields et al. 2000). The bacterium *Fibrobacter succinogenes* is widely considered one of the most active and most important cellulose-digesting anaerobic bacteria in the rumen (Martin & Martin 1998).

The objective of the present study was to determine the anaerobic digestion efficiency of a dilute organic substrate (2% ± 0.2 dry mass) composed of food crops, faeces and green algae by means of anaerobic digestion completed by hydrothermolysis and cellulolytic digestion by *Fibrobacter succinogenes*. The study furthermore explores the potential of digester residue liquefied by a tubular near-critical (T_{crit} = 374°C, p_{crit} = 221 bar) high temperature/high pressure reactor. The carbon liquefaction power and fiber degradation of the hydrothermolysis and *Fibrobacter succinogenes* digestion was evaluated by a series of batch anaerobic digestion tests on the residual solids derived from primary CSTR anaerobic digestion. The overall biogas yield for anaerobic digestion in combination with hydrothermolysis and *Fibrobacter succinogenes* digestion was determined and the applicability of the system for life support was evaluated.

MATERIALS AND METHODS

Substrate composition and preparation

The substrate was composed in such a way that it resembled a concentrated organic waste stream produced by humans in a LSS (Fulget et al. 1999). On DM (dry mass) basis the organic waste consisted of 70% crop residues (1/3 chopped wheat straw, 1/3 green cabbage, 1/3 soya waste), 10% of green algae (*Spirulina platensis*) and 20% of faecal matter. All components were suspended in tap water to obtain a final DM concentration of 2-3%. The suspension was stored at 4°C.

Prior to anaerobic digestion, all substrate components except wheat straw were ground under wet conditions with a conventional kitchen grinder to obtain millimetre-sized particles. Wheat straw was ground in dry state with a rotary cutter that yielded straw particles in the millimetre range (1-3 mm). The characteristics of the individual substrate compounds are given in Table

4.1. The total substrate suspension (2% DM) had the following properties: COD = 21 g l^{-1} (chemical oxygen demand), TAN = 0.41 g l^{-1} (total ammonia nitrogen), Kj-N (Kjeldahl-nitrogen) = 1.4 g l^{-1}, VSS = 24 g l^{-1}, ash-content = 4.4 g l^{-1}, total fibers = 35%, (%) cellulose = 21%, (%) hemicellulose = 10% and (%) lignin = 4%.

Table 4.1. Composition of the compounds of the organic substrate in terms of DM (dry matter), COD (chemical oxygen demand), TC (total carbon) and TN (total nitrogen)

	Mass-%	DM-content	COD	TC	TN
	[g_{DM} g_{DM}^{-1}]	[g_{DM} g^{-1}]	[g_{COD} g_{DM}^{-1}]	[g_{C} g_{DM}^{-1}]	[g_{N} g_{DM}^{-1}]
Straw	0.23	0.93	1.30	0.39	0.0087
Soya	0.23	0.88	1.21	0.39	0.0166
Cabbage	0.23	0.08	1.26	0.37	0.045
Algae	0.1	0.95	1.49	0.42	0.1027
Faeces	0.2	0.2	n.d.	n.d.	n.d.

After anaerobic digestion, the CSTR effluent solids were separated by centrifugation of the CSTR effluent at 7000 g for 15 min. Subsequently, the solids were recovered by decantation and were dried for at least 24 h. These solids were then further treated in two ways (Figure 4.3).

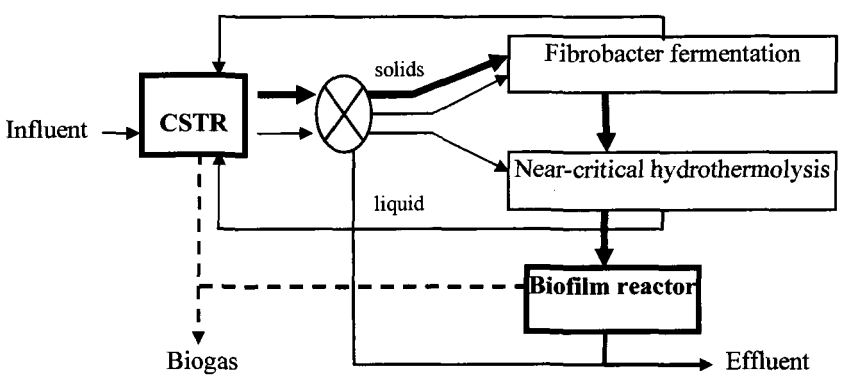

Figure 4.3. Conceptual scheme of the process sequences. The arrows indicate process sequence 1, the **bold** arrows indicate process sequence 2

In process sequence 1, the CSTR solids were treated either by hydrothermolysis or *Fibrobacter* fermentation followed by a second separate digestion for the sake of comparison of the biogas yields of the two treatments. In process sequence 2, the CSTR solids were first treated by *Fibrobacter* fermentation followed by hydrothermolysis and finally diverted to a second digestion (Figure 4.3).

The CSTR solids were subjected to additional size reduction steps prior to hydrothermolysis. Due to the small internal diameters of the high temperature/high pressure tubular reactor, the solid residues had to be ground to a sufficiently small particle diameter in order to prevent clogging of the apparatus. This was accomplished by means of a rotary cutter using two sieves in succession, having a mean mesh size of 1000 µm and 250 µm, respectively. The resulting material was additionally treated in a conventional coffee mill.

CSTR methanogenic reactor

A cylindrical 10 l PVC methanogenic reactor of CSTR-type was incubated at a constant temperature of 34°C and was continuously shaken at 70 rpm (New Brunswick INNOVA, U.K.). The pH in the reactor was at a constant value of 7.3-7.4. The reactor contained 7.5 ± 1 l mixed liquour and was seeded with active methanogenic granular sludge from an anaerobic digester of a potato-processing firm (Primeur, Belgium). The produced biogas volume was measured daily and the biogas composition on a weekly basis.

Because of the particulate nature of the substrate, the reactor was fed manually and fed-batch wise. Prior to sampling, the content of the reactor was homogenized to prevent build-up of solids. The volumetric loading rate (B_v) of the mesophilic CSTR ranged from 1.5-2.5 g of COD l^{-1} day^{-1} over a period of 12 months. The hydraulic retention time (RT) of the reactor was set at 20 d. Batch fermentation tests were performed with raw substrate at reaction times varying from less than 10 days to 65 days and at an initial concentration of 0-2.8 g l^{-1} COD to derive the influence of the initial concentration (g l^{-1} COD) and the RT (d).

High temperature/high pressure tubular reactor

The main building blocks of the tubular reactor are depicted in Figure 4.4. The high-pressure reaction unit is designed as a stainless steel tubular reactor (o.d.= 6.35 mm, i.d.= 3.05 mm) with a variable volume up to 100 ml and capable of withstanding operating pressures up to 300 bar and temperatures up to 450°C.

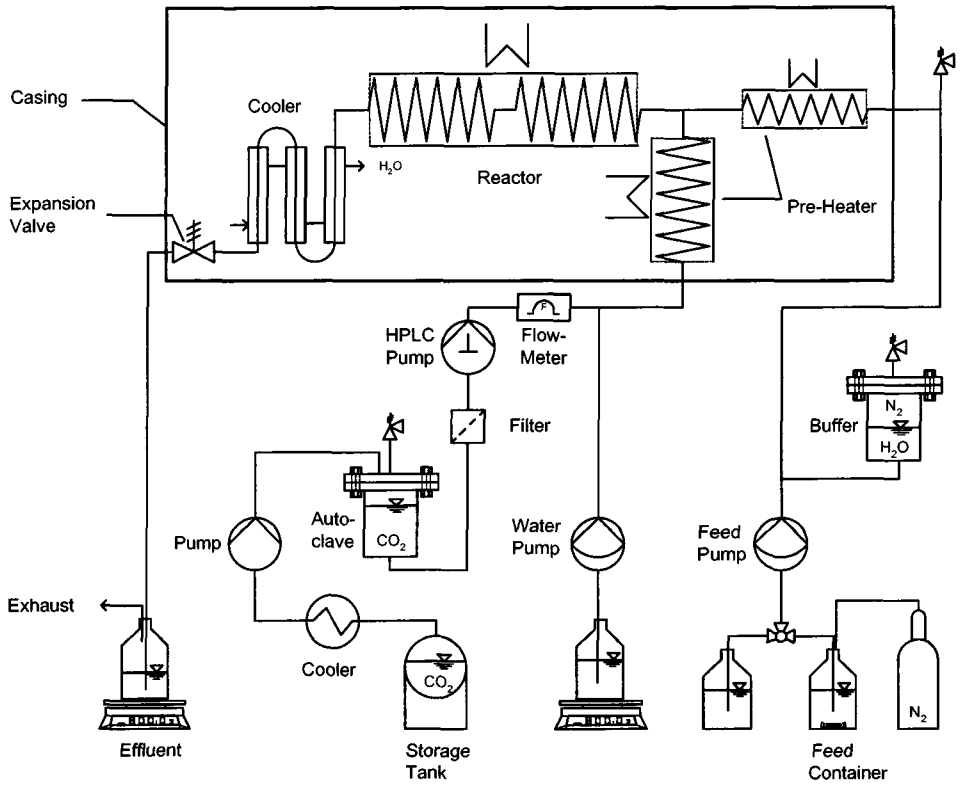

Figure 4.4. Experimental hydrothermolysis apparatus for subcritical liquefaction

Before entering the reaction unit the feed suspension was moderately preheated in an upstream coil, which has an inner volume of V_{Pre} = 38 ml. The reaction was started by mixing the feed suspension with a pure water stream (under nitrogen atmosphere), which was delivered into the system by a high-pressure membrane pump and heated to high temperatures in a second preheater. The preheater and the tubular reactor were electrically heated by means of heating jackets, which could be adjusted separately by a temperature control system (Horst HT-60 controller). In order to decrease the heat losses to the surroundings, the complete high temperature section of the apparatus was thermally insulated. The substrate suspension containing the particulate matter was fed into the system by means of a high-pressure membrane pump (LEWA EK1/V metering pump). Carbon dioxide was delivered from a storage tank, liquefied in a cooler and processed to an autoclave by means of an air-driven pump. Passing a filter unit, the carbon dioxide was introduced into the system by means of a HPLC pump. The amount of carbon dioxide was measured by a mass flow meter.

Fibrobacter succinogenes cultivation and fermentation

Fibrobacter succinogenes S85 (ATCC 19169) was originally isolated from the bovine rumen (Bryant & Doetsch 1954). A pure culture of this strain was grown anaerobically under 100% CO_2 in a sterile basal medium containing (l^{-1}): 450 mg KH_2PO_4, 450 mg K_2HPO_4, 900 mg NaCl, 1.8 g $(NH_4)_2SO_4$, 90 mg $MgSO_4$, 90 mg $CaCl_2$, 3 mg $MnSO_4.6H_2O$, 0.3 mg $CoCl_2.6H_2O$, 8 mg $FeSO_4.7H_2O$, 0.25 mg biotin, 0.005 mg para-aminobenzoic acid, 500 mg cystein, 4 g Na_2CO_3 and a volatile fatty acid mixture (Gaudet et al, 1992). Of this pure culture, 400 ml was used to inoculate a stirred (100 rpm) fermentor (4 l) after a redox potential reduction at -350 mV and temperature equilibration at 39°C. The pH, temperature and redox potential were measured on-line. Na_2CO_3 was added (4 g l^{-1}) by each substrate addition to stabilize the pH to a value of 6.9. Sterilised residual solids from the CSTR-reactor were added in batches (44 g in 2.8 l basal medium) at 1.5% DM to the basal *Fibrobacter* medium. Fermentations were performed for a period of 16 d.

Fermentation of hydrothermolysis and *Fibrobacter* hydrolyzates

Following process sequence 1 (Figure 4.3), batch digestion tests were performed with both the hydrothermolysis and *Fibrobacter* hydrolyzates in erlenmeyer flasks containing either 400 ml (small batch tests) or 800 ml (large batch tests) mixed liquour of the CSTR-reactor (depending on the organic strength of the substrate applied). The reaction times in the batch tests varied from 15 to 75 days. In all batch fermentation tests, a control was included which only contained mixed liquour from the CSTR main digester. The *Fibrobacter* hydrolyzate and hydrothermolysis hydrolyzate were added at various COD-concentrations (g COD l^{-1}) and fermented at various reaction times (d). The residues were added only once at the start of the experiment in amounts ranging from 40-150 ml, representing a COD of 0.1-2.7 g per test bottle. The biogas production and pH were continuously measured for each bottle.

Following process sequence 2 (Figure 4.3), a mesophilic 1.5 l fixed-bed biofilm reactor was employed to determine the biogas yield of the hydrothermolysis hydrolyzate. The reactor was filled with 1 dm^3 of polypropylene carriers, with a specific surface of ca. 500 m^2 m^{-3}. To initiate the biofilm formation, 1 l of tapwater and 500 ml of sludge from the CSTR were added. Subsequently, the liquid was continuously recycled at an upflow velocity of 2 m h^{-1} and at daily basis 5 g of COD $l^{-1}.day^{-1}$ was dosed during a period of 10 weeks. After establishment of the biofilm, the hydrolyzates were added to the fixed-bed biofilm reactor and

continuously recirculated with an upflow velocity of 2 m h^{-1}. The biogas production and parameters as COD_t, COD_s, VFA and pH were followed on a daily basis, during a total period of 21 days per experiment.

Analytical procedures and calculations

Van Soest analysis was performed for the quantitative determination of cellulose, hemicellulose and lignin fraction (Van Soest 1963; Van Soest et al. 1991). The COD, Kj-N, TAN, TSS (total suspended solids), VSS and ash-content of the digester influents and effluents were determined according to Standard methods (Greenberg et al. 1992). Biogas yields (%) were calculated on the basis of COD and VSS mass balances.

The volumetric biogas production was monitored by means of an electronic gas counter (Bergedorf, Hamburg-Harburg, Germany) with a resolution of 1 ml and by means of (acidified) calibrated water displacement columns for the CSTR digester and the batch tests, respectively. Biogas was analyzed for methane and carbon dioxide composition using a Varian 3800 gas chromatograph (PoraPLOT Q column (25 m, I.D. 0.53 mm, 20 µm), helium flow of 7 ml min^{-1}, isothermal 40°C) equipped with a universal dual channel TCD-detector. Individual VFA concentrations (acetic, propionic, butyric, isobutyric, valeric, isovaleric, caproic, isocaproic) were measured with a GC-FID AS800 gas chromatograph equipped with a FID-detector and N_2 as carrier gas. The column used was an Alltech (Deerfield, USA) EC-1000 (30 m, I.D.: 0.32 mm, d_f: 0.25 µm). Formic acid was measured by means of ion-exchange chromatography (Macherey und Nagel EC 200/4 Nucleosil 100 5NH2 column) equipped with a RI-detector. The analyses were conducted isothermally at 40°C with an eluent mixture of 78% acetonitrile and 22% water at a flow rate of 0.7 ml min^{-1}.

The IC (inorganic carbon) buffer of the digester substrate and effluent was measured by means of titration with a Titrino 716 titrator (Metrohm, Switzerland). The sample was titrated as such with 0.1 N HCl (down titration profile) from the actual pH to pH 2.5 and data were automatically acquired and analysed (Van Vooren et al. 1999; Van de Steene et al. 2002).

$SO4^{2-}$ -S and PO_4^{3-} -P concentrations were measured before and after fermentation with a Metrohm IC 761 ion-chromatograph (IC) (metrosep A supp 5 (150 x 4 mm) column) with conductivity detector. Both influent -and effluent samples were diluted 100-fold after centrifugation and filtered over a 0.45 µm filter prior to injection.

Elementary composition analysis was performed with a CNS-analyser at 1100°C (Leco-CNS-2000-Analyser). The dissolved carbon was determined by means of a TOC-analyser

(Elementar "HighTOC + TN_b"). The liquefaction degree of the solids was then calculated by dividing the dissolved carbon after liquefaction by the total influent carbon.

HPLC analysis with a ligand exchange chromatography (LEC) column (L = 300 m, i.d. = 7.8 mm) (Macherey Nagel, Nucleogel Sugar; RI detector) with an isothermal oven temperature of 72°C (distilled water as eluent at 0.5 ml min^{-1}) was performed to determine the composition of the hydrothermolysis hydrolyzate with respect to sugars and degradation products (e.g., hydroxymethylfurfural) thereof.

RESULTS

CSTR-digester performance and biogas yield

Table 4.2 summarizes the digestion parameters for the bioconversion of the raw substrate.

The digester pH remained constant and total VFA concentrations during operation were low, indicating a stable digester performance for the given loading rate (1.5-2.5 g of COD l^{-1} day^{-1}). Cellulose removal corresponded well with VSS and COD removal yields and amounted to 72% on average. The digester efficiently converted the majority (78% on VSS basis) of the organic substrate into biogas with average methane content of 65%. The specific gas production at a RT of 20 d was found to be relatively high (0.37 l of biogas g^{-1} of VSS added). In terms of nitrogen mass balances, an increase of the TAN-level in the effluent was observed while the Kj-N present in the influent (1.4 g l^{-1}) and the effluent (1.2 g l^{-1}) was nearly the same (Table 4.2). Hence, the majority of the organically bound nitrogen (mainly proteins) present in the raw substrate could be converted into ammonium species at a retention time of 20 days (Table 4.2).

Simulation and identification of the IC buffer titration results showed the presence of an IC buffer peak at a pH of 6.3 for both the digester influent and effluent. The bicarbonate concentration increased from 39 mM to 175 mM during biological treatment, whereas the ammonia nitrogen concentration increased from 0.4 to 1 g l^{-1}. For the influent, a third peak was observed but could not be identified (around pH-value 3.3), probably referring to the presence of high-weight proteins and/or acids.

Overall, the PO_4^{3-}-P (mg l^{-1}) concentration of the raw substrate was high (500 mg l^{-1}) relative to domestic sewage. Influent SO_4^{2-}-S concentrations were moderate and resulted in 0.7% H_2S of the volume biogas produced. Van Soest analysis showed that fibers accumulated in the mixed liquour of the digester, leaving a solid digester residue consisting of about 49% of

fibrous matter (cellulose, hemicellulose and lignin). This fibrous solid residue, which accounted for 15-20% of the raw substrate on VSS and COD basis, was the subject of further liquefaction and subsequent biomethanisation (see Figure 4.3).

Table 4.2. Performance data for the CSTR during operation at an average volumetric loading rate of 1.5-2.5 g of COD l^{-1} day^{-1} and a RT = 20 d

Parameter	CSTR
Retention time (d)	20
Methane (%)	65% ± 3
Specific gas production (l biogas g^{-1} of VSS added)	0.37 ± 0.02
Volatile fatty acids: (mg l^{-1})	
Acetate	30 ± 5
Propionate	3 ± 1
Butyrate	1 ± 1
Isobutyrate	1± 1
Valerate	0
Isovalerate	10± 2
Capronate	0
Isocapronate	1± 1
Total VFA (digester)	46± 7
pH	7.4 ± 0.2

Mass balance parameters	Influent (g l^{-1})	Effluent (g l^{-1})	Removal (%)
TSS	28	7.5	73 ± 2
VSS	24	4.8	78 ± 2
COD	21	5.9	80 ± 8
Cellulose	5.9	1.6	72 ± 10
Total Kjeldahl Nitrogen	1.4	1.2	14 ± 4
Total Ammonia Nitrogen	0.4	1	-150 ± 2

Batch fermentation tests with raw substrate showed that for an applied initial concentration of 1.85 g l^{-1} of COD, biogas yields on COD and DM analysis varied from 25% for 10 d to 90% for 65 d reaction time. The increase in biogas yield as a result of an increase of the retention time was most pronounced for the lower retention times (10-20 days) (results not shown). The lower bioconversion found in the batch tests (70%) was not significantly different from the

conversion yield found during continuous operation of the CSTR (78%) for the same reaction time (23 d).

Figure 4.5 shows the CSTR biogas yield at different retention times. At a lower RT (15 d), only 35-50% of the COD of the raw substrate could be transformed into methane. For a more conventional RT of 20-25 d, on average 70-78% of the raw feed could be converted into biogas. At a RT as high as 60-75 d, the raw substrate was converted into biogas with a yield of 80-85%.

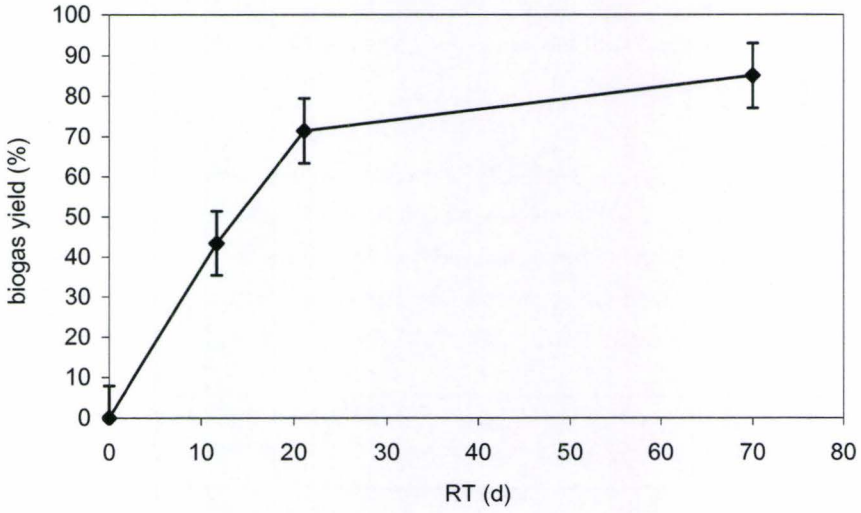

Figure 4.5. CSTR biogas yield from raw substrate at 3 different retention times. 100% biogas yield corresponds to a conversion of 0.5 l biogas for 1 g COD. Standard deviations are based on the biogas yields at 3 different initial concentrations (1.1, 1.8 and 2.8 g/l of COD)

Fiber liquefaction by hydrothermolysis

Despite the variable temperatures and pressures applied, the carbon liquefaction efficiencies for one and the same batch of CSTR solids varied between a relatively narrow range of 44-57% (Table 4.3, run No 2-6). Experiments No 2 and No 3 show that the reproducibility of the thermal reactor was high (less than 2% difference). The fourth experiment was performed at a lower temperature of 300°C and yielded a significantly lower degree of liquefaction of 45%, though the residence time of 87 s was much longer than for the other runs. Even an increase

in temperature to 406°C (experiment No 6), which is well above the critical temperature of pure water, did not result in a higher degree of liquefaction within the residence time employed in the experiments. This implies that for this particular batch, about 40 % of the carbon was very difficult to liquefy without a further increase in residence time. However, a significantly higher carbon liquefaction yield was reached for experiment No 1. This demonstrates that the solids batch used for No 1 presumably contained less inert material compared to the solids batch used for No 2-7.

In order to increase the degree of conversion, carbon dioxide was added to the system (No 7) by which the pH of the influent was considerably lowered. Carbon liquefaction yields higher than 80% could be reached with the same solids batch as No 2-6 by equilibrating the liquor with 50% CO_2 (Table 4.3).

Table 4.3. Carbon liquefaction efficiencies of the CSTR effluent solids at various conditions (T = 301-406°C, p = 233-264 bar). No 1-6: carbon liquefaction of various effluent solid batches without CO_2 saturation; No 7: carbon liquefaction of effluent solids with 50% CO_2 saturation. All experiments were performed with the same batch of CSTR solids except experiment No 1

No	T [°C]	P [bar]	RT [s]	Carbon liquefaction [%]*
1	360	240	25.1	73.9
2	366	238	39.7	56.4
3	360	233	38.8	57.1
4	301	250	87.2	44.8
5	319	247	45.2	58.7
6	406	264	> 35	57.2
7	341	238	50	83.4

* calculated as $C_{soluble\ out}/C_{in}*100$

HPLC analysis of the hydrolyzates at a hydrothermolysis temperature of 310°C and 350°C showed that saccharides were present only in very small concentrations (< 50 mg l^{-1}). Raffinose, maltose, fructose, glucose, pyranose, and hydroxyl-methylfurfural, could be detected at 310°C. For these conditions, distinct peaks were found at residence times shorter than that of raffinose, which are due to the formation of oligo-saccharides. For the 350°C

hydrolyzate, oligo-and mono-saccharides could not be detected. Instead, pyranose and hydroxymethylfurfural were produced in significantly higher amounts. Beside sugars, formic and acetic acid accounted for up to 20% of the total soluble carbon. The concentrations of higher acids were negligible. Due to the production of acidic degradation products during hydrothermolysis, the pH of all thermally treated influents decreased to values of 4.1-4.4.

Essentially all nitrogen (95-100%) initially present in the solid phase (measured by elementary analysis) could be converted to water-soluble components in the course of the hydrothermal degradation. NH_4^+-N and NO_3^--N amounted to about 60% of the total nitrogen detected in the liquid phase after hydrothermolysis. The remaining nitrogen fraction (40%) could not be identified but it is assumed that this fraction is present in the form of other oxidized nitrogen species. The contribution of free amino acids to this unidentified fraction can be considered to be very minor, since it was shown that amino acids are instable and subject to consecutive reactions at the temperatures applied in the experiments (Walter et al. 1967). This finding was supported by own studies on the decomposition behaviour of bovine serum albumin in near-critical water.

With regard to the gas phase, no other components than nitrogen (added at the start) and carbon dioxide could be detected in any of the experimental runs. As can be inferred from the results of these measurements, the amount of carbon in the gas phase had only a minor contribution (2-3%) to the total carbon introduced into the system. In accordance with the high temperatures and pressures applied, the effluents of the hydrothermal treatment were found to be completely sterile.

Fiber fermentation by *Fibrobacter succinogenes*

Fed-batch fermentations were performed by the rumen bacterium *Fibrobacter succinogenes* on the CSTR-effluent solids. The overall liquefaction yield for the recalcitrant digester solids was found to be 41% on DM-basis (data not shown).

Figure 4.6 shows the typical profile of degradation products formed during *Fibrobacter* fermentation of the CSTR-effluent solids with substrate addition at 0 h and 180 h. During the first hours of culture, mainly succinate and acetate were produced as sole metabolites causing a concomitant small decrease in pH (0.3-0.5 units). After 24 hours, the production of succinate stopped and other VFA began to be produced (mainly acetate and propionate). Final VFA concentrations were highest for acetate and propionate corresponding to values up to 3 g l^{-1} and 1.1 g l^{-1} respectively.

Gas analysis showed that CO_2 was the only gaseous compound produced during *Fibrobacter* fermentation in quantities representing less than 10% of the input carbon.

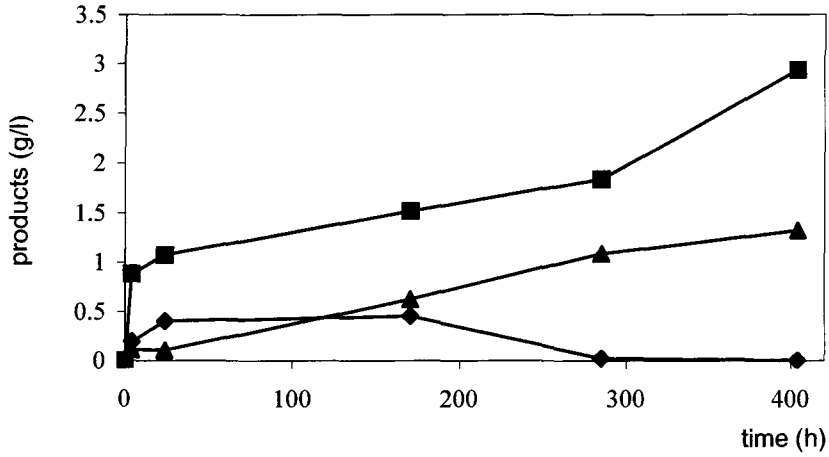

Figure 4.6. Production of organic acids during *Fibrobacter succinogenes* fermentation on CSTR-effluent solids at 15 g l^{-1}. Key: ■ = acetate, ▲ = propionate, ♦ = succinate

Biogas yields of hydrothermolysis and *Fibrobacter* hydrolyzates

CSTR conversion efficiencies for the hydrothermolysis hydrolyzate were significantly higher compared to the *Fibrobacter* effluent (Figure 4.7). For the hydrothermolysis hydrolyzate, biogas yields of 48% and 60% were observed at a reaction time of 20 days and 40 days respectively. As can be derived from Figure 4.5, about 30% of the COD of the *Fibrobacter* residue could be converted into biogas at a reaction time of 20 days or more. Hence, the transformation of the hydrothermolysis hydrolyzate was dependent on the retention time and proceeded at a higher efficiency compared to the *Fibrobacter* hydrolyzate.

Figure 4.8 shows the COD removal and biogas production of the hydrothermolysis hydrolyzate following process sequence 2 (Figure 4.3) employing an upflow biofilm reactor. During the first 7 days, 59.5% of the influent COD could be converted into biogas (Figure 4.8a) with an average methane content of 65%. The VFA-content of the hydrolyzate was low (VFA_{total} = 87 mg l^{-1}) and was completely removed after 1 day of fermentation. The cumulative biogas production mounted to 0.75 l after 7 days or an average biogas production rate of nearly 0.5 l per g COD removed (Figure 4.8b).

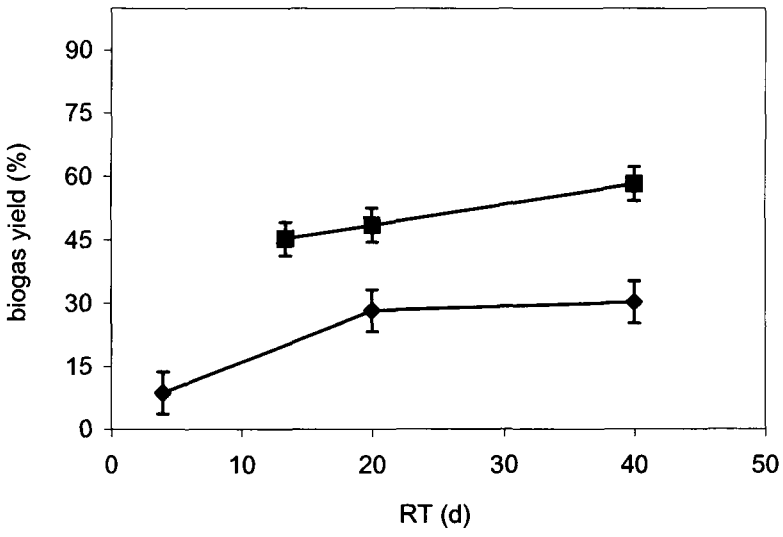

Figure 4.7. Biogas yields of the undiluted hydrothermolysis hydrolyzate (■) and the *Fibrobacter* hydrolyzate (♦) in batch fermentation tests at various reaction times (triplicate tests). Initial concentrations applied were 0.2-0.75 g l^{-1} of COD for the hydrothermolysis hydrolyzate and 2-3 g l^{-1} of COD for the *Fibrobacter* hydrolyzate

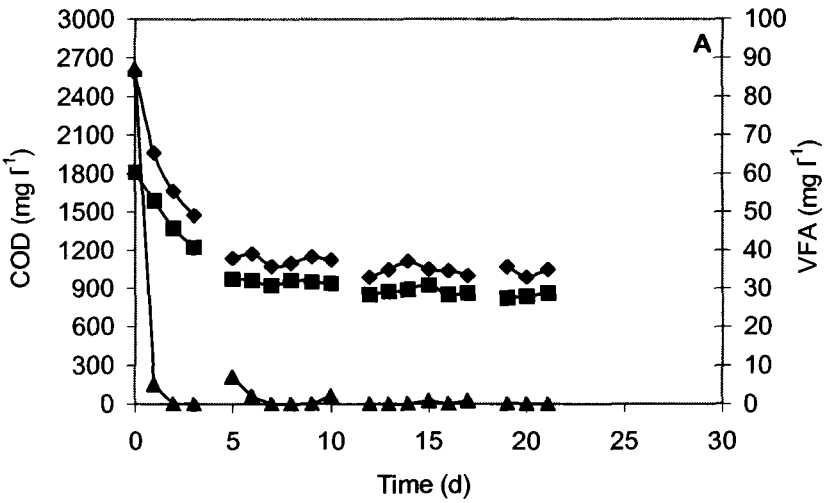

Figure 4.8a. Anaerobic mesophilic digestion of diluted hydrothermolysis hydrolyzate with an upflow methanogenic biofilm reactor. The hydrolyzate was recycled through the biofilm reactor for a period of 21 days at an upflow velocity of 2 m h^{-1}. ***Left Y-axis***; ♦ = COD_{total}, ■ = $COD_{soluble}$, ***right Y-axis***; ▲ = Total VFA

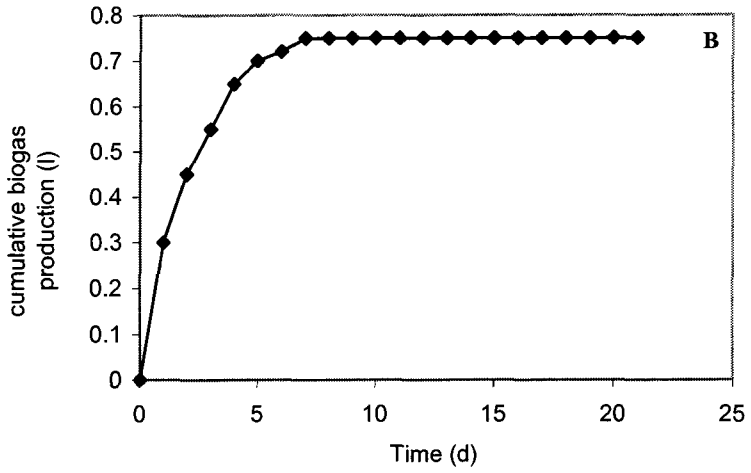

Figure 4.8b. Cumulative biogas production corresponding to Figure 4.8a

Based on the biogas yields from the raw substrate and the liquefied CSTR solids by hydrothermolysis and *Fibrobacter* fermentation, the overall conversion efficiencies for the raw substrate were calculated (Figure 4.9).

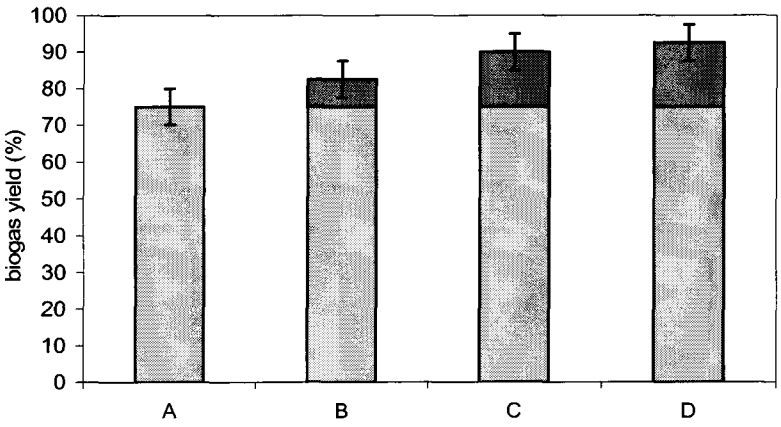

Figure 4.9. Biogas yield of raw substrate for mesophilic digestion (A), mesophilic digestion combined with *Fibrobacter* fermentation (B), mesophilic digestion combined with hydrothermolysis (C) and mesophilic digestion combined with *Fibrobacter* fermentation and hydrothermolysis (D). Key: ***Light grey*** = biogas yield of CSTR; ***Dark grey*** = biogas yield after *Fibrobacter* fermentation and/or hydrothermolysis. The material not converted to biogas was inert to biological transformation

By applying the sequence CSTR digestion/ *Fibrobacter succinogenes* digestion/CSTR digestion, an overall biogas yield of 82% could be reached. The use of hydrothermolysis in combination with CSTR digestion (column C and D) increased the biogas production with 10%, giving rise to an overall biogas yield of 90%. The overall biogas yield found in column D (92%) following process sequence 2 (Figure 4.3) was however not significantly higher compared to column C (Figure 4.9).

DISCUSSION AND CONCLUSIONS

In this work, the nearly-complete anaerobic conversion of a life support substrate consisting of food waste, green algae and faeces was studied. It was shown that a VSS decrease of 78% and a specific gas production of on average 0.37 l biogas per g of VSS added could be reached by means of a one-stage CSTR-type mesophilic digester (RT = 20 d). These performance data are in good accordance with reported conversion efficiencies for non pretreated biosolids (e.g., manure) and lignocellulosic waste (e.g., rice straw) with biogas yields around 50% on COD basis (or 0.2-0.25 l of CH_4 g^{-1} of VSS) (Bonmati et al. 2001) and specific biogas productions in the range of 0.39 L of biogas g^{-1} of VSS (Zhang & Zhang 1999), respectively.

The biogas yield of the CSTR during continuous operation (78%) was statistically in the same range compared to the biogas yields calculated from the batch fermentations (70%). The slightly lower value for the batch test was most probably caused by the subtracted value from the control (mixed liquor without COD loading) used in the batch tests.

The organic waste employed had a high nutrient content with a C/N ratio in the range of 10, mainly due to the presence of faecal matter (20% DM) and the green alga *Spirulina platensis* (10% DM). Hansen et al. (1998) reported that anaerobic digestion of pig manure was inhibited at a pH of 8 corresponding to a free ammonia concentration of 1.1 g l^{-1} or more which caused a decrease in methane yield. Despite the relatively high TAN concentrations in the effluent (1 g l^{-1}), methanogenesis was never inhibited at the applied OLR, presumably because of the lower digester pH (7.4 on average). The IC buffer constituted together with the total ammonia (NH_3 and NH_4^+) a high buffer capacity in the digester, which explained the pH stability of the digester. Since the average pH of the reactor was 7.4, part of the total ammonia (TAN) was present as ammonia and could possibly be transferred to the gas phase. However, it is generally accepted that up to a pH of 7 the total ammonia is only present under the form

of NH_4^+ (Perrin, 1965). Moreover, no significant losses in nitrogen could be detected by TAN -and Kj-N analysis. Therefore, it is assumed that nitrogen losses by means of the produced biogas were minor.

A significant amount of ortho-phosphate was taken up in the digester since the effluent ortho-phosphate concentration was only 1/3 of the influent concentration. Phosphorous is generally much less mobile than nitrogen and can be strongly adsorbed to organic matter and/or sludge (Nowack & Saladin 2000). The enrichment of ortho-phosphate in the digester might thus be explained by adsorption on particulate matter.

The pronounced influence of the RT on the biogas yield (Figure 4.5) gives evidence that after the first 20 d of digestion, the biogas production significantly reduces due to the exhaustion of readily available substrate (day 25-40). Since the digester substrate contained a considerable amount of lignocellulose, it can therefore be hypothesized that the hydrolysis of particulate organic matter (e.g., lignocellulose) became rate-limiting during the course of digestion.

Hydrothermolysis of the CSTR solids resulted in high carbon liquefaction yields, varying between 44-83% (Table 4.3). Sakaki et al. (1996) also showed that cellulose decomposes very rapidly in catalyst free hot compressed water of around 300-400°C, and that the resulting water-soluble products quickly decomposed. The data suggest that adding carbon dioxide to the influent might stimulate hydrolysis kinetics, as can be inferred from the increased degree of liquefaction (Table 4.3). Due to the increased solubility of carbon dioxide in water at elevated temperatures and pressures, the addition of carbon dioxide can serve as a means to lower the pH-value without the need of mineral acids. By decreasing the pH, many acid catalysed reactions like the hydrolysis of glycosidic bonds can be greatly accelerated (Lehninger 1975). This approach bears the advantage of easily recovering the carbon dioxide in the gas phase, such that additional downstream unit operations like neutralisation and precipitation steps become superfluous (Liu 2000).

The hydrolysis temperature during hydrothermolysis played a major role in the formation of degradation products. The production of hydroxymethyl furfural, which is known to be a potential inhibitor of methanogenesis (Rivard & Grohmann 1991), was promoted at higher temperatures. Other potential fermentation inhibitors could however not be detected. Subsequent digestion efficiencies for the undiluted hydrothermolysis hydrolyzate were significantly higher at higher RT (Figure 4.7). Different from CSTR fermentation, the digestion of the diluted hydrolyzate derived from the most recalcitrant solids occurred without any lag phase in the upflow biofilm reactor with a COD removal of 59% (Figure 4.8a) and a high biogas yield (Figure 4.8b). These results indicate that the toxicity of the

hydrothermolysis hydrolyzates to the bacterial consortia in both methane reactors was of no concern for the reliability of the system within the tested time limits. Addition of carbon dioxide to lower the pH of the influent suspension seems to have a catalyzing effect on the hydrolytic degradation and will therefore be systematically investigated in further studies by varying the operating condition, including different degrees of carbon dioxide saturation.

The rumen bacterium *Fibrobacter succinogenes* followed by subsequent methanogenesis was able to convert 30% of the CSTR solids into biogas (Figure 4.7). Initially, *Fibrobacter succinogenes* mainly produced acetate and succinate as dominant fermentation products (Figure 4.6). In other studies, where *Fibrobacter* was grown in cellobiose-limited conditions (5 mM), also succinate and acetate were produced (Maglione and Russell 1997; Fields et al. 2000). However, the reconsumption of succinate and the production of large amounts of acetate (up to 3 g l^{-1}) and propionate (1.1 g l^{-1}) are rather unusual. The production by *Fibrobacter succinogenes* of large amounts of acetate from succinate has already been demonstated by in vivo ^{13}C NMR studies (Bibollet et al, 2000). This phenomenon of reversion of the succinate pathway was observed as well in adherent and non-adherent cells and was favoured by high nitrogen concentration.

The presented thermal/biochemical conversion system demonstrates that a life support organic waste can nearly be completely converted (90% biogas yield) into energy-rich methane gas, leaving a mineral -and nutrient rich effluent and carbon dioxide suitable for the growth of secondary foods in space.

Due to its efficiency, the presented system is highly attractive for life-support systems where hygienic, rapid and total conversion of organic waste is of major importance (Fulget et al. 1999). The recovery of energy from the the high temperature hydrothermolyis step is in principle feasible, the heat integration of the complete system being an issue that has to be solved in future work.

ACKNOWLEDGEMENTS

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Chapter 5

ALKALINE WET OXIDATION PRETREATMENT OF ORGANIC MUNICIPAL WASTE FOR SIMULTANEOUS SACCHARIFICATION AND FERMENTATION INTO ETHANOL[1]

ABSTRACT

The feasibility of efficient ethanol production from the cellulose fraction of food waste enriched with wheat straw and woody yard waste by means of simultaneous saccharification and fermentation (SSF) by Saccharomyces cerevisae was investigated after (thermal) wet oxidation pretreatment. The effects of varying wet oxidation parameters (e.g., temperature (185-200 °C), pH, and oxygen pressure (3-12 bar)) on the enzymatic cellulose and hemicellulose degradation of the organic waste were evaluated by means of enzyme assays with commercial cellulases and β-glucosidase.

The SSF procedure at 10% dry solids (DS) revealed cellulose to ethanol conversion efficiencies ranging from 50-70% for the food waste and 40-79% for the yard waste at cellulase loadings varying from 5-25 FPU (filter paper units) g^{-1} of DS, corresponding to 22 and 24 g L^{-1} ethanol for the highest enzyme loading. At moderate enzyme loadings (15 FPU g^{-1} of DS), the ethanol yield was 65% and 69% of the theoretical yield for the food and yard waste, respectively. It could be unambiguously shown that the wet oxidized filtrates did not exhibit any toxicity to the yeast, a frequently encountered phenomenon observed during ethanol production from various biomasses.

Finally, carbon mass balances illustrated that 66% and 49% of the lignin could be converted into biodegradable fatty acids (mainly acetate) for the food and yard waste respectively, making the SSF residue suitable for further biological treatment.

This study shows that carbohydrate recovery from organic lignocellulosic waste in the form of ethanol is feasible from a biotechnological point of view, leaving a low-value residue potentially suitable for methane recovery.

Keywords: *municipal waste, wheat straw, cellulose conversion efficiency, simultaneous saccharification and fermentation, wet oxidation*

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INTRODUCTION

Municipal solid waste (MSW) is produced abundantly and its disposal is of ever growing concern worldwide. Cellulose and hemicellulose (holocellulose), derived from e.g., yard waste, food waste, and paper waste, are the principal biodegradable components of municipal waste and are found together with lignin in rigid hemicellulose complexes. These two polysaccharides, which can make up to 80% of lignocellulose for some refuse components (*i.e.* paper), are of particular interest for the production of bio-ethanol from biomass (Bjerre et al., 1996).

The rate and extent of microbial degradation of MSW-associated lignocellulose is severely limited due to the shielding effect of lignin on holocellulose (Liu et al., 2002). Various MSW refuse components have been reported to have moderate to high lignin levels (11-44%) (Eleazer et al., 1997). The lignin concentration and structure are major factors determining the rate of biological degradation of MSW (Eleazer et al., 1997). Woody yard waste for instance can contain up to 30% lignin on DS basis (Gellens et al., 1995). However, also the crystalline structure of cellulose plays a role as it prevents penetration by enzymes or microorganisms and even by small molecules such as water (Lynd et al., 2002).

The natural availability of the native materials is an important parameter in the overall feasibility of a biofuel process. MSW is a ubiquitous byproduct from human activity and is either source-separated collected (e.g., yard and kitchen waste) or separated from the non-organic fraction in grey waste processing plants (De Baere, 2000; Gellens et al., 1995).

In order to make holocellulose accessible during fermentation, a pretreatment of the waste is required. The biochemical utilization of lignocellose for bio-ethanol production requires the fractionation or separation of the cellulose, hemicellulose and lignin prior to fermentation, often referred to as the "biorefinery approach". Biological pretreatments most often involve the use of lignin-degrading organisms and cellulose-degrading enzymes derived from cellulolytic bacteria and mostly filamentous fungi (Curling et al., 2002; Thygesen et al., 2003). These methods are promising due to their high specificity for cellulose or hemicellulose (Thengerdy and Szakacs, 2003). However, in many cases chemical treatment is required to enhance the enzymatic efficiency in subsequent saccharification and fermentation (Bjerre et al., 1996). Moreover, biological pretreatment does not ensure sanitation of contaminated lignocellulosic waste (*i.e.* MSW) prior to fermentation.

Thermal pretreatments with or without catalysts have the benefit to render lignocellulose more accessible to enzymatic attack by solubilizing part of the hemicellulose and lignin

fraction and to decrease the cellulose crystallinity (Schmidt and Thomsen, 1998). Thermal treatments involving steam (*i.e.* steam explosion) (Liu et al., 2002) and thermal hydrolysis (Schieder et al., 2000) are by far the most investigated processes for pretreatment of the MSW and yard waste prior to biomethanation or bio-ethanol production (Emmel et al., 2003; Garrote et al., 2001a; Garrote et al., 2001b; Garrote and Parajo, 2002; Josefsson et al., 2002; Sawada and Nakamura, 2001; Tengborg et al., 2001). Some studies also involved the addition of acidic reagents (mostly H_2SO_4) to achieve acid-catalyzed hydrolysis of the waste (Nguyen et al., 1999). Although these studies have demonstrated enhanced fermentation yields, the utilization of hemicellulose hydrolyzates after the steaming processes is often restricted due to the presence of dehydrated degradation products of both sugar and lignin, *i.e.*, 2-furfural and 5-hydroxymethyl-2-furfural (Bjerre et al., 1996).

Alternatively, wet oxidation mostly in combination with alkaline addition has been investigated as a pretreatment for wood (Schmidt et al., 2002; Chang et al., 2001a; Chang et al., 2001b) and other cellulosic substrates such as wheat straw (Klinke et al., 2002; Chang et al., 2001a; Chang et al., 2001b). Wet oxidation has been reported to have significant advantages over other thermal pretreatment technologies such as lower production of sugar degradation products (*i.e.* furan derivatives) and significant decrease of cellulose crystallinity (Schmidt and Thomsen, 1998). Furthermore, wet oxidation under alkaline conditions has been reported to permit fast lignin fragmentation and therefore greatly favours biomass biodegradability (Verenich and Kallas, 2002).

In this study, the wet oxidation process as a pretreatment for bio-ethanol production was applied to two carbohydrate-rich waste fractions, namely food waste enriched with wheat straw and woody yard waste. The influence of three wet oxidation process parameters (T, O_2 pressure and initial pH) on the enzymatic convertibility for ethanol production was studied and the optimal wet oxidation conditions were determined by means of a cellulase convertibility assay. Simultaneous saccharification and fermentation (SSF) was performed on the enzymatically most accessible wet oxidized wastes at different enzyme loadings in function of the ethanol yield.

MATERIALS AND METHODS

Raw substrate

Food waste was collected from a municipal waste plant in Frederikssund (Denmark) during wintertime. The food waste consisted of source-sorted kitchen waste mainly and was collected in plastic bags. During treatment in the waste plant, the waste was shredded (< 1 cm) and plastics were removed using a rotating drum. Shredded wheat straw was added to the drum at a final concentration of 8% of the total DS (dry solids) content of the MSW. This was done to increase the DS content and for stabilising the waste. Fresh woody yard waste was collected from a local site in Denmark (DTU) during wintertime and was composed of small branches (< 2 cm diameter) of different kinds of trees (mainly oak and birch). Both wastes were used for the study after air drying until a DS content of 95-96% and after subsequent cutting of the waste into millimetre (mm) particle size with a cutting-knife mill.

Wet oxidation reactor and sample preparation

WO (wet oxidation) experiments were carried out in a high-pressure autoclave with a tubular loop and an impeller constructed at Risø National Laboratory as described by Bjerre *et al.* (1996). The autoclave was designed as a cylindrical vessel (V = 1890 ml) made of Sandvik Sanicro 28 (27% Cr, 31% Ni, 3.5% Mo, 1% Cu) with an impeller that continuously pumped the liquid through the tubular loop (Figure 5.1).

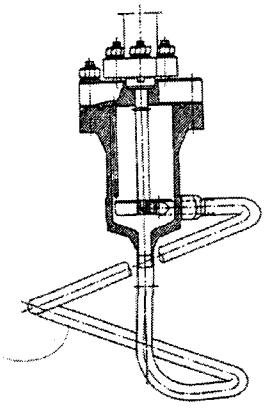


Figure 5.1. Wet oxidation reactor with tubular loop constructed at Risø National Laboratory

Prior to heating, the reactor lid was closed and oxygen pressure was supplied from a gas cylinder. The autoclave was mounted on a rack, facilitating temperature control by raising or lowering it in a heating bath. After wet oxidation, the reaction was terminated rapidly (< 3 min) by immersing the reactor in a water bath.

WO experiments were performed batch-wise by suspending 60 g DS of substrate in 1 litre of deionized water (6% DS). To determine the effects of temperature, initial pH and oxygen pressure, four wet oxidation conditions were tested (Table 5.1 and Table 5.2) for both wastes whereby 2 parameters were changed per experiment. The holding time (10 min for food waste and 15 min for yard waste) was kept constant during all experiments. Because of the good heat-transfer conditions of the reactor, both the heating and cooling period could be restricted to approximately 2.5 minutes. The initial pH of the 6% DS solution was made alkaline by addition of 2 g l^{-1} Na_2CO_3 (sodium carbonate) prior to closure and pressurization of the autoclave with oxygen. The pH of the solutions was measured before and after wet oxidation. After WO, the wet oxidized solids and the filtrate were separated by vacuum filtration. Subsequently, the solids were washed with deionized water and dried in a climate chamber at 20°C and 65% relative humidity. After drying, the solids were stored in paper bags. Wet oxidized filtrates were stored at -18°C.

Table 5.1. Wet oxidation pretreatment conditions for the food waste. All wet oxidation experiments were performed at 6% DS

WO condition	**A**	**B**	**C**	**D**
Temperature (°C)	185	185	195	195
Time (min)	10	10	10	10
Oxygen Pressure (bar)	3	12	3	12
Na_2CO_3 addition (g l^{-1})	0	2	2	0
pH before wet oxidation	4.8	7.2	7.2	4.8
pH after wet oxidation	4.4	4.6	5.1	4.0

Table 5.2. Wet oxidation pretreatment conditions for the yard waste. All oxidation experiments were performed at 6% DS

WO condition	A	B	C	D
Temperature (°C)	185	185	200	200
Time (min)	15	15	15	15
Oxygen Pressure (bar)	3	12	3	12
Na_2CO_3 addition (g l^{-1})	0	2	2	0
pH before wet oxidation	6.3	9.5	9.5	6.3
pH after wet oxidation	3.4	3.7	4.2	2.7

Chemical analysis

Analysis of the solid fiber fraction

The solid fractions derived from WO were shredded and hammer milled to pass a 1 mm screen prior to analysis. The wet oxidized solids and raw waste were analysed for their contents of glucan, xylan, arabinan, Klason lignin and ash after strong acid hydrolysis (72% w/w H_2SO_4 at 30°C for 60 min) followed by dilute acid hydrolysis (4% w/w H_2SO_4 at 121°C for 60 min) (Gilbert et al., 1952). Subsequent sugar analysis was carried out by HPLC analysis (Klinke et al., 2002).

For the raw materials, the non-cell wall material was characterised by two methods. First, a triple extraction procedure according to Puls (1993) was performed prior to strong and dilute acid hydrolysis. The method consisted of extracting the 1 mm sieved substrate by means of soxhlet extraction with petrol-ether/acetone/70% methanol (in water) for a period of 3 h for each solvent. The removal of the different non-cell wall compounds (*i.e.* fats, waxes, resins) was determined gravimetrically. Second, the water solubles, pectin/NCWM (non-cell wall material) and resins/fats/waxes fraction of the raw material were determined by a modified gravimetric grass fiber analysis method (Browning, 1967) by extracting the raw wastes with water (30 min, 25°C) to remove the water solubles, and 3% EDTA at pH 3.3 (4 h, 84 °C) to extract the pectin and NCWM fraction.

Analysis of the liquid fraction and strong acid hydrolyzates

Total glucose, xylose and arabinose concentrations (sum of monomeric and polymeric sugars) in the wet oxidized filtrates were determined after dilute sulfuric acid hydrolysis (4% w/w H_2SO_4 at 121°C for 10 min) (Gilbert et al., 1952). Quantification of free monomeric sugars and carboxylic acids present in the wet oxidized filtrates was carried out after pH adjustment to pH 2-2.3 with 0.1 M H_2SO_4. Sulfate ions were precipitated by an equivalent amount of barium hydroxide ($Ba(OH)_2$) and separated by centrifugation. Samples were filtered (0.45 µm) prior to HPLC analysis and diluted 10-fold with HPLC eluent (4 mM H_2SO_4) when necessary.

Glucose, xylose, arabinose, ethanol and total carboxylic acids (sum of malic, succinic, glycolic, formic and acetic acid) as well as furan derivatives (sum of 5-hydroxy-2-methylfurfural (5-HMF) and 2-furfural) were quantified by HPLC analysis according to Klinke *et al.* (2002).

The total reducing sugar concentration of the WO filtrates, acid hydrolyzates and enzymatically treated samples were analyzed spectrophotometrically by a dinitrosalicylic acid (DNS) assay according to Miller (1959) using xylose as a standard. Samples were diluted 2.5-25 fold depending on the concentration of the hydrolyzates measured.

Carbohydrate recovery calculations

Carbohydrate recoveries (cellulose and hemicellulose) were calculated to estimate their losses during WO following

$$\text{Carbohydrate recovery } \%[w/w] = \frac{(\text{Carbohydrate}_{HPLC})}{\text{Carbohydrate}_{\text{raw MSW}}} \quad \text{(i)}$$

with $\text{carbohydrate}_{HPLC}$ being the glucan concentration (for cellulose) or the sum of xylan and arabinan (for hemicellulose) concentration for the liquid phase (*recovery liquid phase*) or for the solid phase (*recovery solid phase*) in % DS. $\text{Carbohydrate}_{\text{raw MSW}}$ represents the glucan or arabinoxylan content of the raw material (% DS).

Enzymatic hydrolysis

A modified enzymatic convertibility assay (Varga et al., 2003) based on commercial cellulase (Celluclast 1.5 L from *Trichoderma reesei*) and β-glucosidase (Novozym 188) (Novozymes A/S, Denmark) was used for both wastes to determine the efficiency of the four WO pretreatment conditions tested. The celluclast enzyme activity was previously determined to be 67 FPU (filter paper units) ml^{-1} (Thygesen et al., 2003). Enzymatic conversion of WO solids was performed at 2% DS either in the presence of 0.2 M acetate buffer (pH = 4.8) or WO filtrate with an adjusted pH of 4.8. Enzymatic hydrolysis was carried out in triplicate in 10 ml test tubes, which were placed in an incubator at 50°C and were shaken at 150 rpm. Applied enzyme loadings were 25 FPU g^{-1} of DS for all assays. The total hydrolysis time was 72 h with 3 sampling times (24, 48 and 72 h). Samples were withdrawn under sterile conditions, centrifuged (4000 rpm, 5 min), 10-fold diluted with HPLC eluent and filtered over a 0.45 μm filter before HPLC analysis.

The enzymatic convertible cellulose (ECC) expressed as % DS was calculated as

$$ECC = \frac{(Glucose_{HPLC})}{DS} x100x0.9 \qquad (ii)$$

with $glucose_{HPLC}$ being the measured glucose concentration after the assay (g l^{-1}), DS the dry solid content during the assay (g DS l^{-1}) and a molar weight multiplication factor for conversion of glucose to cellulose concentration. The cellulose conversion efficiency (%) was calculated as

$$Conversion\% = \frac{ECC}{Cellulose_{filtercake}} x100 \qquad (iii)$$

with ECC being the enzymatic convertible cellulose (% DS) and $cellulose_{filtercake}$ the total cellulose amount present in the WO solids (% DS).

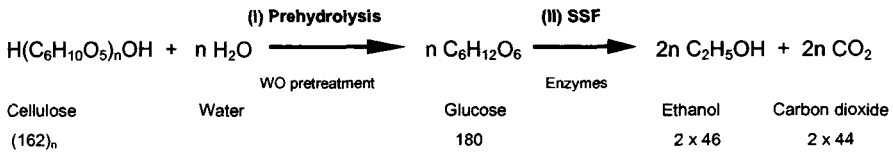
Conversion efficiencies for the assay including the WO filtrates were calculated following

$$Conversion\% = \frac{Glucose_{HPLC} - Glucose_{filtrate}}{(Cellulose_{solids} + Cellulose_{filtrate})x1.11} x100 \qquad (iv)$$

with $glucose_{HPLC}$ being the measured glucose concentration after hydrolysis (g l^{-1}), $glucose_{filtrate}$ the free monomeric glucose present in the filtrate (g l^{-1}), $cellulose_{solids}$ the cellulose content of the WO solids, $cellulose_{filtrate}$ the polymeric glucose present in the filtrate (g l^{-1}) and a hydrolysis factor for conversion of cellulose to glucose concentration. Conversion efficiencies and ECC values for the hemicellulose fraction were calculated similarly by replacing glucose by xylose in the formula and by taking into account the hydrolysis loss factors for pentose sugars.

Simultaneous saccharification and fermentation (SSF)

A SSF method was developed to determine the ethanol yield from the cellulose fraction of the wet oxidized and raw wastes. The method consisted of two steps: enzymatic prehydrolysis of cellulose (and hemicellulose) to sugar monomers and fermentation by *Saccharomyces cerevisiae* of the glucose fraction to ethanol (theoretical yield of 0.51 g ethanol g^{-1} glucose).



Prehydrolysis (presaccharification) and SSF was performed in 100 ml fermentation flasks at increased DS content (10% DS) because of the low carbohydrate content of the waste employed. Prehydrolysis (liquefaction) of the WO solids was performed at 50°C for 24 h at 5 FPU g^{-1} of DS with the same celluclast mix (Varga et al., 2003). After liquefaction, the fermentation flasks were supplemented with a second batch of enzymes at an enzyme loading of 0, 5, 10 and 20 FPU g^{-1} of DS and inoculated with 0.16 g yeast. During the fermentation, 0.24 ml of sterile filtered urea (16 mM) was supplemented as a source of nitrogen along with the yeast. In a second assay, the ethanol yield of wet oxidized food waste pretreated for 10 min and 15 min during WO was compared while for the yard waste, additional nutrients were supplied under the form of yeast extract (Difco, USA) and bacto tryptone (casein extract, BD, France). In all assays, the headspace of each fermentation flask was flushed with nitrogen and sealed with a yeast lock filled with glycerol. Duplicate flasks were incubated at 32°C for 8 days and were shaken at 90 rpm to prevent mass transfer limitation.

The cellulose to ethanol conversion was monitored gravimetrically by CO_2 loss. The ethanol yield during fermentation was calculated by multiplication of the molar ratio of EtOH/CO_2 (= 1.045) with the CO_2 loss. The final ethanol concentration was also determined by HPLC analysis (as described earlier). The cellulose to ethanol conversion efficiency (ethanol yield) was determined following

$$\text{EtOH yield} = \frac{\text{EtOH}_{\text{gravimetric/HPLC}}}{\text{Totalglucan}_{\text{flask}} \text{x} 0.51} \text{x} 100 \qquad \text{(v)}$$

with $EtOH_{gravimetric/HPLC}$ being the ethanol amount per flask (g) and total $glucan_{flask}$ the total glucose amount per flask (g), multiplied with the theoretical ethanol conversion factor.

RESULTS

Wet oxidation pretreatment

The experimental conditions for wet oxidation of MSW were chosen based on the wet oxidation of wheat straw for high cellulose convertibility and recovery (Klinke et al., 2002). For all conditions, a pH decrease was observed with 0.4-2.6 units for the food waste and 3-5.8 units for the woody waste (Table 5.1 and Table 5.2).

To evaluate the effect of the WO pretreatment on the carbon mass balances of both wastes, chemical analysis was carried out before and after WO. The composition of the raw food waste on DS basis was as follows: 28% water solubles (non-cell wall material such as salts and protein), 4.3% pectin, 15.6% resins/fats/waxes, 20.1% glucose, 7.2% xylose, 0.9% arabinose, 21.8% lignin and 1.9% total ash. The raw woody waste contained 5% water solubles (non-cell wall material such as salts and protein), 7% pectin, 27.4% resins/fats/waxes, 24.8% glucose, 11.5% xylose, 2.2% arabinose, 22% lignin and 0.1% total ash. The effect of the WO experimental conditions on the material mass balances is shown in Figure 5.2 for the food waste and Figure 5.3 for the yard waste.

For both wastes, the solid fraction significantly increased in cellulose content (up to 125% for yard waste and up to 100% for food waste) as a result of hemicellulose and lignin solubilization. The cellulose content of the WO food waste ranged from 39.4 to 45.7 % DS compared to 20.1 % DS for the untreated waste. Cellulose enrichment of the WO solids was

highest for condition B for both wastes. Total cellulose recovery (glucan) was in all cases nearly complete and varied from 89-99% (Figure 5.2 and Figure 5.3).

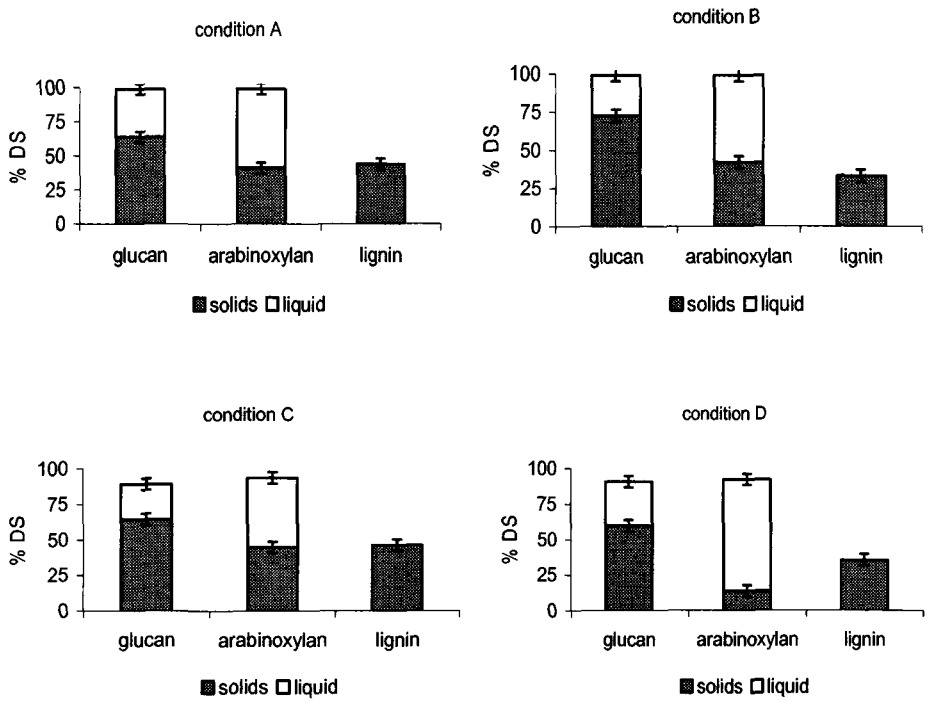


Figure 5.2. Characteristics of the WO food waste solids (solid fraction) and the WO filtrates (liquid fraction) after wet oxidation (g/100 g of DS raw solids). Error bars represent standard deviations on triplicate samples

As a whole, the extent of hemicellulose solubilization was considerably higher for the woody yard waste whereas cellulose solubilization was higher for the food waste. Figure 5.2 shows that the amount of solubilized hemicellulose for the food waste was comparable for conditions A, B and C but was much higher for the most severe condition D (high temperature, high O_2 pressure and acidic pH). This could also be confirmed by measuring the total reducing sugar content of the filtrates by means of the dinitrosalicylic acid (DNS) assay. Overall, the total hemicellulose recovery was more than 95% for condition A and B but was significantly lower at 195°C (Figure 5.2). Besides hemicellulose solubilization, considerable amounts of cellulose (up to 36% for condition A) and lignin (up to 67% for condition B) were

solubilized during wet oxidation pretreatment. Cellulose was most efficiently solubilized under acidic conditions (A and D). Delignification of the waste was much higher at high oxygen pressure (12 bar) and neutral to alkaline pH (condition B) compared to the other conditions tested (Figure 5.2).

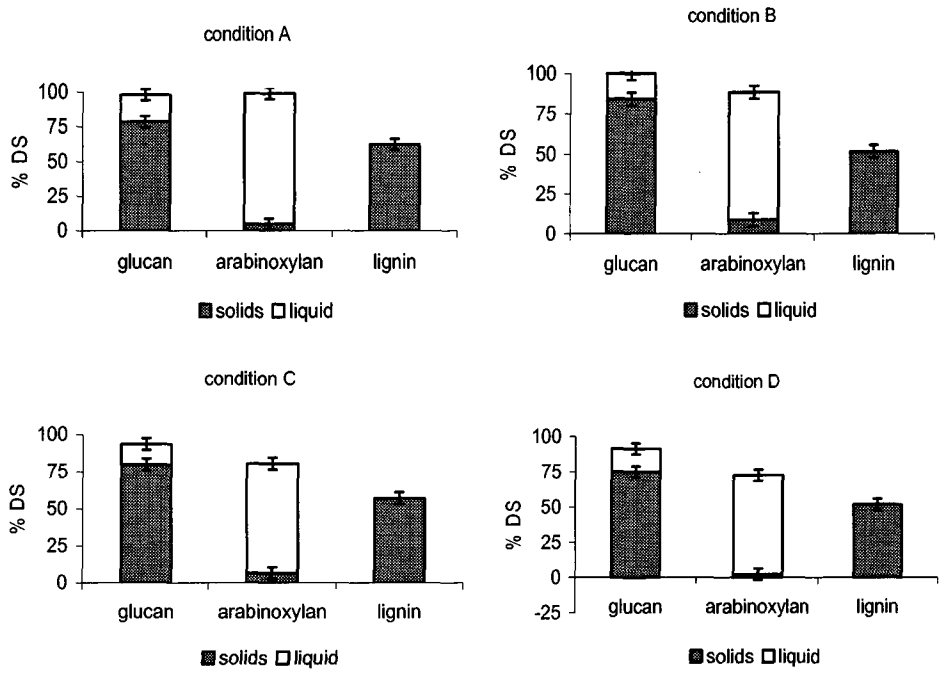


Figure 5.3. Characteristics of the WO yard waste solids (solid fraction) and the WO filtrates (liquid fraction) after wet oxidation (g/100 g of DS raw solids). Error bars represent standard deviations on triplicate samples

For the yard waste, high amounts of original hemicellulose could be solubilized during WO, ranging from 70% (condition D) to 95% (condition A) (Figure 5.3). The total hemicellulose recovery was in the range of 88-100% for conditions A, B and C but was significantly lower for the most severe WO conditions (D). Beside the temperature, hemicellulose recovery was also influenced by the oxygen pressure and was consistently lower at higher oxygen pressure (12 bar). WO condition A resulted in the highest hemicellulose recovery and solubilization. Similar to the food waste, delignification of the woody solids during WO was lowest for condition A (38%) and was highest for condition B (49%). Lignin removal generally increased with increasing oxygen pressure (condition B and D). The high hemicellulose and

lignin recovery for condition A related with the total carboxylic acid concentration, being significantly lower (3.1 g per 100 g DS) for condition A compared to the other WO conditions.

The total free acids concentration in the WO filtrates were highest at alkaline pH (condition B and D) and varied from 2.2-7.4 % on DS basis with the highest values for the woody waste (data not shown). For both wastes, the production of 5-HMF and 2-furfural was stimulated at higher WO temperature and oxygen pressure. However, the concentration of furan derivatives was in all cases low (0.08-0.9% DS) as measured by HPLC analysis.

Enzymatic convertibility of the wet oxidized solids and filtrates

Food waste

In a first assay, the enzymatic accessibility of the washed WO solids of both wastes in acetate buffer was evaluated for the four WO experimental conditions at 2 different incubation times. Figure 5.4 shows the enzymatic conversion efficiency for the glucan and xylan fraction of the raw and wet oxidized food waste. The conversion yields of cellulose and hemicellulose did not further increase after 24 h of incubation (data not shown). Hence, maximum cellulose and hemicellulose enzymatic digestibility at 25 FPU g^{-1} of DS was reached after 24 h.

The extent of enzymatic cellulose conversion of the solids in acetate buffer was relatively similar for all conditions tested with slightly higher conversion efficiencies for conditions C and D (Figure 5.4). However, the hemicellulose conversion was far lower for condition D compared to the other conditions. This was due to the comparatively lower hemicellulose content of the WO solids of condition D as a result of increased hemicellulose solubilization at these conditions (Figure 5.2). Overall, up to 72% of the glucan (condition D) in the food waste could be enzymatically hydrolyzed into monomeric sugars. The enzymatic conversion efficiency of the raw waste was far lower compared to the treated waste, with a conversion efficiency of 36-46% for cellulose and hemicellulose, respectively (Figure 5.4).

By replacing the acetate buffer with the WO filtrates (second assay), the conversion efficiencies of the polymeric sugars present in the WO filtrates could be evaluated along with the enzymatic conversion efficiencies of the WO solids. Figure 5.4 shows the enzymatic conversion efficiencies for the enzymatic assay including the filtrates. Again, the difference in conversion yield for WO conditions A, B and C was relatively small (< 10%). The enzymatic digestibilities for cellulose and hemicellulose were generally in the same range for the WO

filtrate assay compared to the acetate buffer assay. The DNS-numbers of the enzymatically hydrolyzed WO showed the same tendency (data not shown).

As a whole, the enzymatic digestibilities of both assays did not differ more than 9% from each other for the 4 WO conditions tested except for the xylan fraction in the wet oxidized slurry assay, which was significantly lower for conditions A and C. Based on the analytical error (± 5%) made in the various sample preparation steps, the differences in enzymatic conversion yield were found not to be statistically significant. Hence, it was decided to perform a simultaneous saccharification and fermentation procedure (SSF) at 10% DS with the WO solids and filtrate of condition B because of the lowest amount of furan derivatives and the highest total hemicellulose recovery found for this condition.

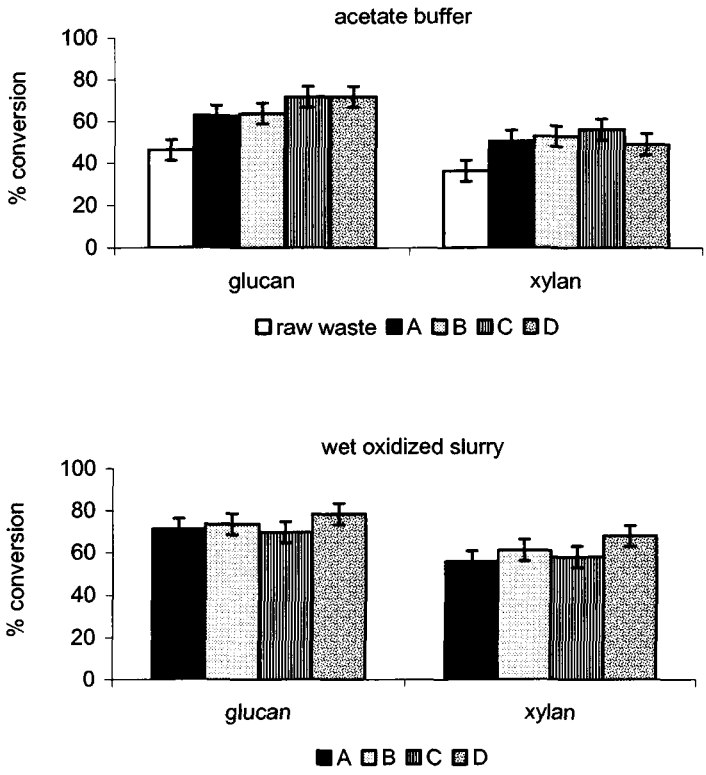


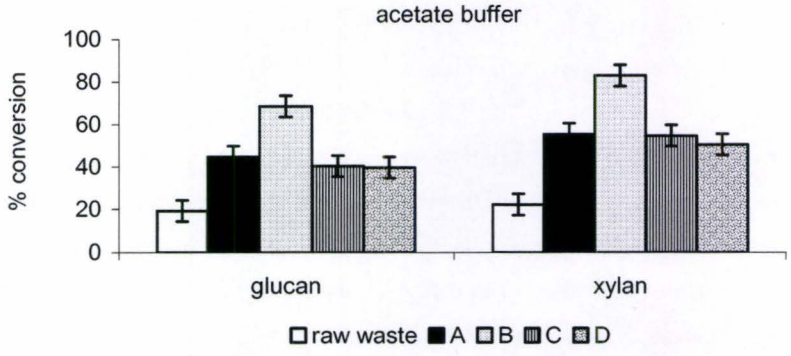
Figure 5.4. Enzymatic conversion efficiency (%) for glucan and xylan of the raw and wet oxidized food waste (condition A, B, C and D) in acetate buffer and of the wet oxidized slurry. Enzyme loading: 25 FPU g^{-1} of DS. Error bars represent standard deviations on triplicate test tubes

Yard waste

Similar to the food waste, a first assay in acetate buffer was performed. Whereas the enzymatic convertibility for the different WO conditions was rather minor for the food waste, the enzymatic conversion for condition B was on average 24-29% and 28-33% higher compared to the other conditions for the cellulose and hemicellulose fraction, respectively (Figure 5.5). The cellulose to glucose convertibility mounted to 68.6% after 48 h incubation time for WO condition B. This WO condition also resulted in a high enzymatic accessibility of 83% of the remaining hemicellulose contained in the WO solids. These observations could also be confirmed by DNS analysis of the enzymatic hydrolyzates (data not shown).

The enzymatic conversion efficiency of the native wood was far less compared to the WO solids. Only about 20% of the cellulose and hemicellulose contained in the raw material could be efficiently liquefied into the corresponding monomeric sugars if no pretreatment was considered.

A second enzymatic assay was set up in which the acetate buffer was replaced by the WO filtrates (Figure 5.5). While the cellulose conversion efficiencies are 3-11% lower for the filtrate assay compared to the acetate buffer assay, no similar straightforward statement can be made regarding the hemicellulose conversion efficiencies. However, the largest increase in hemicellulose conversion efficiency was observed for condition A and C when including the WO filtrates in the assay. Similar with the first assay, condition B showed the highest enzymatic convertibility.



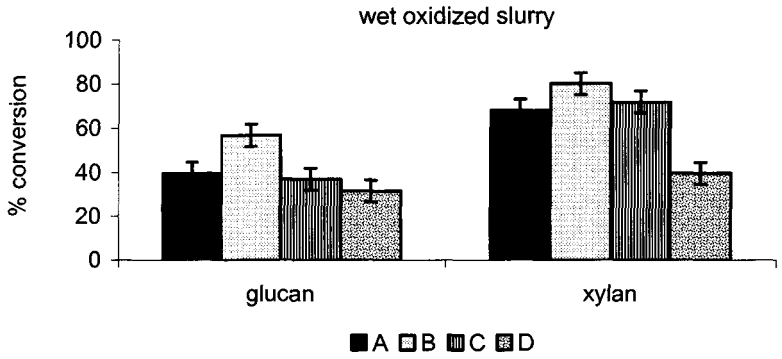


Figure 5.5. Enzymatic conversion efficiency (%) for glucan and xylan of the raw and wet oxidized yard waste (condition A, B, C and D) in acetate buffer and of the wet oxidized slurry. Enzyme loading: 25 FPU g^{-1} of DS. Error bars represent standard deviations on triplicate test tubes

Simultaneous saccharification and fermentation (SSF)

Food waste

It was found that during prehydrolysis at 5 FPU g^{-1} of DS, on average 33% of the total glucan contained in the fermentation flask could be hydrolyzed into hexose sugars (data not shown). The liquefaction step decreased the viscosity of the slurry considerably and produced readily fermentable carbohydrates (17-18 g l^{-1} of glucose) suitable for fermentation.

Different cellulase loadings were tested during SSF to optimize the enzyme loading in function of the ethanol yield. Depending on the total enzyme loading during SSF (5-25 FPU g^{-1} of DS), final ethanol concentrations in the range of 16.5 (5 FPU g^{-1} of DS) up to 22 g l^{-1} (25 FPU g^{-1} of DS) could be reached after 8 days incubation time (Figure 5.6). The fermentation curves as depicted in Figure 5.6 show a typical growth pattern common for yeast sugar fermentation. In fact, more than 80% of the ultimate ethanol yield was already achieved after 48 h of fermentation for all enzyme loadings tested. The glucose concentrations of the slurries after SSF were in all flasks lower than 0.15 g l^{-1}, indicating that the yeast fermented virtually all solubilized glucan.

The ethanol yield increased with higher cellulase loading (Figure 5.6). However, an increased enzyme loading (5-25 FPU g^{-1} of DS) did not provide an equally proportional increase in the ethanol yield.

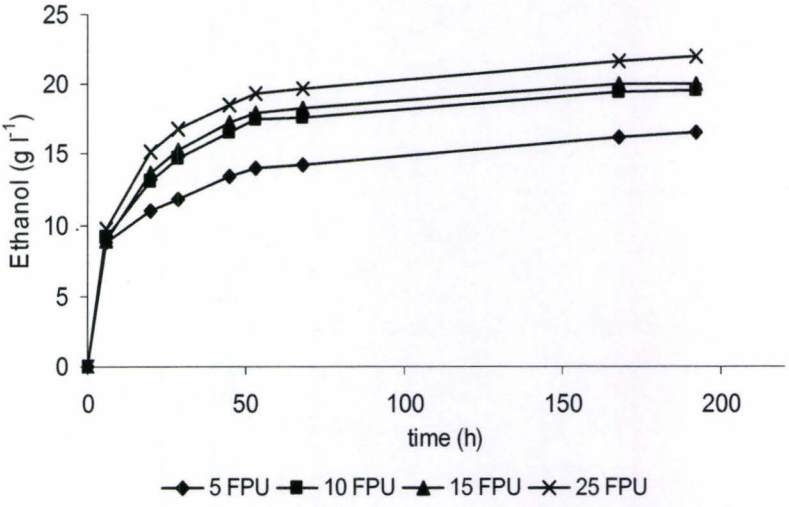


Figure 5.6. Ethanol production by *Saccharomyces cerevisiae* during simultaneous saccharification and fermentation of wet oxidized solids (condition B) of food waste dissolved in wet oxidized filtrate at 10% DS (solids were prehydrolyzed before inoculation at 5 FPU g^{-1} of DS for 24 h at 50°C for all enzyme loadings tested). Enzyme loadings are expressed per g DS. Data points are average values of duplicate samples

Figure 5.7 shows the ethanol yield of the treated waste at the different total enzyme loadings tested as well as the corresponding decrease in cellulose content of the WO solids. The ethanol yield increased with total cellulase loading and mounted to a yield of 70% for 25 FPU g^{-1} of DS. The cellulose to ethanol conversion efficiency ranged between 50% and 70% for a total enzyme loading of 5 FPU g^{-1} of DS and 25 FPU g^{-1} of DS, respectively. Moreover, the ethanol yields at 10 and 15 FPU g^{-1} of DS were very similar, namely 62% and 65%, respectively. Even at a very low enzyme loading of 5 FPU g^{-1} of DS, an ethanol yield of 50% was still achieved. A second SSF assay with WO MSW slurry oxidized for 15 min instead of 10 min retention time showed on average a 5-10% lower ethanol yield (data not shown). Hence, a longer pretreatment time did not improve the ethanol yield.

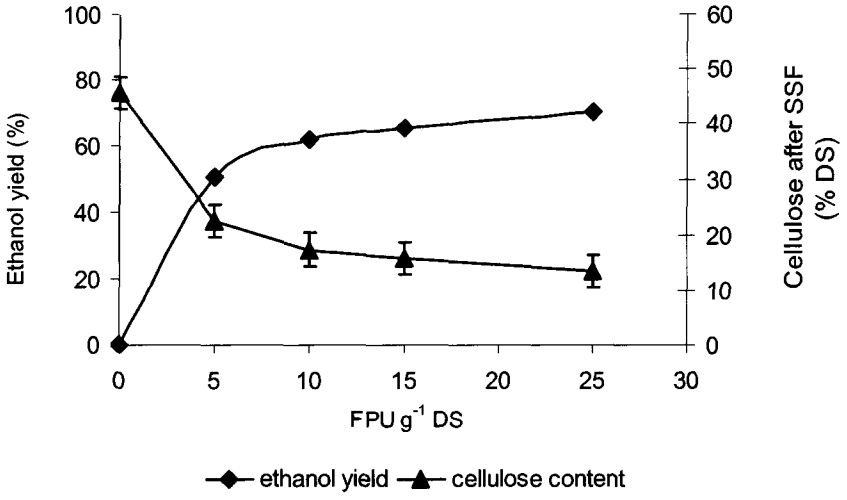


Figure 5.7. Ethanol yield (%) during SSF of wet oxidized solids (condition B) of food waste by different enzyme loadings after 8 days of incubation. Error bars represent standard deviation on triplicate samples. Ethanol yields are average values of duplicate samples

Yard waste

During prehydrolysis of the WO yard waste (condition B), it was found that at 5 FPU g^{-1} of DS, on average 22% of the total glucan could be hydrolyzed into monomeric glucose (data not shown).

Similar to the food waste, different enzyme loadings were tested during SSF with respect to ethanol yield and cellulose conversion efficiency. Depending on the total enzyme loading during SSF (5-25 FPU g^{-1} of DS), final ethanol concentrations in the range of 11.7 (5 FPU g^{-1} of DS) up to 24.4 g l^{-1} (25 FPU g^{-1} of DS) could be reached at 8 days incubation time. However, it was found that the fermentation was characterized by a typical lag phase. Effectively, ethanol production at higher enzyme loadings only increased significantly after an incubation time of 48 h (data not shown). Hence, further experiments were made with respect to inhibition of the filtrate and/or nutrient requirements of the yeast.

A second SSF was carried out at 25 FPU g^{-1} of DS under exactly the same conditions as the first assay except that extra nutrients and minerals were added prior to SSF under the form of yeast and casein extract. As can be inferred from Figure 5.8, an ethanol concentration of 20 g

l^{-1} could already be reached after 68 h in the presence of the extra nutrients while more than 120 h were needed in the first assay to reach the same ethanol level. The fermentation curves also show a typical growth pattern reaching a maximum ethanol concentration of 22 g l^{-1} after approximately 150 h of fermentation (Figure 5.8). Final glucose concentrations of the SSF filtrates were in all flasks that were supplemented with extra nutrients lower than 0.2 g l^{-1}, indicating that the yeast fermented virtually all solubilized glucan (data not shown).

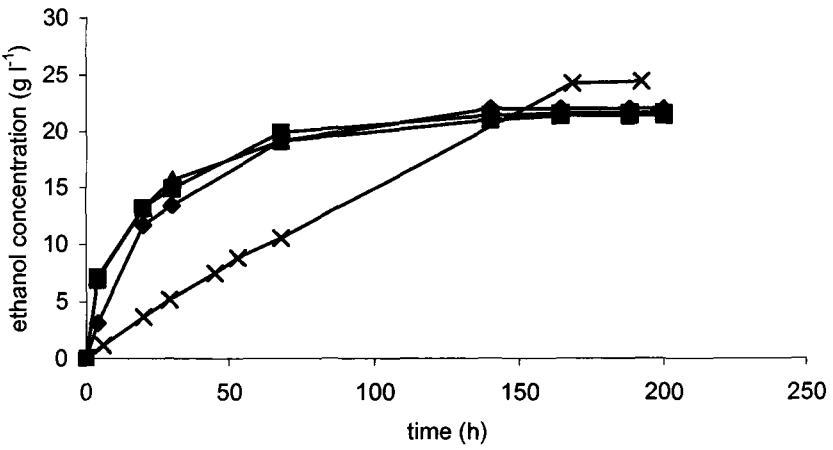


Figure 5.8. Ethanol production by *Saccharomyces cerevisiae* during simultaneous saccharification and fermentation of wet oxidized solids (condition B) of yard waste dissolved in wet oxidized filtrate at different dilutions. Applied enzyme loading was 5 FPU g^{-1} of DS during prehydrolysis and 20 FPU g^{-1} of DS during SSF. Key: X: undiluted filtrate, no yeast/casein extract; ♦: undiluted filtrate, with yeast/casein extract; ■: 1:1 diluted filtrate, with yeast/casein extract; ▲: 1:2 diluted filtrate, with yeast/casein extract

Figure 5.8 also shows the fermentation pattern of SSF flasks to which diluted WO filtrates (1:1 and 1:2) had been added. Ethanol production proceeded at a similar rate with the undiluted and 1:1 and 1:2 diluted filtrates.

Figure 5.9 shows that the ethanol yield exponentially increased with total enzyme loading and was highest for 25 FPU g^{-1} of DS (maximum yield of 79%). However, at a total loading of 15 FPU g^{-1} of DS, cellulose to ethanol conversion efficiency of 69% was still achieved (Figure 5.9). Total cellulase loadings equal or lower than 10 FPU g^{-1} of DS resulted in ethanol yields

lower than 60%. The cellulose contents of the WO solids after SSF matched very well with the calculated ethanol yields.

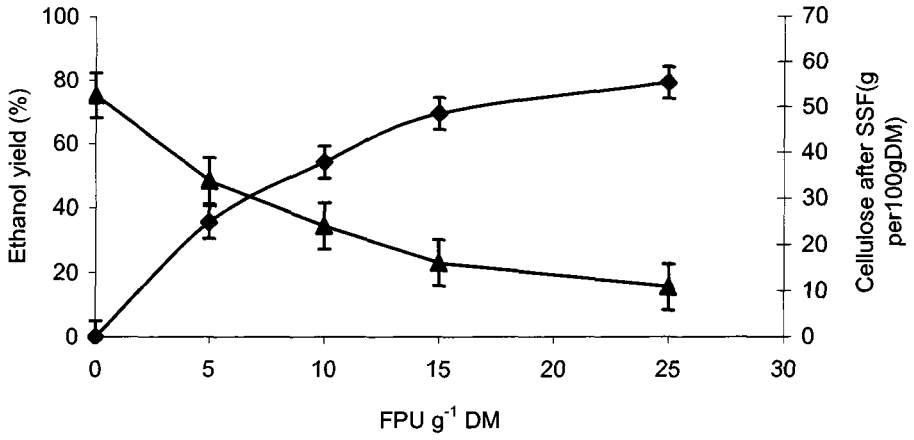


Figure 5.9. Cellulose conversion efficiency into ethanol during SSF of wet oxidized solids of yard waste (condition B) after 8 days incubation. Key: ♦: ethanol yield (left Y-axis), ▲: cellulose content of solids after SSF as determined by strong acid hydrolysis (right Y-axis). Error bars represent standard deviation on triplicate samples. Ethanol yields are average values of duplicate samples

DISCUSSION

Effects on carbohydrate mass balances

In this study, wet oxidation was investigated as a means to increase the enzymatic convertibility for bio-ethanol production of carbohydrate-rich waste fractions, namely food waste enriched with wheat straw and woody yard waste.

The oxidative conditions caused a consistent pH decrease for all tested WO conditions as a result of carboxylic acid production from the hemicellulose and lignin fraction (Klinke et al., 2002; Kolaczkowski et al., 1999). For both wastes, the most proncounced pH-decrease could be observed under alkaline conditions (condition B and C) and can be explained by increased lignin oxidation as a result of the addition of alkaline under the form of Na_2CO_3 (Verenich and Kallas, 2002) (Table 5.1 and Table 5.2). The delignification of lignocellulosic biomass under oxidative conditions proceeds most efficiently at alkaline pH (pH > 9), causing a higher

production of hydroxyl radicals and low molecular acids (Klinke et al., 2002). For the food waste, the final filtrate pH was however very similar (around 4-5) for all 4 WO conditions tested and can probably be attributed to the high buffer effect of the treated slurry, created by soluble salts (*i.e.* sodium) present in the waste combined with weak acids (*i.e.* acetic acid) formed during WO. This weak acid-salt buffering system together with the relatively low hemicellulose content of the raw food waste largely explains the relatively high filtrate pH after WO compared to other cellulosic biomasses, *i.e.* corn stover (Varga et al., 2003). In this respect, Bjerre and Sørensen (1992) stated that the presence of catalysts such as salts promotes the further oxidation of carboxylic acids such as formate into bicarbonate during WO, causing a second buffering effect in the reaction mixture. This oxidation effect probably caused the low total carboxylic acid content (< 4.5 % DS) of the food waste WO filtrates despite the relatively high oxidative lignin removal (54-67%) (Figure 5.2).

In general, oxidative hemicellulose degradation and solubilization was highest at higher WO temperature and lower pH. Hence, hemicellulose solubilization was much higher for condition D compared to the other conditions (Figure 5.2 and Figure 5.3). Oxidative hemicellulose degradation was promoted at a higher oxidation temperature in first instance (condition C and D). Klinke *et al.* (2002) also found significantly lower hemicellulose recoveries for wheat straw at 195°C compared to 185°C. Total hemicellulose recovery was lowest for condition D and was linked to the production of furan derivatives, which were highest for condition D (0.2-0.9% on DS basis).

The hemicellulose solubilization was much higher for the yard waste compared to the food waste. This phenomenon was probably due to an enhanced autohydrolysis reaction, which is mainly generated by the formation of acetic acid derived from acetylated xylan chains present in hemicellulose (Garrote et al., 2001b). This mechanism is particularly important during hydrothermolysis of hardwood because of its high acetyl content that provides increased catalytic action (Biermann et al., 1984).

The lower cellulose reactivity (linear configuration, high polymerization degree and crystalline structure) compared to the reactivity of the highly branched hemicellulose and lignin during wet oxidation caused a relatively low solubilization of cellulose and a high total cellulose recovery. Thermal cellulose degradation by loss of chemical water is believed only to occur at temperatures higher than 200°C (Scheirs et al., 2001). Cellulose solubilization was significantly higher for the food waste compared to the yard waste, which was probably due to the higher amount of soluble and more accessible carbohydrates present in the food waste.

Oxidative lignin removal was moderate (49% for the yard waste) to high (67% for the food waste) at 185°C and under alkaline conditions (condition B). Oxidative (lime) alkaline treatment was previously found to enhance lignin removal and enzymatic digestibility for wheat straw and high-lignin poplar wood (Bjerre et al., 1996; Chang et al., 2001b). Furthermore, Verenich and Kallas (2002) also stated that wet oxidation under alkaline conditions is more effective to break up lignin in biodegradable compounds and remarked that this process does not impair high organic losses (to CO_2). Hence, alkaline wet oxidation at 185°C was very suitable for the selective removal and oxidation of lignin from carbohydrate-rich waste into low weight carboxylic acids and CO_2.

Effects on enzymatic convertibility and ethanol yield

For the food waste, the enzymatic cellulose (and hemicellulose) conversion efficiency between the different WO conditions only displayed small differences up to 9% (Figure 5.4). In all cases, enzymatic digestibility ranged from 70-78% for the WO slurries and from 63-72% for the acetate buffer assay. This is rather contradictory to previous studies applied to pure feedstocks (*i.e.* cornstover) where the differences in conversion efficiency for the various WO conditions tested were more pronounced (Varga et al., 2003). Hence, it is assumed that the heterogeneous carbohydrate composition of the different refuse components level out the effect of the different WO conditions. In this respect, one can expect that the highly variable and season-dependent composition of organic waste is crucial for further optimization of ethanol production from household waste. However, the enzymatic degradation for the yard waste fractions showed more distinct differences (Figure 5.3). Chang et al. (2001b) also found that combining oxidative and alkaline conditions enhanced enzymatic accessibility extensively. In this respect, it can be assumed that alkaline conditions favoured in particular deacetylation, thereby enhancing the enzymatic digestibility of the yard waste.

Enzymatic conversion and fermentation yields of thermally pretreated biomass are generally higher when the WO liquid fraction is omitted due to the presence of inhibitory compounds, particularly at high dry matter content (> 5% DS). Therefore, most described SSF and enzymatic procedures have been carried out with only (washed) WO solids (Spindler et al., 1991). However, this study shows that the presence of the WO filtrates in the enzymatic and SSF procedure did not exhibit any inhibition or toxicity towards *Saccharomyces cerevisiae,* even at a high solids content of 10% DS. In fact, enzymatic conversion efficiencies including the WO filtrates were in the same range as the conversion yields found in the absence of the

filtrates. Alkaline wet oxidation pretreatment results in comparatively lower sugar degradation product levels and more biodegradable WO filtrates compared to other (mostly) steam-based pretreatments. In this respect, Nguyen *et al.* (1999) reported that up to 10% of the xylan contained in mixed solids waste was converted into furfural by applying steam explosion and dilute-acid pretreatment. In this study, only 0.08-0.9% DS of the original raw solids was converted into furan derivatives during WO. It was also shown that the wet oxidized food waste contained all necessary nutrients and minerals for subsequent fermentation whereas extra nutrients had to be supplied to ferment the wood carbohydrates. Furthermore, a longer WO retention time of 15 min did not result in a higher ethanol yield for the food waste. This shows that the WO reaction occurred mainly during the first 10 minutes, giving rise to the formation of compounds (e.g., carboxylic acids) which are recalcitrant to further oxidation (Verenich and Kallas, 2002).

At moderate enzyme loadings (10-15 FPU g^{-1} DS), 60-70% of the cellulose present in wet oxidized food and yard waste could be converted into ethanol whereas for the raw wastes, only 18-45% of the cellulose could be enzymatically converted at 25 FPU g^{-1} DS. Further research is however warranted on the development of more specific cellulolytic enzymes for the production of ethanol from cellulosic biomass and waste.

CONCLUSIONS

This work shows that wet oxidation (T = 185-195°C, O_2 pressure = 3-12 bar, 2 g l^{-1} of Na_2CO_3 and 10 min) is an effective pretreatment for the simultaneous saccharification and fermentation of food and yard waste into ethanol. The effect of high oxygen pressure under alkaline conditions showed to be decisive parameters for extensive delignification (up to 67%) of organic waste during wet oxidation. Solubilized lignin was further oxidized into non-toxic degradation products, namely low weight carboxylic acids and CO_2.

By applying an SSF procedure with *Saccharomyces cerevisiae* and commercial cellulases at 10% DS, it was shown that a final ethanol concentration of 16.5-24 g l^{-1} of ethanol can be reached from the WO slurry at a cellulose conversion efficiency of 50-79% and a total cellulase loading of 5-25 FPU g^{-1} of DS. Moderate enzyme loadings of 10-15 FPU g^{-1} of DS still resulted in 60-70% ethanol yields from the cellulose fraction of the wastes. The WO filtrate did not exhibit any toxicity to the yeast during fermentation.

This study shows that alkaline wet oxidation can considerably decrease the enzyme loading and hence decrease the operational costs in the production of ethanol from carbohydrate-rich

wastes. Furthermore, the presented wet oxidation process could be particularly attractive for the treatment of fibrous, carbohydrate-rich and source-separated municipal waste for the production of bio-ethanol.

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Chapter 6

ENHANCEMENT OF THE ANAEROBIC DIGESTION PROCESS OF RAW AND DIGESTED BIOWASTE BY ALKALINE WET OXIDATION[1]

ABSTRACT

Anaerobic digestion of solid biowaste generally results in relatively low methane yields of 50-60% of the theoretical maximum. Increased methane recovery from organic waste would lead to reduced handling of digested solids, lower methane emissions to the environment and higher green energy profits. The objective of this research was to enhance the anaerobic biodegradability and methane yields from different biowastes (food waste, yard waste, and digested biowaste already treated in a full-scale biogas plant (DRANCO, Belgium)) by assessing thermal wet oxidation. The biodegradability of the waste was evaluated by using biochemical methane potential assays and continuous 3-L methane reactors. Wet oxidation temperature and oxygen pressure (T, 185-220°C; O_2 pressure, 0-12 bar; t, 15 min) were varied for their effect on total methane yield and digestion kinetics of digested biowaste. Measured methane yields for raw yard waste, wet oxidized yard waste, raw food waste, and wet oxidized food waste were 345, 685, 536, and 571 mL of CH_4/g of volatile suspended solids (VSS), respectively. Higher oxygen pressure during wet oxidation of digested biowaste considerably increased the total methane yield and digestion kinetics and permitted lignin utilization during a subsequent second digestion. The increase of the specific methane yield for the full-scale biogas plant by applying thermal wet oxidation was 35-40%, showing that there is still a considerable amount of methane that can be harvested from anaerobically digested biowaste.

Keywords: *biogas, lignin degradation, digested biowaste, food waste, yard waste, wet oxidation*

[1] Redrafted after:
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INTRODUCTION

Recent estimates show that about 1.3 billion tons of organic waste and 700 million tons of agricultural wastes are produced annually within the European Union (EU). This represents a yearly biodegradable fraction of municipal solid waste (MSW) production of 107 million tons of dry matter or approximately 2.2 tons of dry organic matter per European citizen, of which more than 60% is still landfilled (EEA, 2002b).

In recent years, the EU policy is diverting the disposal of organic waste away from disposal routes such as landfilling because of the production of (toxic) leachates and greenhouse gas emissions (e.g., methane) (Eleazer et al., 1997) and because organic waste is increasingly regarded as a potentially valuable resource for renewable and green electricity production (Gellens et al., 1995; De Baere, 2001). It is generally recognized that anaerobic digestion is a more controlled and sustainable way of treating organic waste as compared to other disposal routes (i.e., landfilling or composting) (Verstraete et al., 2000). Despite the higher investment and treatment costs, anaerobic digestion is expected to gain considerable importance soon due to its valuable energy recovery in the form of biogas (Mata-Alvarez et al., 1999). So far, full-scale anaerobic digestion facilities have often relied upon a 15-20 days digestion phase transforming the readily biodegradable fraction, followed by a post-digestion stabilization of the remaining lignocellulosic solids (De Baere, 2000; Lissens et al., 2001; Van Lier et al., 2001; Liu et al., 2002). Hence, post-treatments (typically composting) are necessary to obtain a high-quality stable digestion product that can be stored and reused for agricultural purposes.

Cellulose and hemicellulose (holocellulose) are the principal biodegradable components of biowaste and are found together with lignin in rigid hemicellulose complexes (Ress et al., 1998). The degradation of these lignocellulose complexes, which can make up to 80% of the fiber content for some refuse components (e.g., paper), is however, limited to yields of at most 50% (< 200 mL of CH_4/dry g) of those achievable with the pure carbohydrates (Eleazer et al., 1997). This is due to the shielding effect of lignin on holocellulose and the low biodegradability of lignin under anaerobic conditions (Ress et al., 1998). Hence, in the light of the EU green electricity certificates, additional treatments that enhance the biodegradability of waste carbohydrates and lignin could lead to a considerable increase in methane yields from renewable feedstocks.

Thermal treatments have been reported to fractionate the lignocellulose by solubilizing part of the hemicellulose and lignin fraction, to decrease the cellulose crystallinity and to hygienize the lignocellulose during pretreatment (Schmidt and Thomsen, 1998; Klinke et al., 2002). Thermal treatments involving steam (e.g. steam explosion) (Liu et al., 2002) and thermal hydrolysis (Schieder et al., 2000) are the most investigated processes for pretreatment of biowaste prior to digestion. Alternatively, wet oxidation, mostly in combination with alkaline addition has been investigated as a pretreatment for other pure biomasses such as wheat straw for the production of bio-ethanol (Klinke et al., 2002; Chang et al., 2001a; Chang et al., 2001b). Wet oxidation (WO) has been reported to have significant advantages over other thermal pretreatment technologies such as lower production of toxic sugar degradation products, significant decrease of cellulose crystallinity and high delignification potential (Schmidt and Thomsen, 1998).

In this study, the anaerobic biodegradability of three wet oxidized wastes (raw food waste, digested biowaste and raw yard waste) was compared with the untreated organic wastes by measuring methane yields in batch and continuous tests. For digested biowaste originating from a full-scale anaerobic digester (DRANCO, DRy ANaerobic COmposting), WO parameters (temperature, oxygen pressure) were optimized for maximum enhancement of the methane yield during a second digestion of the biowaste and the results were compared relative to the methane yield achieved during the first full-scale digestion.

MATERIALS AND METHODS

Seed preparation and adaptation

A blended seed from a pig manure digester and a food waste digester in a 2:1 ratio was used as a starter seed in two 3-L reactors. The seed was gradually adapted to food waste for a period of 1 month by using an increasing feeding ratio of food waste to pig manure. Next, both digesters were run in parallel for a period of 1 month with the food waste. During this time, seed from the 3-L reactors was used for the BMP (Biochemical Methane Potential) assays. Seeds were subsequently adapted to digested biowaste from a full-scale plant over a period of several weeks. Finally, to compare the methane yield and the reactor performance in continuous mode, reactor 1 was fed with untreated digested biowaste and reactor 2 was fed with WO digested biowaste for a period of 2 weeks.

Organic waste sources

Raw source-separated biowaste was collected from a municipal waste plant in Frederikssund (Denmark) during wintertime. The waste consisted mainly of source-sorted food waste (hereafter called food waste) collected in plastic bags. Upon collection in the waste plant, the waste was shredded (< 1 cm) and plastics were removed using a rotating drum. Shredded wheat straw was added to the drum at a final concentration of 8% of the total dry matter (DM) content of the food waste to increase the DM content and to bind the wet waste together for a better removal of the plastics.

Fresh woody yard waste was collected from a university campus (DTU, Denmark) during wintertime and was composed of small branches (< 2 cm diameter) of different kinds of trees (mainly oak and birch). Both raw food waste and raw yard waste were air-dried for 48 h and ground to 3 mm particle size with a cutting-knife mill prior to WO and digestion. Prior to anaerobic digestion, the ground particulates were suspended in tap water to a final concentration of 50 g/L and 34 g/L of dry matter (DM) for raw food waste and raw yard waste, respectively.

Digested biowaste was collected during springtime from a full-scale anaerobic digester (DRANCO, Belgium) in which 50,000 tons/year of source-separated biowaste (yard and food waste) is treated. The digester residue was screw pressed on the site and was subsequently shredded in the lab with a slow-speed meat mincer to obtain a uniform sample size no greater than about 5 cm long by 2 cm wide. Next, tap water was added to the shredded waste to 40 g/L of total suspended solids (TSS). All suspensions were stored at 4°C prior to WO.

Wet oxidation (WO) equipment and sample preparation

Raw yard waste and food waste were oxidized under the same conditions (except the WO time) (Table 6.1), while the digested biowaste was oxidized under four different conditions (referred to as A-D). WO experiments with digested biowaste were performed batch-wise (duplicate) at 40 g/L of TSS. The WO conditions for the raw food waste and raw yard waste as well as the four experimental conditions performed on the digested biowaste (A-D) are summarized in Table 6.1. For the digested biowaste, the reaction time was set at 15 min for all experiments. For experiment D, the initial pH was made alkaline by the addition of 2 g/L of Na_2CO_3 prior to closure and pressurization of the autoclave with oxygen. The pH of the solutions was measured before and after wet oxidation (Table 6.1).

Table 6.1. Wet oxidation (WO) conditions and oxidative losses for raw yard waste, for raw food waste, and for digested biowaste (Conditions A-D)

Parameter	**Yard waste**	**Food waste**	**Digested biowaste**			
WO conditions			**A**	**B**	**C**	**D**
Temperature (°C)	185	185	185	185	185	220
Time (min)	15	10	15	15	15	15
O_2 Pressure (bar)	12	12	0	3	12	12
Na_2CO_3 (g/L)	2	2	0	0	0	2
pH before WO	9.5	7.2	8.3	8.3	8.3	10.1
pH after WO	3.7	4.6	7.3	6.6	4.4	6.4
COD/TSS/VSS$_{after\ WO}$						
COD total (g/L)	-	-	27.2	26.1	25	20.7
COD soluble (g/L)	-	-	2.3	3	4.8	5.9
TSS (g/L)	31	44	38	32	30	26
VSS (g/L)	30	37	19	18	17	13
% total COD loss (%)*	-	-	9	13	16	31
% total VSS loss (%)*	9	10	9	14	20	32

* losses based on (COD/VSS $_{before\ WO}$ – COD/VSS $_{after\ WO}$)/(COD/ VSS $_{before\ WO}$) * 100

WO experiments were carried out in a high-pressure autoclave with a tubular loop and an impeller constructed at Risø National Laboratory (Bjerre et al., 1996). The autoclave was designed as a cylindrical vessel (V = 1890 mL) made of Sandvik Sanicro 28 (27% Cr, 31% Ni, 3.5% Mo, and 1% Cu) with an impeller that continuously pumped the liquid through the tubular loop. Prior to heating, the reactor lid was closed and oxygen pressure was supplied from a gas cylinder. The autoclave was mounted on a rack, facilitating temperature control by raising or lowering it in a heating bath. After WO, the reaction was terminated rapidly (< 2 min) by immersing the reactor in a water bath.

After WO, the solids of the wet oxidized slurry of the first batch were separated by vacuum filtration. Subsequently, the solids were washed with deionized water, dried in a climate chamber at 20°C and 65% relative humidity and stored in paper bags for analysis. The wet oxidized filtrates were stored at -18°C for analysis. The second batch was stored at 4°C without solids separation.

Biochemical methane potential assays

All organic wastes were wet oxidized in duplicate batches, and the enhancement in methane yield and kinetics was measured. For the raw food waste and raw yard waste, WO parameters had already been optimized previously (Lissens et al., 2004a; Lissens et al., 2004b). For digested biowaste, four WO conditions were tested for their effect on methane yield and kinetics. To compare the actual methane yield of the reference and wet oxidized materials, BMP assays were conducted in quadruplicate 100 mL serum flasks sealed with rubber stoppers. The BMP assays allowed selecting for the WO conditions resulting in the highest cumulative methane yield in subsequent digestion. The seed (from 3-L reactors) made up 33% wt% of the content of each flask and the organic loading of each flask was set at 0.5 g of volatile suspended solids (VSS). A 2.6 g/L of bicarbonate solution was added to each flask to bring the volume of each flask to 60 mL and to ensure an initial pH of 7-8. Four control flasks containing seed and bicarbonate only were used to measure background methane production. Quadruplicate flasks were incubated at 55°C for a period of 28 days. Methane analysis was performed daily during the first 12 days and every two days from day 12 to day 28. All flasks were monitored until no further significant gas production was detected. For the WO conditions resulting in the highest cumulative methane yield in the BMP assays, the methane potential of the reference and WO digested biowaste was determined by employing two continuous 3-L anaerobic reactors (see next section).

Anaerobic reactors

Two stainless steel 3-L reactors manufactured at the Technical University of Denmark (DTU, Denmark) were used for continuous feeding of digested biowaste (Reactor 1) and WO digested biowaste (Reactor 2) (Angelidaki and Ahring, 1993). The reactors contained an automatic internal stirring device, which stirred the reactor for 3 min every 5 min. Reactor inlets and outlets were constructed from PVC-piping with 1 cm diameter. Reactors were fed manually once a day with a 50 mL syringe, thereby causing a simultaneous withdrawal of the same volume of effluent by liquid displacement. The reactors were kept at a constant temperature of 55 ± 1°C by means of external water heating jackets connected to a Heto (Denmark) warm water bath. The reactor loading rate (B_v) was on average 2.6 g of VSS/L of reactor volume per day for raw food waste and varied between 0.9 and 1.1 g of VSS/L of reactor volume per day for the WO materials. Biogas was collected at the top of each reactor

and was monitored by means of an electronic liquid displacement column with an accuracy of 10 mL (modified version as described by Angelidaki et al., 1992) (DTU, Denmark). The COD (Chemical Oxygen Demand), Kj-N (Kjeldahl-Nitrogen), TSS, VSS, and ash content of the digester influent and effluent were determined according to Standard methods (Greenberg et al., 1992). VFA (volatile fatty acid) and biogas composition (carbon dioxide and methane) of both reactors were determined on a daily basis and weekly basis, respectively. Individual VFA concentrations (acetic, propionic, butyric, isobutyric) were measured with a 5890 series II Hewlett-Packard HPLC with Helium as the carrier gas. Biogas analysis was performed with a Shimadzu 8A GC-FID with Nitrogen as the carrier gas.

Analytical procedures

The solid fractions derived from WO were shredded and hammer-milled to pass a 1-mm screen prior to analysis. The WO solids and raw waste were analyzed for their contents of glucan, xylan, arabinan, Klason lignin, and ash after strong acid hydrolysis (72% w/w H_2SO_4 at 30°C for 60 min) followed by dilute acid hydrolysis (4% w/w H_2SO_4 at 121°C for 60 min) (Gilbert et al., 1952). Subsequent sugar analysis was carried out by HPLC analysis (Klinke et al., 2002).

Total glucose, xylose (including galactose and mannose) and arabinose concentrations (sum of monomeric and polymeric sugars) in the WO filtrates were determined after dilute sulfuric acid hydrolysis (4% w/w H_2SO_4 at 121°C for 10 min) (Gilbert et al., 1952). Quantification of free monomeric sugars and carboxylic acids present in the wet oxidized filtrates was carried out after pH adjustment to pH 2-2.3 with 0.1 M H_2SO_4. Sulfate ions were precipitated by an equivalent amount of $Ba(OH)_2$ and separated by centrifugation. Samples were filtered (0.45 μm) prior to HPLC analysis and diluted 10-fold with HPLC eluent (4 mM H_2SO_4) when necessary.

Glucose, xylose, arabinose, ethanol and total carboxylic acids (sum of malic, succinic, glycolic, formic, and acetic acids) were quantified by HPLC analysis according to Klinke et al. (2002).

Carbohydrate recoveries (cellulose and hemicellulose) were calculated to estimate their losses during WO following

$$\text{Carbohydrate recovery}\,[\%(w/w)] = \frac{(\text{Carbohydrate}_{\text{HPLC}})}{\text{Carbohydrate}_{\text{raw waste}}}$$

with carbohydrate$_{HPLC}$ being the glucan concentration (for cellulose) or the sum of xylan and arabinan (for hemicellulose) concentration for the liquid phase (recovery liquid phase) or for the solid phase (recovery solid phase) in g/100 g of DM. Carbohydrate$_{raw\ waste}$ represents the glucan or arabinoxylan content of the raw material (g/100 g of DM).

RESULTS

Wet oxidation treatment

Table 6.1 shows the pH of the three waste suspensions (food waste, yard waste and digested biowaste [conditions A-D]) before and after WO. For all cases, the WO treatment caused a pH drop from 1 to 5.8 units, with the most pronounced decrease in pH at the highest oxygen pressure (conditions C and D). The final pH for case D was not as low as for case C because of the addition of a buffering agent prior to WO. The decrease in pH was related to total carboxylic acid production during WO, with increasing VFA concentrations at higher oxygen pressure (A, 0.28 g/L; B, 0.58 g/L; C, 1.41 g/L; and D, 2.29 g/L). Furthermore, Table 6.1 shows that generally 9-20% of the VSS contained in the waste or 9-16% of the COD content of the waste is oxidized during wet oxidation at a WO temperature of 185°C. At a WO temperature of 220°C, approximately 32% of the organic content is oxidized during WO (Table 6.1). These losses were based on the fact that the raw yard waste, raw food waste, and digested biowaste originally contained 33, 41, and 21 g of VSS/L, respectively. The COD of the untreated digested biowaste was 30 g/L. Table 6.1 also shows that the degree of liquefaction, measured as the $COD_{soluble}$ of the WO digested biowaste, was significantly higher at higher oxygen pressure (conditions C and D).

In Table 6.2, the carbohydrate composition of the raw wastes and digested biowaste before WO are given, as well as the effect of the variable WO conditions (A-D) on the carbohydrate composition of the digested biowaste after WO.

Table 6.2. Characteristics of the WO treated and untreated wastes (solids and liquid fraction) (g/100 g of solids)

BEFORE WO (g/100 g DM raw waste)			
	Raw Yard Waste	Raw Food Waste	Digested Biowaste
Glucan	24.8	20.1	5.2
Arabinoxylan	13.7	8.1	2.5
Lignin	22	21.8	16.5

DIGESTED BIOWASTE AFTER WO (g/100 g DM raw waste)									
SOLID FRACTION					**LIQUID FRACTION**				
Polym. sugars	A	B	C	D	*Monom. sugars*	A	B	C	D
Solids recovery	66.7	58.3	30	25	Glucose	0.12	0.31	0.69	0.86
Glucan	4.2	4.4	4.1	2.7	Arabinoxylan	0.02	0.09	0.41	0.12
Arabinoxylan	1.11	0.83	0.36	0.28	*Polym. sugars*				
Lignin	17	13.7	5.9	4.33	Glucose	0.17	0.21	0.11	0
Ash	40.8	40.2	32.7	38.9	Arabinoxylan	1.12	1.41	1.45	0.18
					Total free acids	0.70	1.45	3.54	5.74
Recovery (%)					**Recovery (%)**				
Glucan	80.7	84.6	78.8	51.9	Glucan	5.6	10.0	15.4	16.6
Arabinoxylan	44.4	33.2	14.4	11.2	Arabinoxylan	45.3	60	74.4	11.8
Lignin	100	83	35.7	26.2	Lignin	-	-	-	-

TOTAL recovery (%)				
	A	B	C	D
Glucan	86.3	94.6	94.2	68.5
Arabinoxylan	89.7	93.2	89.1	23

For all conditions tested, WO solids after WO increased considerably in cellulose content with increasing oxygen pressure (6.3 and 13.7 g/100 g of DM WO solids for condition A and C, respectively). However, due to the comparatively lower solids recovery at higher oxygen pressure, the cellulose content expressed per 100 g of raw digested solids was 4.1-4.4 g/100 g of DM raw solids for WO conditions A-C, which is comparable with the untreated waste (5.2

g/100 g of DM raw solids). Only for WO condition D, the cellulose recovered in the solid phase was much lower (Table 6.2).

The higher solubilization effect for conditions C and D was also reflected in their comparatively low lignin content after WO (Table 6.2). Up to 64% and 74% of the original lignin present in the digested biowaste could be solubilized for conditions C and D, respectively. At lower oxygen pressure (0-3 bar), however, the majority of the lignin (> 80%) was recovered in the solid fraction. As a whole, the glucan recovery in the liquid fraction during WO was low and averaged from 6 to 17% for glucan whereas the arabinoxylan solubilization was 12-74% (Table 6.2) with highest values for WO condition C. The total glucan and arabinoxylan recoveries were high for conditions A-C (WO temperature of 185°C) and varied between 86 and 95%. However, for condition D, the total carbohydrate recovery was much lower, which indicates that the majority of the arabinoxylan fraction (77%) and part of the cellulose fraction (32%) was oxidized (Table 6.2).
Concomitantly with a lower total hemicellulose recovery and high lignin solubilization, the production of total free acids during WO in the liquid phase was highest for conditions C and D (Table 6.2). Acetic acid was the principal carboxylic acid found in the WO hydrolyzates (data not shown).

Anaerobic biodegradability of wet oxidized yard waste and food waste

In Figure 6.1a, the cumulative methane yields of raw food waste and raw yard waste are compared with the yields of the corresponding WO materials in the BMP assays. A final methane yield of 685 mL of methane/g of VSS could be achieved for the WO yard waste while 345 mL of methane/g of VSS was reached for the untreated yard waste. This corresponds to a doubling of the methane yield following wet oxidation pretreatment. For the food waste, the methane yield of the WO waste was only 7% higher as compared to the untreated waste. For both wastes, the fermentation started at a lower initial rate for the WO materials but proceeded at a comparatively higher rate compared to the untreated materials after a lag period of about 5 days.

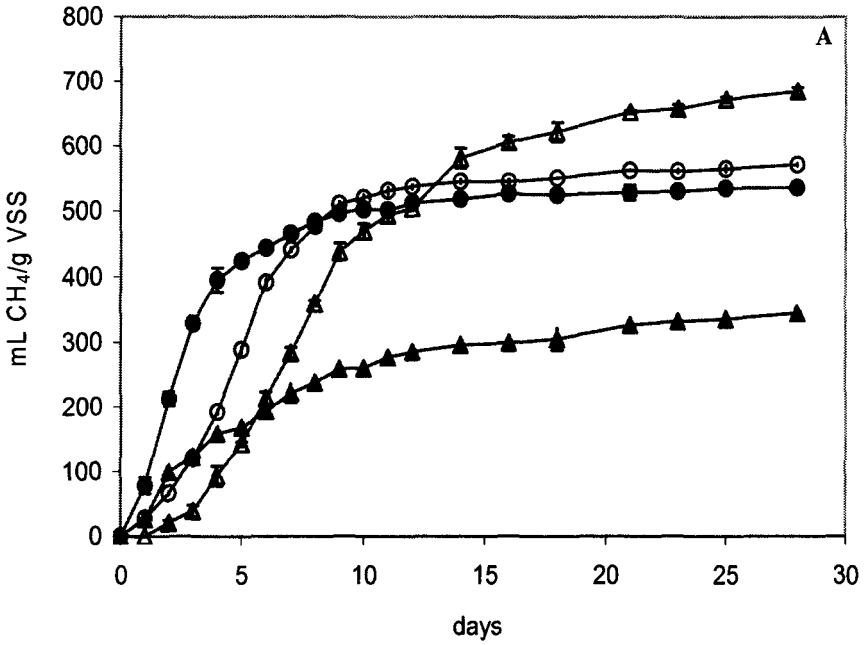

Figure 6.1a. Cumulative methane production in the BMP assays of the raw wastes. Error bars: standard deviations on quadruplicate serum flasks (error bars may be too small to be visible on the figure). Key: -▲- Yard waste, -●- Food Waste, -Δ- WO Yard waste, - ○- WO Food Waste

Anaerobic biodegradability of wet oxidized digested biowaste

Figure 6.1b and Table 6.3 show the cumulative methane yields of the untreated digested biowaste as compared to the WO digested biowaste for the four experimental WO conditions tested (A-D). Taking into account an oxidative loss of 9-32% of the organic content during WO (Table 6.1), the specific methane yields in the BMP assays were 50-76% higher for the WO digested biowaste as compared to the untreated biowaste in the second digestion (Table 6.3). The highest methane yield was reached for conditions C and D, despite the higher oxidative losses inherent to a higher oxygen pressure (12 bar). As a whole, the methane yields were 15-20% higher for conditions C and D as compared to conditions A and B. However, a higher oxygen pressure during WO provoked a lag phase of about 5 days before methane production started (Figure 6.1b). Next, a rapid burst of methane production was observed for conditions C and D for a period of about 10 days. Alternatively, the methane production for

the digested biowaste of conditions A (0 bar oxygen) and B (3 bar oxygen) was instantaneous, very similar, and increased more gradually (Figure 6.1b).

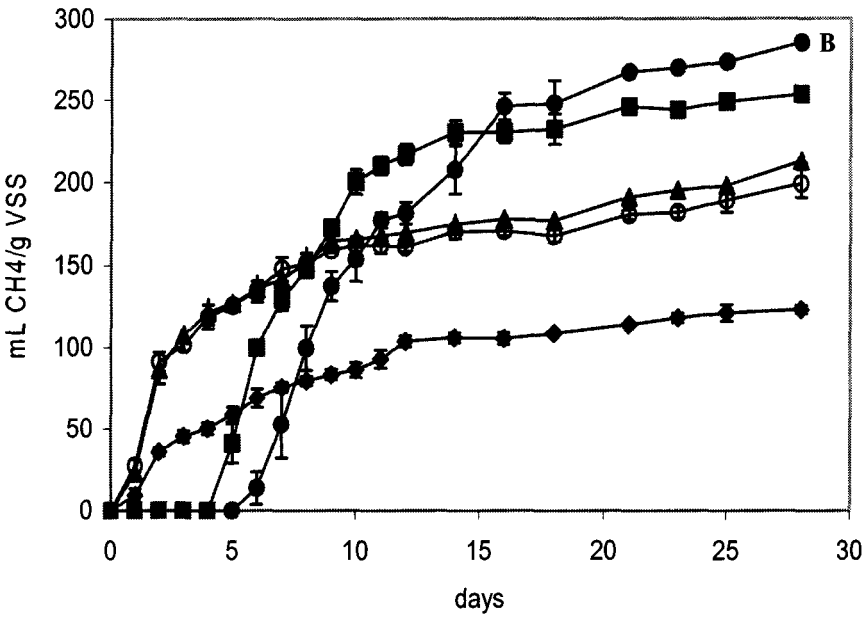

Figure 6.1b. Cumulative methane production in the BMP assays of the digested biowaste. Error bars: standard deviations on quadruplicate serum flasks (error bars may be too small to be visible on the figure). Key: -♦- Untreated Biowaste, -▲- WO Biowaste [B], -○- WO Biowaste [A], -■- WO Biowaste [C], -●- WO Biowaste [D]

Relative to the specific methane yield in the first digestion (0.25 L of CH_4/g of VSS raw biowaste), a gain in methane production of up to 60-62% could theoretically be reached in the second digestion by applying the WO conditions C or D (Table 6.3). At lower WO oxygen pressures (0-3 bar), a gain of 52% in methane yield could be achieved (Table 6.3). For the untreated waste, 36% increase in methane yield was reached relative to the first digestion.

Table 6.4 summarizes the methane yields and the reactor performance of the two 3-L reactors on raw food waste and on the first (DRANCO) and second digestions (3-L reactors) of the biowaste (Figure 6.2a).

Table 6.3. Enhanced cumulative methane yields in the BMP assays (28 days) of WO digested biowaste for the second digestion only (BMP Assays) and including the first digestion

Parameter	**Unit**	**Control**	**A**	**B**	**C**	**D**
Second digestion						
Specific CH_4 yield	L CH_4/g WO VSS	-	0.20	0.21	0.25	0.29
Specific CH_4 yield	L CH_4/g VSS digested biowaste*	0.12	0.18	0.19	0.21	0.22
Increase in yield	%	-	50	51	72	76
First + second digestion						
Gain in specific CH_4 yield	L CH_4/g of VSS raw biowaste**	0.09	0.13	0.13	0.15	0.16
Total specific CH_4 yield	L CH_4/g of VSS raw biowaste***	0.34	0.38	0.38	0.40	0.41
Increase in yield	%	36	52	52	60	62

*Values calculated from the COD losses shown in Table 6.1

**1 g VSS digested biowaste = 1.37 g of VSS raw biowaste (Table 6.4)

***Specific CH_4 yield in first digestion = 0.25 L of CH_4/g of VSS raw biowaste (Table 6.4)

For the raw food waste (days 0-22, Figure 6.2a), the specific methane yield averaged around 0.35 L of methane/g of VSS, which was about 1.5 times lower than the specific methane yield found in the BMP assays (0.54 L of methane/g of VSS).This corresponded to an average biogas production rate of 3.8 L/day (Figure 6.2a) with an average methane content of 59% and a TSS/VSS removal in the range of 50%. The reactor performance was stable with a pH of 8.0 and a low total VFA concentration (< 2 mM) (Table 6.4). The standard deviations for both reactors were determined on at least 4 samples taken at regular time intervals (Table 6.4). During days 22-35 (Figure 6.2a), the seeds of both reactors were gradually adapted for 2 weeks with digested biowaste by using a blended feed of raw food waste and digested biowaste and from day 35 on a feed of 100% digested biowaste (Figure 6.2a).

From days 35-46 (Figure 6.2a and 6.2b), a second digestion of the WO digested biowaste was performed by using reactor 1 as a control reactor (untreated waste) and using reactor 2 for the WO waste (Table 6.4).

Table 6.4. Methane yields and performance data of the 3-L reactors during digestion of raw food waste (day 0-22) and for the first (DRANCO) and second (day 35-46) digestion of the biowaste. For the biowaste : Reactor 1, Untreated Waste; Reactor 2, WO Waste

Parameter	**Units**	**Raw Food Waste (day 0-22)**		**First digestion**	**Second digestion (day 35-46)**	
		Reactor 1	Reactor 2	DRANCO Digester	Reactor 1	Reactor 2
Daily VSS loading rate	g VSS/L.day	2.1	2.1	7-14	1.45	0.9-1.2
Retention time	d	20	20	15-25	15	15
% Methane in biogas	%	59 ± 1	59 ± 1	50-60	22 ± 5	46 ± 6
Specific methane production	L CH_4/g VSS	0.35 ± 0.03	0.35 ± 0.03	0.25	0.26 ± 0.03*	0.34 ± 0.02*
Acetate	mM as HAc	0.9 ± 0.5	0.9 ± 0.5	-	3 ± 1.4	2 ± 1.2
Propionate	mM as HAc	0.6 ± 0.2	0.6 ± 0.2	-	2 ± 0.8	1.3 ± 1
Butyrate	mM as HAc	0	0	-	0.5 ± 0.2	0.2 ± 0.1
Isobutyrate	mM as HAc	0.3 ± 0.2	0.3 ± 0.2	-	0.3 ± 0.1	0.23 ± 0.1
Total VFA (digester)	mM as HAc	1.8 ± 1	1.8 ± 1	-	5.8 ± 2	3.7 ± 1.7
pH	S.U.	8 ± 0.2	8 ± 0.2	8	7.7 ± 0.2	7.8 ± 0.2
TSS removal	%	45 ± 4	45 ± 4	25	26*	35*
VSS removal	%	56 ± 3	56 ± 3	37	39*	50*

*Total values for first and second digestion

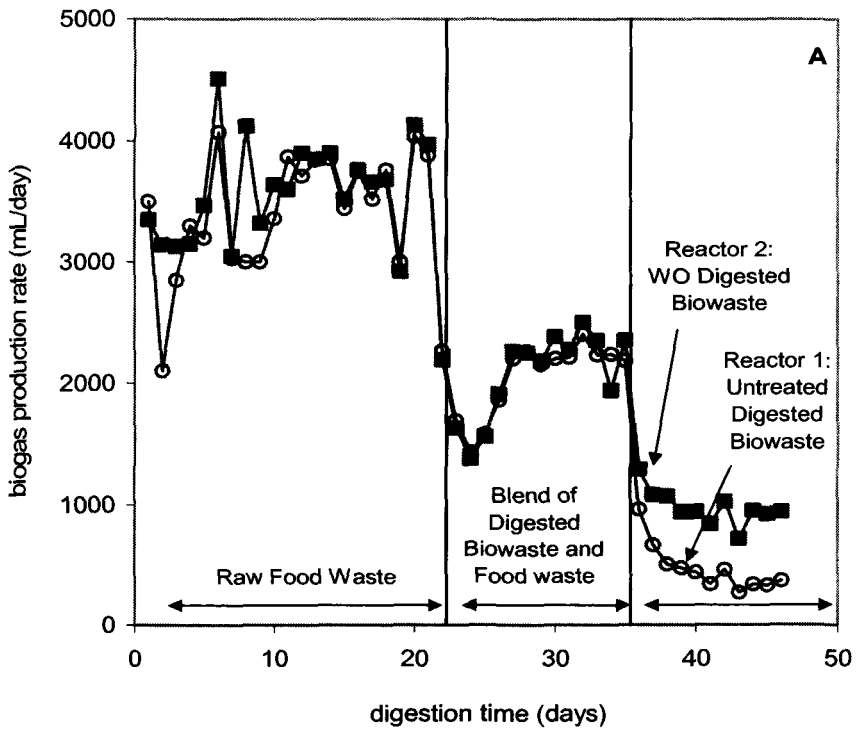

Figure 6.2a. Biogas production rate with raw food waste (days 0-22), with a blend of raw food waste and digested biowaste (days 22-35) and digested biowaste (days 35-46) for reactor 1 (○) and reactor 2 (■)

In Figure 6.2b, the biogas production rate as well as the cumulative biogas yield of both reactors for the second digestion is depicted from day 35 to day 46. The sharp decrease in biogas production from day 35 on for both reactors (Figure 6.2a) was due to the change of the feed from a mixture of digested and raw waste to only digested waste. Furthermore, the loading rate of the reactors at day 35 was decreased from 150 mL to 100 mL. During second digestion, reactors 1 and 2 generated a daily biogas production of 350 mL and 950 mL of biogas, respectively. The average methane content of the biogas was 22% for reactor 1 and 46% for reactor 2. Taking into account an average VSS removal of 37% during the first digestion (Table 6.4), these figures corresponded to an extra specific methane production of 0.01 L of methane/g of VSS raw biowaste for the untreated biowaste (Reactor 1) and 0.09 L of methane/g of VSS raw biowaste for the WO biowaste (Reactor 2). Compared to the specific methane yield during first digestion (0.25 L of methane/g of original VSS), the wet

oxidation treatment followed by a second digestion increased the total specific methane yield by approximately 35-40% (0.34 L of methane/g of original VSS). Without WO treatment, the second digestion resulted in only 4-6% gain in methane yield (0.26 L of methane/g of original VSS) (Table 6.4). The methane yields obtained with the 3-L reactors were approximately 1.1-1.3 times lower as compared to the yields found in the BMP assays. During days 35-46, the biogas production for conditions C (first week) and for D (second week) did not differ significantly (data not shown). The VFA concentrations in both reactors were low (< 10 mM total VFA) (Table 6.4).

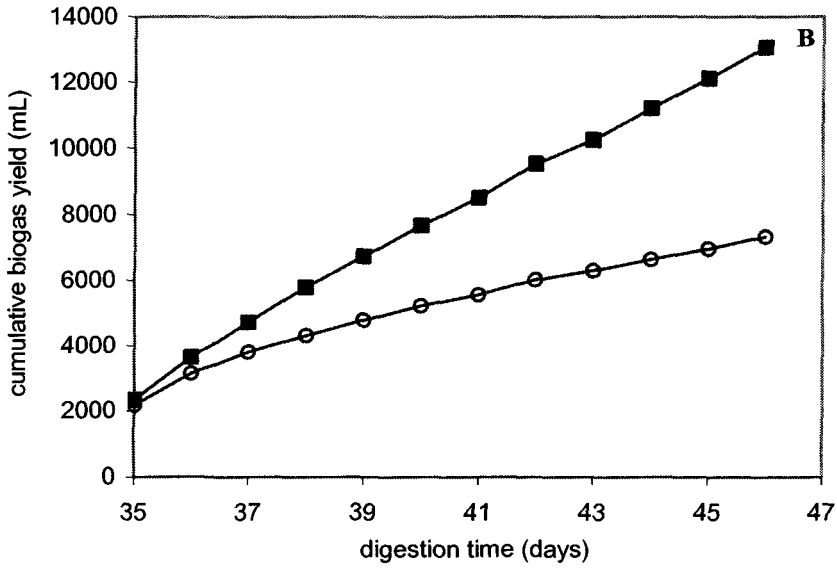

Figure 6.2b. Subset of Figure 6.2a: cumulative biogas yield for the untreated digested biowaste (○) and the WO digested biowaste (■) (days 35-46)

Discussion

Effects of wet oxidation on carbohydrate mass balances

Wet oxidation treatment of the different organic wastes resulted in clear effects on the carbohydrate composition of the materials. The O_2 pressure and temperature during WO were

decisive parameters for the material mass balances and for the subsequent anaerobic biodegradability of the wastes (Tables 6.1 and 6.2). WO involves a chain reaction mechanism in which oxygen and (hydroxyl) free radicals actively participate (Kolaczkowski et al., 1999; Robert et al., 2002). Due to the oxidative conditions, a decrease in the pH could be noticed for all tested WO conditions as a result of the production of acids from the hemicellulose and lignin fraction (Table 6.1) (Klinke et al., 2002; Kolaczkowski et al., 1999). The most pronounced pH decrease (up to 5.8 units) could generally be observed for the highest oxygen pressure (12 bar) mainly due to the enhanced lignin oxidation (Klinke et al., 2002). The lignin oxidation was much higher (64-74%) for oxygen pressurized WO (conditions C and D) as compared to WO at low oxygen pressure (17%, condition B) or in the absence of oxygen (0%, condition A). This can be explained by the occurrence of high amounts of phenoxyl linkages in lignin, which are excellent radical mediators during oxidative processes (Dorrestijn et al., 2000). The main degradation products of lignin after wet oxidation have been reported to be carboxylic acids and partially CO_2 (Lissens et al., 2004a; Lissens et al., 2004b). Hence, the total free acid concentrations were highest for conditions C and D. Apart from the higher oxidation temperature, the superior lignin oxidation for condition D was due to the addition of Na_2CO_3 since alkaline treatment was previously found to enhance lignin oxidation for other biomasses (Chang et al., 2001b).

Hemicellulose solubilization, and to a lesser extent cellulose solubilization, was also promoted at higher oxygen pressure and oxidation temperature (Table 6.2). The lower cellulose reactivity (linear configuration, high polymerization degree and crystalline structure) compared to the reactivity of the highly branched hemicellulose and lignin during wet oxidation caused a high enrichment of the WO solids in cellulose (Table 6.2) and a high total cellulose recovery. Only for condition D, the majority of the hemicellulose fraction was oxidized to CO_2 and possibly to sugar degradation products such as furan derivatives. It is assumed that the carbohydrate losses were due to oxidation to CO_2, which coincided with the high COD loss (33%) for condition D. For the other conditions, thermal cellulose degradation was insignificant since it is generally believed only to occur at temperatures higher than 200°C (Scheirs et al., 2001).

The release of soluble organic material (COD) was also significantly higher for the WO runs at high oxygen pressure as compared to the WO runs at low oxygen pressure. Compared to the controls, the soluble COD level was 4.7-5.8 times higher at high oxygen pressure whereas it was only a factor 2.3-3 times higher for low pressure (Table 6.1). These solubilization

levels are higher compared to the ones found by Liu et al. (2002), who found a factor 3 increase for steam pressure disruption applied to primary digestate of MSW.

Effects of wet oxidation on anaerobic biodegradability of raw waste

Figure 6.1 shows the effect of the composition of a waste stream (Figure 6.1a) as well as the effect of the applied WO conditions (Figure 6.1b) on the anaerobic biodegradability of raw and digested waste after assessing WO. While a doubling of the methane yield was achieved for WO yard waste compared to the reference, a minor increase (7%) in methane yield was observed in case raw food waste was subjected to WO. These observations can be explained by inherent differences in lignocellulose composition and characteristics of the lignin fraction of both wastes. Although it was previously shown that both wastes have a similar lignin content (21-22 g/100 g) and also rather similar cellulose and hemicellulose content (Table 6.2) (Lissens et al., 2004a; Lissens et al., 2004b), it can be assumed that the amount of readily biodegradable and soluble organics in the food waste is much higher as compared to the woody yard waste (Eleazer et al., 1997). Hence, the WO pretreatment could provoke a substantial beneficial effect on the biodegradability of the fibrous yard waste while this was not the case for the food waste.

Effects of wet oxidation on anaerobic biodegradability of digested biowaste

The oxygen pressure during WO was a decisive parameter for the subsequent anaerobic biodegradability of digested biowaste (Figure 6.2). Higher oxygen pressure (conditions C and D) during WO greatly promoted the methane formation from digested biowaste. Hence, since the characterized VSS fraction of digested biowaste consisted of mainly lignin (Table 6.2), the oxygen pressure during WO is a crucial parameter to convert lignin into biodegradable low-molecular compounds and to enhance lignin utilization during anaerobic digestion. The generally low lignin conversion under anaerobic conditions and the potential toxicity of its principal components to many organisms support the assumption that lignin degradation products may have caused the delay in methane production observed for conditions C and D (Liu et al., 2002). However, the release of significant amounts of bacterial inhibitors during WO was very unlikely due to the rapid burst of methane after 5 days in the BMP assays, the high feed-to-seed ratio (1:1 to 1.5:1) in the BMP assays, and the satisfactory reactor performance of the 3-L reactors. Moreover, it has been shown that (alkaline) wet oxidation

does not produce substances that are inhibitory to yeast in bio-ethanol production from biomass (Klinke et al., 2002; Bjerre et al., 1996). Therefore, it is more likely that the low pH of the WO wastes caused the delay in methane production.

As a whole, the specific methane yields found in the BMP assays for raw food waste and digested biowaste were approximately a factor 1.1-1.5 higher than the ones found for the 3-L reactors (Tables 6.3 and Table 6.4). This was most likely caused by the longer retention time in the BMP assays (28 d versus 15-20 d).

Extrapolation to full-scale enhanced methane production

On the basis of the methane yields achieved with the 3-L reactors, a theoretical gain of about 35-40% in methane production can be expected if WO (12 bar oxygen pressure) followed by a second digestion would be applied on digested biowaste from the full-scale DRANCO plant (Table 6.4). Liu et al. (2002) also reported an improved methane yield of 40% for MSW after steam disruption and a second digestion However, they applied a longer digestion retention time (22-30 days) and the digested solids contained a comparatively higher amount of VSS (cellulose and hemicellulose) and lower lignin levels. Furthermore, Liu et al. (2002) reported that the digested MSW after the second digestion was substantially enriched in lignin, thereby postulating that lignin conversion in the second digestion was rather low. This confirms the finding that pressurized oxygen during thermal pre- or intermediate treatment of organic waste acts as a catalyst to make lignin bio-available during subsequent digestion. This partially explains the much higher improvement in methane yield compared to previously reported physicochemical and biological procedures with reported beneficial yields in the range of mostly 10-25% (Mata-Alvarez et al., 1999).

The extrapolation of the results in this study to the full-scale DRANCO plant (50,000 tons of organic waste per year) would impair that the gain in methane yield expressed as electrical power (at 3.98 kWh/m^3 of methane) needs to be weighed off against the estimated costs made for the wet oxidation pretreatment (on raw waste) or intermediate treatment (on primary digested waste). The first scenario refers to wet oxidation as a pretreatment for primary digestion, giving rise to an estimated increase of the total methane yield of 70% (based on raw yard waste). At an average European feed-in tariff of 0.068 € for each kilowatt hour provided into the grid (Cerveny and Resch, 1998), the beneficial electricity production would correspond to 11 €/ton of original input waste. Applying the second scenario (WO as an intermediate treatment followed by a second digestion) at an estimated increase of the total

methane yield with 40% (Table 6.4), the electricity profit would mount to 6 €/ton of original input waste (at 75% of the original input tonnage). The operational costs made for WO encompass the use of chemicals (mainly pressurized oxygen) and electricity consumption. The electricity requirement can be considered to be minor as only energy is required to heat up the reactor (once) to 150°C. Beyond that temperature, the WO reaction is exothermic (Kolaczkowski et al., 1999; Lendormi et al., 2001) and consequently generates heat corresponding to 4100 kJ/kg of DM biomass (Thomsen, 2003). Hence, the effect of oxygen pressure on the operational cost is rather high, whereas the effect of treatment time and temperature (185°C vs 220°C) is rather minor due to the self-sustaining character of the WO reaction above 150-160°C. Furthermore, it has previously been found that only 1/12 of the oxygen supply is effectively consumed during the process (Thomsen, 2003). Hence, the recovery and reuse of oxygen during the process can considerably decrease the oxygen supply costs. Considering both the operational and capital costs (depreciation time of 15 years) of the WO unit, a first estimation shows that the gain in beneficial electricity production might cover the total costs made for WO treatment. Further pilot-scale studies are required to determine the effect of heat and oxygen recovery during WO on the economical feasibility of the process and to evaluate the plausibility to omit the conventional oxygen-requiring aerobic post-treatment after digestion (Liu et al., 2002). The decrease in the amount of solids after the second digestion will further lower the cost of solids handling and the WO process will ensure a full sanitation of the effluent.

In current full-scale applications, typically only 50% of the organic content present in the organic waste is converted into biogas. In light of the Kyoto agreements and the EU green electricity certificates, additional technologies to enhance the methane yield from various wastes and to ensure a biologically safe digested product are needed. The WO process as presented in this work was shown to enhance methane yields by approximately 35-70% from raw and digested lignocellulosic biowaste. Wet oxidation has a higher techno-economical feasibility as compared to other pretreatment technologies for anaerobic digestion due to the low oxygen consumption for the presented WO conditions, the self-sustaining character of the WO reaction, and the opportunity for heat and oxygen recovery. Pilot-scale studies are currently carried out to establish the technical and economical benefits of the WO technology in addition to methane and ethanol recovery from various biomasses and wastes.

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Chapter 7

GENERAL DISCUSSION, FUTURE PERSPECTIVES AND CONCLUSIONS

7.1. THE VERSATILITY OF WET OXIDATION IN MSW TREATMENT

Biological treatment is by far the most applied method for the purification of wastewater and, to a lesser extent, for the conversion of solid organic waste. This is due to the fact that it is generally less expensive compared to non-biological treatments. Furthermore, from an operational point of view, biological treatment of waste mostly involves straightforward processes at ambient pressures and temperatures and it can handle a wide variety of wastes.
As a whole, anaerobic biodegradation of organic waste is even slower than aerobic degradation and hence conversion or removal efficiencies are lower. This results in relatively carbon-rich and recalcitrant effluents requiring further processing prior to reuse and recycling.

Clearly, biological treatment methods cannot efficiently cope with all wastes. This is reflected in the slow or incomplete degradation of certain fractions and the left-over of slowly biodegradable and recalcitrant by-products. Moreover, toxic substances (e.g., xenobiotics) can inactivate microorganisms and in case they can be biologically degraded, the time needed for complete biodegradation is mostly longer than the retention times typically applied in biological treatment. In addition, biological safety of treated effluents for direct reuse purposes can often not be guaranteed by biological treatment alone.

In this context, non-biological treatments play a significant role. In this discussion chapter, the significance of wet oxidation processes in both wastewater and solid waste treatment is discussed in the light of Chapters 3, 5 and 6 of this work. In a second part, the meaning of bioregenerative life support in organic waste treatment (Chapter 4) is given and the lessons learned from it for integrated waste management are illustrated. In a last part, the future opportunities for wet oxidation technology in integrated waste management and for biofuel production are highlighted.

7.1.1. The role of advanced oxidation processes (AOP's) in wastewater treatment

Advanced oxidation processes have in common that they produce highly reactive hydroxyl radicals which are useful for two purposes: the oxidation of chemical substances and the kill-off of waterborne living organisms. The oxidation reaction of the radicals with organics is mostly non-selective and is based on hydrogen abstraction (Kraft et al., 2003). This is one of the main differences with biological degradation, whereby organic substances can be degraded selectively by specific enzymatic reactions. Because of their non-selective behaviour, AOP's can be applied for the destruction of a wide range of hazardous organic (e.g., halogenated hydrocarbons, aromatic compounds, phenols and pesticides) and inorganic (ammonia, cyanide, sulfide and nitrite) compounds in water (reviewed by Vogelpohl, 2001).

Because of the broad spectrum action of AOP's, the main issue consists of the application of oxidation processes either as a stand-alone treatment process or as a post-or pretreatment step to (mostly biological) conventional processes as part of an integrated treatment system. The success of AOP's as single treatment processes to raw wastewaters has mostly been seriously impaired by the high operational costs (> 5 €/kg COD removed) involved. This is due to the non-selectiveness of the technique, namely that organic substances different from the target molecules also react with the generated hydroxyl radicals and hence considerably decrease the efficiency of the process. Therefore, Scott and Ollis (1995) and Ollis (2001) suggested that the potential advantages for water treatment via process integration are larger than for single technology processing. These authors suggested that the treatment of four types of wastewater can benefit from an integrated process approach:

- Biorecalcitrant or totally non-biodegradable wastewaters
- Wastewaters containing insoluble compounds
- Wastewaters containing polymeric compounds with high molecular weight
- Biologically inhibitory wastewaters

7.1.1.1. Selection of most emerging AOP's in wastewater treatment

More than 100 examples in literature have been described that indicate the plausibility and sometimes the utility of sequential chemical and biological oxidation of recalcitrant

wastewaters (Ollis, 2001). Besides the earlier mentioned studies on (mostly) synthetic wastewaters containing single recalcitrant compounds (Vogelpohl, 2001), numerous studies have been applied to industrial multicomponent feed streams such as effluents from the textile, paper, tannery, vinasse, olive, pesticide and metal plating industry (Vogelpohl et al., 2001).

Undoubtedly, one of the most successful applications of AOP's sofar both as single treatment and as a combination with biological treatment have been described with effluents from the textile wet-processing industry (Vandevivere et al., 1998; Li and Zhao, 1999). The main reason for this success is the very recalcitrant character of textile effluents and hence its limited biological degradation, containing a wide range of hazardous compounds (dyes, chelating agents, lignin, surfactants, AOX and heavy metals). Other promising applications are situated within the pesticide industry and metal plating industry where heterogeneous photocatalysis (e.g., with TiO_2 catalyst) and the photo-Fenton process have been successfully applied on pilote-scale to combust pollutants (pesticides, EDTA) at a high yield (> 90%) by a solar energy driven process (Vogelpohl, 2001; Babay et al., 2001; Blanco and Malato, 2001).

Because of their intrinsic advantages over other AOP's, the most emerging technologies in the field are ozonisation, photoassisted Fenton oxidation, photocatalysis and electrolysis.

Only for these technologies, pilote scale and even full-scale studies have been reported (Vandevivere et al., 1998; Vogelpohl et al., 2001). However, the photocatalysis technology can only be applied as a final polishing step as the process efficiency is seriously impaired by the presence of suspended solids and other competitive organics. Although ozonisation is a well-established technology for a wide variety of wastewaters, the production of toxic intermediates recalcitrant to further biological treatment (e.g., aldehydes), the short half-life of ozone and its high total cost (4-8 €/kg of COD removed of which up to 75% of the total costs are due to electricity needs) limit its competitiveness (Vandevivere et al., 1998). Despite the promising results for photoassisted Fenton reaction (Acero et al., 2001; Aplin et al., 2001) and the consequent decrease in the production of iron sludge, this relatively new Fenton process still involves the handling and consumption of high amounts of excess hydrogen peroxide (COD:H_2O_2 ratio of 1:1) (Kim et al., 1997).

Until recently, the electrolysis process has seriously been impeded by low electrode lifespan and anode materials with low oxygen overpotential (De Francesco and Costamagna, 2002). However, due to the development of a new type of electrode material (boron-doped diamond

anodes), the electrochemical oxidation process is suggested to become one of the most emerging AOP's in the near-future (Kraft et al., 2003).

7.1.1.2. The electrochemical advanced oxidation process (EAOP)

In Chapter 3 of this work, the application potential of a newly developed electrode material, namely boron-doped diamond thin film electrodes, was illustrated for both the partial decomposition and complete oxidation of chelating agents and surfactants. This material has clear advantages over other electrodes as discussed in Chapter 2 and therefore is one of the most attractive electrode materials in wastewater treatment applications (Kraft et al., 2003). Table 7.1 shows the operational costs of the EAOP's involved in this work (Chapter 3) and an operational cost calculation with BDD electrodes based on equation 1 (Kraft et al., 2003):

$$C_E = \frac{P_{COD} \text{ x } (U_{ec} + (j \text{ x } d)/\Omega)}{(298.5 \text{ mg } O_2/Ah) \text{ x } \eta \text{ x } EC} \qquad (1)$$

with C_E the energy consumption for COD removal (€), P_{COD} the eliminated COD (g O_2), U_{ec} the cell voltage (V), j the current density (mA/cm^2), d the electrode distance (cm), Ω the conductivity of the solution (mS/cm), η the current efficiency for COD removal and EC the electricity cost (€/kWh). According to the law of Faraday, 298.5 mg O_2/Ah are produced.

Table 7.1. Comparison of the operational cost (at 0.1 €/kWh) for the electrochemical treatment of surfactants and chelating agents in aqueous medium and raw industrial wastewater

Surfactants (Chapter 3)		**Chelating agents** (Chapter 3)		**Wastewater** (Kraft et al., 2003)
Deactivation	*COD removal*	*Decomplexing*	*COD removal*	*COD removal*
kWh/kg COD	kWh/kg COD	kWh/kg COD	kWh/kg COD	kWh/kg COD
50-100	50-100	18-20	30-45	16.8
€/kg COD	€/kg COD	€/kg COD	€/kg COD	€/kg COD
5-10	5-10	1.8-2	3-4.5	1.7

It can be deducted that on average, the operational costs for the electrochemical decomplexing and removal of chelating agents approaches the figure (16.8 kWh/kg of COD) found by Kraft

et al. (2003) the most. This is evident since the current efficiencies found for the chelating agents (71-95%) were closest to the 90% current efficiency assumed by Kraft et al. (2003). The much lower current efficiencies found in the surfactant study (5-12%) caused the 3-6 fold higher energy consumption compared to the study of Kraft et al. (2003). As discussed in Chapter 3, the very low surfactant concentrations employed in the surfactant study resulted in mass transfer limitations (decreased adsorption rate onto the BDD surface). Hence, to treat wastewaters with very low COD values (< 200 mg/l), the use of three dimensional diamond anodes (e.g., spheres) is inevitable (Kraft et al., 2003; Fryda et al., 2000). Indeed, at increased anode surface the current density will drop, resulting in less unwanted side reactions of the hydroxyl radicals at low COD concentrations and thus higher current efficiency. Furthermore, the hydrodynamic operating conditions in the cell should favour a turbulent wastewater flow near the electrode surface rather than a laminar flow (Tröster et al., 2002).

When it comes to investments costs, the major capital cost involved in the EAOP process is the BDD anode. Because the BDD film deposition process is still under up-scaling development (Tröster et al., 2002), the prices for diamond electrodes are still very high and are in the range of 10 €/cm^2 surface at this stage (Kraft et al., 2003). Therefore, the application potential for the EAOP process appears to be highest for moderately concentrated (mostly industrial) wastewaters (COD of a few g/l) with a high amount of toxic and/or persistent organics, for which lower BDD anode areas are required compared to very concentrated or diluted solutions. Equation 2 shows which parameters are determining for the calculation of the required electrode area in the EAOP process:

$$A = \frac{C_{COD} \times v}{((298.5\,mg\,O_2/Ah) \times \eta)/j} \qquad (2)$$

with A the diamond anode area (cm^2), C_{COD} the COD concentration which should be removed (g O_2/l) and v the flow through velocity of the water to be treated (l/h) (Kraft et al., 2003). For highly concentrated wastewaters (e.g., COD of > 5 g/l), the required anode area and thus the cost proportionally rises with the organic loading and with the flow. For very dilute solutions (< 200 mg/l of COD), larger anode areas are needed in order to avoid mass transfer limitations. Furthermore, cell design parameters such as the electrode distance (d, equation 1) also need to be optimized to lower the overall cost of the process.

If we assume a current efficiency of 80-90% and an applied current density of 30 mA/cm^2, a BDD anode surface of at least 1 m^2 would be required to efficiently treat a wastewater with 1 g/l of COD at an average flow rate of 100 m^3/hour (100 kg COD/hour). This would correspond to an investment cost of about 0.5 €/kg of COD for the BDD anode (1000 €/100 cm^2 of BDD surface according to DiaCell®) over a 2 year depreciation time. Besides, a second important capital cost is the requirement of a rectifier to produce direct current from alternate current, which is estimated at maximum 0.1 €/kg of COD for a payback time of 2 year. Together, this would correspond to an estimated investment cost of 0.5-1 €/kg of COD for a payback time of 2 years. These costs are lower than ozonisation, for which the capital costs are typically 1-2 €/kg of COD (or 25-40% of the total costs) removed at a comparable depreciation time. Furthermore, the life time of BDD electrodes is much higher compared to other electrodes because they are resistant to corrosion and fouling (Tröster et al., 2002).

In Table 7.2, the operational cost of the EAOP process is compared with two other common AOP's. While ozonisation clearly involves higher operational and total costs, H_2O_2 based processes such as the Fenton process show comparable costs with the EAOP process. However, the fact that handling with chemicals becomes superfluous, that no (toxic) sludges are produced and that the EAOP process is highly suitable for automation can make the EAOP process one of the most promising AOP's for the future.

Table 7.2. Comparison of the operational cost of biological treatment and three most promising AOP's

Biological treatment	**Ozonisation** (Munter, 2001)	**H_2O_2 based AOP** (Munter, 2001)	**EAOP process** (Kraft et al., 2003)
kWh/kg COD	kWh/kg COD	kWh/kg COD	kWh/kg COD
1-3	40-60	15-30	15-20
€/kg COD	€/kg COD	€/kg COD	€/kg COD
0.1-0.3	4-6	1.5-3	1.5-2

To conclude, the EAOP process with DiaChem® electrodes (Tröster et al., 2002) shows that full-scale industrial applications are on their way. Most likely, the process will be applied in a two-step process whereby the EAOP process is followed by a biological treatment. This way, the costs involved in EAOP can be reduced (Table 7.2). One of the most promising

applications in this regard is the treatment of metal plating effluents containing high amounts of EDTA and NTA. Meanwhile, the EAOP process on the chelating agents in this work (Chapter 3) has also been investigated by other authors with promising indications for a two-step process (Kraft et al., 2003; Tröster et al., 2002).

Another but so far less studied application field of BDD electrodes is the final polishing (tertiary treatment) of biologically treated effluents. Whereas disinfection of drinking and process waters (only when COD is sufficiently low) by means of diamond coated electrodes has been established successfully on an industrial scale (E-disinfector, Ecodis NV, Belgium), the simultaneous removal of recalcitrant organic matter is less obvious. Indeed, the practical implication of the EAOP process for removal of low concentrations of residual organic matter is ruled by mass transfer conditions and is largely determined by the BDD surface area.

7.1.2. The role of alkaline wet oxidation in organic waste treatment and management

Wet oxidation (WO) in solid and semi-solid waste treatment is a well-known technology already for years (Kolaczkowski et al., 1999). Nevertheless, full-scale applications of the WO process have been limited to the complete oxidation and destruction of mostly organic wastes (e.g., sewage sludge) under severe conditions. In none of these applications, recovery or reuse of materials was aimed at but the WO process was rather used as an "end-of-pipe" technology to get rid of hazardous materials.

The results in Chapters 5 and 6 show that the WO process operated under mild conditions ($T < 220°C$, $p < 20$ bar) is a versatile technology that can be used for completely other purposes, namely the increased recovery of biofuels from organic wastes. This was illustrated for two cases, namely the production of bio-ethanol from raw carbohydrate-rich municipal waste (Chapter 5) and the enhanced production of biogas from lignin-rich raw and digested biowaste (Chapter 6). Since biological pretreatments are mostly substrate-specific, slower than non-biological pretreatments and do not ensure a complete sanitation of the waste, biologically-based treatments (e.g., enzymes or thermophilic bacteria) to open up the lignocellulosic complexes from municipal waste were not considered to be appropriate. Instead, it was decided to investigate a thermochemical pretreatment to sanitize and open up the lignocellulose at the same time. Because of the heterogeneous substrates involved, the process needed to have a broad non-specific substrate spectrum, a high automation potential

and should result in low production of fermentation inhibitors. Furthermore, the thermal treatment should not involve the use of expensive corrosion resistant alloys and should preferentially allow the recovery of process heat and used chemicals. To meet all of these criteria, inspiration was sought and found at the Risø National Lab of Denmark where a mild wet oxidation process for the production of bio-ethanol from feedstock biomass (e.g., corn stover, bagasse and wheat straw) had been developed in collaboration with the Technical University of Denmark over the last 10 years (Bjerre et al., 1996).

7.1.2.1. The advanced wet oxidation process (AWO)

As discussed in Chapters 5 and 6, one of the most important features of the AWO (alkaline wet oxidation) process compared to other physicochemical pretreatments (Weemaes et al., 2000; Liu et al., 2002) is its ability to largely convert polymeric lignin into soluble monomeric lingo-aromatic compounds and short-chain carboxylic acids. Most likely, this delignification effect was the major contributor in the enhanced bioethanol and biogas production from the investigated wastes.

Chandler et al. (1980) formulated a mathematical correction for bioavailability of an organic substrate based on its lignin content:

$$B = - 0.028\ X + 0.830 \qquad (2)$$

with B the biodegradable fraction of the volatile solids and X the % lignin of the volatile solids. This formula provides evidence that the bioavailability of a substrate linearly decreases with the lignin content of that substrate. This means that for an average lignin content of 15-20% (e.g., wood and municipal solid waste), the biodegradable fraction under anaerobic conditions would only be 30-45% (Chandler et al., 1980).

The study of Healy and Young (1979) demonstrated already in 1979 that more than half of the organic carbon contained in ligno-aromatic compounds (e.g., catechol, cinnamaldehyde, vanillic acid and syringaldehyde) derived from heat treatment under alkaline conditions can be converted into methane gas. These authors concluded already at that time that the amount of ligno-aromatic wastes needing disposal can be reduced by their biological conversion into a useful product, namely methane gas (Healy and Young, 1979). The lack of a clear waste management policy on biowaste at that time however retarded further research in that direction.

Apart from waste management policies and environmental concerns, the potential application of the AWO process will largely be determined by the economical costs of the process. Partially based on personal communication (Thomsen, 2003; Haagensen, 2003; De Baere, 2003), a cost estimation was made of the AWO process when applied at a regional scale in conjunction with an anaerobic digestion plant treating 50,000 tons biowaste/year (AD) (Table 7.3). A cost calculation of the AWO process for bio-ethanol production from raw waste (Chapter 5) was not considered because of the involved scaling effects in bio-ethanol production.

As suggested in Chapter 6, the AWO process can be applied before or after AD. Based on the enhanced biogas yields when applying the AWO process before (1.7-2-fold increase in biogas for AWO-AD process) or after AD (up to 1.4-fold increase in biogas for AD-AWO-AD process), an economical comparison was made between the profit in biogas yield (kWh/ton or €/ton input waste) and the operational costs made for the AWO process (€/ton input waste) (Table 7.3).

Table 7.3. Comparison of the total costs (euro) in conventional AD process with the AWO-AD and the AD-AWO-AD process for an AD plant treating 50,000 tons biowaste/year

Cost (€/ton input waste)	**AD**	**AWO-AD**	**AD-AWO-AD**
Digestion	60-70	60	70
Composting*	8	8 (1.6)	8 (4.8)
Electricity recovery**	-15	-26	-21
AWO total cost***	/	11.2	6.7
TOTAL cost	58	53.2 (47)	63.7 (60.5)

* Numbers between brackets: composting costs for proportionally lower digester amounts at enhanced methane yields

** The enhanced electricity recovery is based on 80% and 40% increase in methane production for the AWO- AD process and AD-AWO-AD process, respectively.

*** Total cost based on the operational cost and the capital cost (depreciation time of 15 years)

Based on an average tonnage of 50,000 tons/year, an AD plant treats biowaste at an average cost of 60-70 €/ton input waste. The post-digestion step involves composting, which is usually only 5-10% of the anaerobic digestion cost or 5-8 €/ton waste (Table 7.3). In case the AWO process is applied prior to AD (AWO-AD process), a gain of 180 kWh/ton waste or 11

€/ton waste (at an average feed-in tariff of 0.068 €/kWh green electricity) can be achieved. For the AD-AWO-AD process, on average 80-90 extra kWh/ton waste or 7 €/ton waste can be recovered. Compared to the AD process, it is assumed that the total digestion costs for the AWO-AD and the AD-AWO-AD process are 10-15% lower and higher, respectively (Table 7.3). This difference can be attributed to the loss of organic material in the AWO-AD process (10-20%) and the increased input flow in the digester for the AD-AWO-AD process.

The major cost involved in the AWO process is the operational cost and more specifically the use of oxygen. Based on a total oxygen requirement of 0.25 g O_2/g DM waste to create 12 bar oxygen pressure, the operational cost (including Na_2CO_3 costs and maintenance) for the AWO-AD process mounts to 9 €/ton waste and for the AD-AWO-AD process to 3.7 €/ton waste. For both processes, the capital costs for the AWO unit are about 2-3 €/ton waste.

If the total costs made for the AWO process are compared with the gain in methane yield, it can be derived that the costs of the integrated AWO processes are in the same range (up to 5 €/ton waste difference) as the costs of the sole AD process (Table 7.3). However, when it is assumed that the composting costs proportionally decrease with the gain in methane yield or that composting could be completely omitted, an overall profit on the total costs can potentially be achieved. Furthermore, the calculation made in Table 7.3 did not take into account the potential oxygen and heat recovery (exothermic process) during AWO treatment as discussed before in Chapter 6.

From these perspectives, it can be concluded that both the technical, environmental and economical data of the integrated AWO process justify tests at pilot-scale. Important issues of the AWO process that are currently under investigation are the application of much higher dry matter contents (up to 30% DM) and the integrated production of bio-ethanol, biogas and hydrogen from selected biomass.

7.1.2.2. Advanced biogas, bioethanol or hydrogen production from biowastes?

The presented AWO process offers new perspectives for the advanced production of biogas, bio-ethanol and hydrogen gas from biowastes. When it comes to the selection of a biofuel process for a determined biomass or waste, three important considerations have to be made:

- The total mass-based and volume-based calorific yield of the biofuel from glucose as a model compound
- The operational cost to produce the biofuel from the feedstock
- The market value of the biofuel and its potential applications

The total calorific yield for each of the biofuels is partially based on their (theoretical) stoechiometric reactions during fermentation:

Bio-ethanol:

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$$

Biogas:

$$C_6H_{12}O_6 \longrightarrow 3\ CH_4 + 3\ CO_2$$

Hydrogen gas:

$$C_6H_{12}O_6 + 6\ H_2O \longrightarrow 12\ H_2 + 6\ CO_2$$

Based on mass weight, the theoretical and practical yield for bio-ethanol production is clearly highest (Table 7.4). The practical yields shown in Table 7.4 are based on reported average substrate to biofuel conversion efficiencies, namely 50-80% for methane (Liu et al., 2002), 50-90% for bio-ethanol (Bjerre et al., 1996) and 15-33% for hydrogen gas (Logan, 2004). The lower efficiencies count for conversion of slowly biodegradable lignocellulose (e.g., in agricultural and household waste) whereas efficiencies higher than 80% are reached with cellulolytic food crops. Despite the much higher energy content of hydrogen gas, the total calorific yield is about 3 times lower for hydrogen gas production from glucose (Table 7.4) than for methane (biogas) and bio-ethanol production.

Table 7.4. The theoretical and practical yields of conversion of glucose into biogas, bio-ethanol and hydrogen gas during fermentation. The total calorific yield is based on the yield in practice and the energy content of each of the biofuels (after Lay et al., 1999; Logan, 2004)

Methane	**Bio-ethanol**	**Hydrogen gas**
Theoretical yield	*Theoretical yield*	*Theoretical yield*
(g/g glucose)	(g/g glucose)	(g/g glucose)
0.27	0.51	0.13
Yield in practice	*Yield in practice*	*Yield in practice*
(g/g glucose)	(g/g glucose)	(g/g glucose)
0.14-0.22	0.3-0.46	0.02-0.04
Total calorific yield*	***Total calorific yield****	***Total calorific yield****
(kJ/g glucose)	**(kJ/g glucose)**	**(kJ/g glucose)**
7.8-12.2	8-12.3	2.4-4.9

* Energy content: 55.5 kJ/g methane; 26.7 kJ/g ethanol; 122 kJ/g hydrogen; 15.6 kJ/g glucose

The volumetrically based calorific yield of biogas is much higher than the calorific hydrogen yield because of the nearly 10-fold lower gas density of hydrogen gas compared to methane gas. This implies the need for much larger storage volumes of hydrogen gas compared to other biofuels. It must be mentioned that other non-biological process routes for hydrogen production from biomass have proven to result in considerable higher hydrogen yields and lower costs: Nath and Das (2003) compared all of the processes including the fermentative process and concluded that apart from natural gas-steam reforming, biomass gasification and pyrolysis are the most economical processes for renewable hydrogen production from (semi-) solid biomass. Besides, methanol production by catalytic hydrogenation of carbon from biomass is also expected to become a competitive fuel of tomorrow (Hamelinck and Faaij, 2002).

Hence, biological hydrogen production is expected to be rather limited to low-cost carbohydrate-rich wastes (e.g., from the food industry), unless high-performance hydrogen producing strains are developed in the future (> 60% efficiency). Nevertheless, hydrogen production from wastewater might be an interesting option because the market value of hydrogen gas is nearly 20 times higher per kg of hydrogen gas compared to methane gas (Logan, 2004) and because of the "negative cost" of wastewater.

Compared to biogas, bio-ethanol has the main advantage that it is a liquid fuel with high performance in internal combustion engines. Despite its decreasing production cost over recent years thanks to the development of more efficient pretreatment methods and enzymes, bio-ethanol production even from refined materials (e.g., sugar cane or pure starch) is still not cost competitive with gasoline production. The main cost involved in the process is the need for high enzyme loadings during the simultaneous saccharification and fermentation process (Sheehan and Himmel, 2001). The distillation costs have already decreased considerably and will probably further decrease in the future because of increased heat recovery (Seeman, 2003). While the difference in costs between gasoline and bio-ethanol from crop-based cellulosic biomass has become relatively small, bio-ethanol production costs from organic waste are still considerably higher due to its inherent lignocellulosic structure. However, it is predicted that cellulosic compounds from municipal waste will also be utilized in the future, provided that they can be efficiently separated from the waste matrix (Askew, 2003).

The biogas production process is a well-established technology and can undoubtedly handle the widest variety of all kinds of wastes. Furthermore, the anaerobic digestion technology is

straightforward which makes it also very suitable for downstream processing. This is illustrated in a suggested scheme in Figure 7.1 where the AWO process is integrated in an overall biofuel production scheme from biowaste.

From an economical point of view, it is preferred that the high calorific compounds (e.g., starch, cellulose and hemicellulose) of presorted organic wastes are converted into high value biofuels such as hydrogen gas and bio-ethanol whereas the low-value residues (ligno-aromatic compounds, carboxylic acids) can be further converted into biogas (Figure 7.1). Both the hydrogen production from the liquid phase and the ethanol production from the solid phase benefit from the AWO pretreatment: the AWO process completely sanitizes the waste and leaves a liquid phase rich in soluble carbohydrates and lignin derivatives whereas the cellulose contained in the solids can be used for ethanol production. The hydrogen and ethanol produced from both fractions could be sold to the market (e.g., transportation fuel) whereas the biogas and heat are locally recovered and reused (by combustion) in the system.

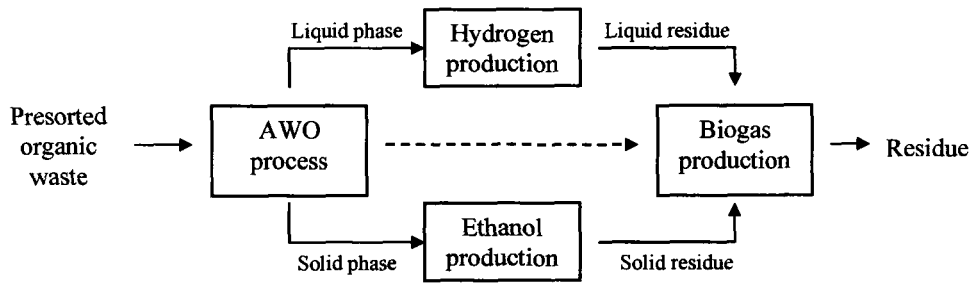

Figure 7.1. Conceptual process scheme for the maximization of valuable biofuel production from solid organic waste

Alternatively, it was shown in Chapter 6 that the AWO process can be applied either before or after anaerobic digestion for the enhancement of biogas production only. This option would be most beneficial when treating lignin-rich mixed waste since anaerobic digestion in combination with AWO is the only biological way to efficiently recover energy from this type of waste. Hence, the AWO-AD process can become a main competitor of composting, which is at the moment the most common technology to deal with lignin-rich waste (EEA, 2001b). Although the total cost of AD is 1.1-1.3 times higher than composting, the enhanced biogas yield, the considerably smaller amount of end-product (solids) and the prevention of harmful emissions are key drivers in diverting biowaste away from composting.

7.2. BIOREGENERATIVE LIFE SUPPORT FOR ORGANIC WASTE RECYCLING

A life support system can be defined as "*any natural or human-engineered system that furthers the life of the biosphere in a sustainable fashion. The fundamental attribute of life support systems is that together they provide all of the sustainable needs required for continuance of life.*" (according to Encyclopedia of Life Support Systems, EOLLS).

In this definition, it is crucial that the functions of the earth are duplicated or mimicked without the benefit of the earth's large buffer systems: oceans, atmosphere and land mass (Lasseur, 2002). This implies that there is no "dilution effect" and that all elements are cycled in a closed waste-to-food and food-to-waste materials loop from and towards the crew on a short time basis. From an engineering point of view, this requires a very close control of the internal mass balances of such a system and the guarantee of a (nearly) 100% complete and biosafe turn-over of all elements.

With regard to space applications such as manned long-term space flights (2-3 years), this last element is crucial since external food supplies will not be available during the flight and the original food supply taken from the earth will not last for the whole journey (Silverstone et al., 2003). Hence, all elements present in the waste generated by the crew need to be thoroughly recycled in a life support system and reconverted into elementary food components.

7.2.1. The role of biological life support systems in advanced organic waste treatment

In Chapter 4, an integrated system for the advanced bioconversion of waste generated by the crew into biogas was proposed. This system, which is based on microbiological as well as thermal treatment technologies, was developed over a period of 2 years by also gathering the knowledge and expertise of other research groups within France (University of Blaise-Pascal) and Germany (Technical University of Hamburg).

The system, which is based on a unique integrated combination of anaerobic digestion, fermentation by the cellulolytic *Fibrobacter succinogenes* and thermal treatment at near-critical conditions, shows for the first time that a dilute lignocellulosic substrate can be converted into energy-rich methane gas and carbon dioxide at a biogas yield of 90-95% of the theoretical yield (Chapter 4). While the technical merits of the work are clear, the remaining issues are the potential use of methane gas in space, the overall energy balance of the system and the behaviour of the system in micro-gravity.

The technology to achieve high-quality single cell protein (SCP) from methane gas by methanotrophic bacteria is well-established and documented (Litchfield, 1983). This technology however requires oxygen and thus extra supply of energy (e.g., electrolytic production of oxygen). Another interesting option remains the conversion of methane gas into electricity and carbon dioxide by the use of combustion engines or direct carbonate fuel cell technology (Katikaneni et al., 2002).

In all cases, the overall energy balance of the system is negative due to high heat requirements of the thermal liquefaction unit (at least 120 kJ/g of solids treated based on 4.2 kJ energy needed to heat 1 liter of water with 1°C) compared to the comparatively small gain in methane (1.7 kJ/g solids treated). Assuming that no process heat would be recovered, this implies that about 70 times more energy has to be provided to the system than there is energy recovered under the form of extra methane (20% increase at 55 kJ/g methane). However, in case heat recovery is considered and external energy supply can be provided from space (e.g., UV radiation), it can be concluded that the proposed system in Chapter 4 has potential applicability for manned long-term space flights to recycle all essential elements in a complete, fast and safe way.

The well-functioning of the system on earth is however no guarantee for the reliability of the system in micro-gravity. Before a system like MELiSSA (see Chapter 4) can be effectively applied in space, the main challenge will first consist of a long-term demonstration on earth.

7.2.2. Bioregenerative life support: lessons learned for integrated waste management

Efficient planning for integrated municipal solid waste (MSW) management requires accounting for the complete set of environmental effects and costs associated with the entire life cycle of MSW. In integrated waste management, this means that no real side-products are generated but that all materials and energy contained in the waste are reused and recycled (Gajdos, 1998). Hence, the residue generated after the integrated biofuel process depicted in Figure 7.1 needs to be further processed for recycling purposes.

Artificial life support systems show that biowaste can be efficiently recycled on a regional scale. This is important since the transport costs associated with the collection of organic waste can make up to 50% of the total costs of a biofuel production process (Askew, 2003). At local scale, biogas is the most preferred biofuel since electricity and heat can be locally recycled, whereas hydrogen and bio-ethanol need more expensive equipment and thus centralised large-scale installations (Nath and Das, 2003; Sheehan and Himmel, 2001).

7.3. FUTURE OPPORTUNITIES FOR ANAEROBIC DIGESTION AND THE AWO PROCESS IN SUSTAINABLE ORGANIC WASTE MANAGEMENT

7.3.1. The AD-AWO-AD approach for enhanced carbon recycling from biowaste

Figure 7.2 shows a sequential anaerobic digestion approach for the conversion of organic waste into biogas by intermediate AWO treatment.

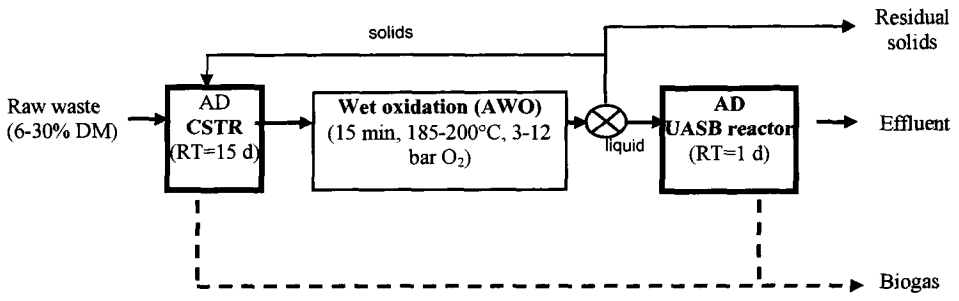

Figure 7.2. Integrated anaerobic digestion of organic waste for enhanced biogas recovery and sanitation

The AD process represented in Figure 7.2 involves the use of a CSTR type of reactor in the first digestion while a UASB reactor with a much shorter hydraulic retention time is used to further convert the soluble organic matter released during AWO in a second stage.

The use of wet oxidation as an intermediate treatment bears the advantage that the first digestate has a high buffer capacity with a pH of typically 8-9 units. This approach allows the readily available organic matter to be converted into biogas and only the more recalcitrant organic material to be subjected to wet oxidation. The solids after wet oxidation, which largely consist of cellulose, could be returned to the main digester for biogas conversion. The wet oxidation liquid contains the majority of the nutrients and salts, solubilized hemicellulose (xylose), lignin degradation products (e.g., acids) and possible pollutants (e.g., di (2-ethylhexyl) phthalate (DEHP) from MSW). A UASB reactor could subsequently be employed to stabilize the liquid and to convert remaining carbon into biogas or the solids could be recycled to the first digester. The final effluent would be rich in nutrients and organic salts, suitable for nutrient and salt recovery. The remaining solid fraction would largely consist of inert recalcitrant matter such as lignin residues and ash and would be much smaller compared to the solid fraction after conventional composting.

Alternatively, the wet oxidation process could be applied as a pretreatment to the raw waste. This option might be particularly attractive for more pure lignocellulosic biomasses such as woody waste (e.g., yard waste), as it is known that the methane yield of these materials in AD is only of the order of 0.08-0.21 l CH_4/g VSS added (Owens and Chynoweth, 1993).

7.3.2. The AD-AWO-AD approach for enhanced nutrient recycling from biowaste[1]

To make anaerobic digestion (AD) a real player in the main stream of waste management, it appears warranted to step away from its thus far positioning. Indeed, at present, AD is pictured as an omnipotent total recycling process. However, the reality is that one of its major end-products, i.e. stable organic matter (e.g., compost, humotex) has no real demand in many, not to say most industrialised countries nowadays. The key feature of AD consists of the recovery of green energy (kWh) and mineral fertilizer (N and P) from organic matter. The first is already receiving recognition in the context of the Kyoto agreements and is in a number of countries sold to the grid at a good price (0.07-0.17 €/kWh). Since both ammonia and phosphate represent fuel equivalents, one should also strongly strive to obtain recognition of these materials in the framework of the Kyoto agreements (see Chapter 2). Hence, within the context of sustainable environmental management, guaranteed price supporting systems for green kWh, green N and green P should be obtained. Once this is achieved, there is a major potential for large scale AD of organic wastes in which the AD permits to deliver 3 green products. Moreover, AD can decrease with 50-90% the amount of organic matter which at the end has to be disposed of by incineration.

7.3.2.1. Market shifts

At present, biowaste from households is subjected to anaerobic digestion to generate green kWh and an organic residue which is marketed as compost. However, mainly due to the stringent quality and regulatory reuse standards as discussed in Chapter 2 of this thesis, market demands are shifting away from the production of a residue to be used as an organic fertilizer. A new approach consists of the unsorted collection, drying, separation and recycling

[1] Redrafted after :
Verstraete, W., Rabaey, K., Fernando, M., Aiyuk, S. and Lissens, G. Anaerobic digestion as a core technology in sustainable management of organic waste. Closing lecture at the *10th World Congress Anaerobic Digestion*, 29 August- 2 September 2004, Montreal, Canada.

or digestion of the MSW and burning of the RDF (refuse derived fuel) e.g., in the cement industry. This approach does however not allow to optimally recover the energy and nutrient potential of the material. This is partially due to comparatively high emissions and losses of organic material during the drying and separation steps.

In a modern market economy driven by the consumer, AD should be entirely positioned in the framework of the growing demand of green energy and clean nutrients. As a matter of fact, the mineral nutrients present in biowaste can be expressed in terms of energy equivalents. Indeed, the fossil fuel based fertilizer production is responsible for about 1.2% of the world energy consumption or 1/3 of the energy use in industrial agriculture. This is due to the fact that 1.1-1.6 L of gasoil (11-16 kWh equivalent) is used for the manufacturing of 1 kg of ammonia from natural gas for N fertilizer and 0.2-0.4 L of gasoil (1.4-2.6 kWh equivalent) for the production of 1 kg of phosphoric acid for P fertilizer from phosphate ore, respectively (Helsel, 1992; Kongshaug, 1998).

7.3.2.2. The green energy and clean nutrient concept

Figure 7.3 shows the proposed default scheme with AD as a key technology for the recovery of 3 green products from source separated organic waste, namely green kWh, green N and green P.

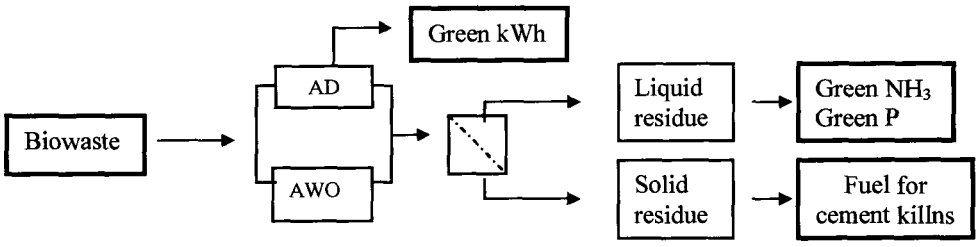

Figure 7.3. Integrated concept for green energy recovery (kWh) and green nutrient recovery from biowaste. AWO: thermal alkaline wet oxidation (T: 185-200°C, p_{O2}: 12 bar, Na_2CO_3: 0-6 g/kg of waste, t: 15 min)

Biogas is collected and converted into electricity at an efficiency of 3.98 kWh/m^3 CH_4 (Figure 7.3). The NH_3 could be recovered free of contaminants via stripping from the liquor while PO_4^{3-} can be selectively precipitated (e.g., with iron or aluminium salts) in an acceptable

form. It must be stressed that source separated collection (SSC) of the waste is a prerequisite to avoid contamination of the recovered phosphorous. The concept proposes to subject the residual solids to total destruction by co-incineration.

To optimize AD in the proposed default scheme, technologies that can increase the energy and nutrient recovery from organic waste are welcome. AWO (Alkaline Wet Oxidation) has been shown to enhance the biogas yield of source separated biowaste with 40% (Chapter 6). Apart from increased energy recovery, AWO can enhance N and P recovery and guarantees absolute sanitation of recovered P. Furthermore, AWO could permit the sanitation and thus disposal of slaughterhouse wastes category 1&2 (Chapter 2).

Energy based calculations show that the gain in energy production from extra green energy recovery (up to 1.2 GJ/ton waste considering the omission of the composting step) and fossil fuel savings by green nutrient recovery (0.3-0.5 GJ/ton biowaste) can compensate for the extra costs made for the AWO treatment, the N and P recovery steps, the dewatering and the incineration of the residue. Based on experimental results and literature data, the digestion of 1 ton biowaste (25% DM) following the default scheme would add an extra 40 m^3 of biogas or 159 kWh to the average 100 m^3 biogas/ton waste. Furthermore, assuming that 80% of the N and P can be recovered (presume 1% N and 0.3% P on DM basis for biowaste), 90-140 kWh (6-10 €) equivalent for NH_4-N recovery and 3-6 kWh (0.2-0.4 €) equivalent for PO_4^{3-}-P recovery can potentially be saved for every ton waste treated. Hence, including the omission of the composting step, the total gross recovery for the 3 green products mounts to 350 kWh (24.5 €)/ton biowaste.

Obviously, the acceptability of the 3 green AD products by the public has also to be investigated. Incentives for the incineration industry to step into the default scheme will have to be explored. Finally, with regard to organic farming and soil health, green and perfectly safe N and P can be applied to these soils to grow so-called soil organic matter enriching crops with soil improving characteristics.

This new AD concept, focusing on 3 green recovery products but totally abandoning the reuse of organic matter, warrants in depth evaluation and particularly overall economic appraisal. It offers an alternative treatment route which is, although somewhat complicated, rigorously safe in terms of unwanted chemical and biological agents. It also is an ethically sound treatment path for SSC biowaste.

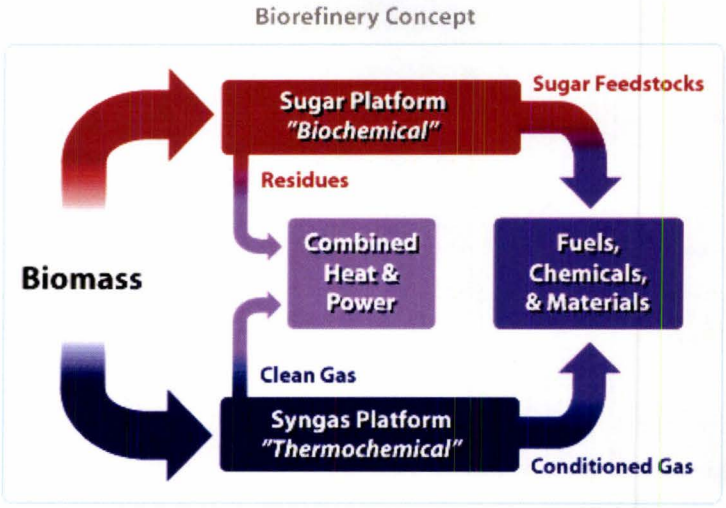

Figure 7.4. The biorefinery concept as an alternative to the petrochemical refinery. The term *biomass* comprises energy-crops (e.g., sugar cane), agricultural wastes (e.g., bagasse) and organic waste (e.g., biowaste)

Eventually, the integrated anaerobic digestion approach will be positioned in the context of the rapidly growing biorefineries (Lynd et al., 1999). The biochemical (e.g., fermentation technology) and thermochemical (e.g., wet oxidation) processing routes at all biomass quality levels (from high grade such as starch derived from corn to low grade such as mixed biowaste) will never reach such a strong synergy as in the presented biorefinery concept. In biorefineries, the fractionation of agricultural feedstocks into intermediate basic products and further into final products is put forward. This approach will place waste management and treatment technologies in a completely new perspective whereby the total reuse and recycling of biowaste will become evident.

SUMMARY

In the year 2000, a European citizen produced on average 330 kg of biodegradable municipal waste. This represents for the EU-15 a yearly total biodegradable waste production of 107 million tons, an enormous amount of waste which is expected to increase with 2% per year. The majority of this biodegradable waste in Europe is still being landfilled (66%) or incinerated, while only a minor fraction (< 15%) is recycled by biological treatment. Due to the serious threats that landfilling poses to the environment (acidification, eutrophication, climate change, human health and pollution), the EU landfill directive of 1999 (1999/31/EC) states that the biodegradable municipal waste (BMW) going to landfill must be decreased to 75% by 2006, to 50% by 2009 and to 35% by 2016 based on the BMW produced in 1995. Incineration of BMW requires extensive energy-input prior to incineration due to the high moisture content of the waste and the overall energy yield is thus low.

Up to now, one of the most economical and thus most applied biological treatments for BMW is aerobic composting or a combination of anaerobic digestion of 15-20 days followed by short-term aerobic composting. The latter approach is currently the most sustainable, since the plant nutrients (N, P and K) and bioenergy (biochemically bound energy) in organic waste are upgraded in controlled bioconversion systems, whereby plant nutrients and digested organics are recycled under the form of compost and bioenergy under the form of methane gas can be used. The digestion efficiency of BMW is however limited to methane yields of typically 50-60% because of the slow or incomplete degradation of certain fractions (e.g. lignocellulosic fibers). Moreover, toxic substances (e.g. xenobiotics) can inactivate microorganisms and in case they can be biologically degraded, the time needed for complete biodegradation is mostly longer than the retention times typically applied in biological treatment. In addition, the biological safety of treated effluents and solids (e.g. compost) for direct reuse purposes can often not be guaranteed by biological treatment alone.

The wet oxidation technology was originally developed in the 80's as an end-of-pipe technology for the complete destruction and oxidation of hazardous waste streams (e.g. sewage sludge). Similarly, advanced oxidation processes were first explored to completely

oxidize and remove hazardous pollutants in wastewater. The high costs involved for both technologies however prevented their widespread application.

The approach of this work consisted of the exploration of wet oxidation technologies and a non-oxidative thermal treatment coupled to biological treatment for the recycling of municipal waste. From an integrated waste management perspective, this coupling was investigated from a technical, environmental and economical point of view.
In a first part, the anodic electrochemical oxidation of commonly occurring pollutants in municipal and industrial organic waste was investigated at newly developed boron-doped diamond (BDD) electrodes. More specifically, the deactivation and oxidation of cationic (hexadecyltrimethyl ammonium chloride) and anionic (sodium dodecylbenzenesulfonate) surfactants as well as the decomplexing and oxidation of common chelating agents (EDTA and NTA) was studied in what was called the EAOP process (electrochemical advanced oxidation process). In both studies, the BDD electrodes showed a higher stability in the investigated solutions (e.g. graphite) and superior oxidation and deactivation rates of the target molecules compared to other carbon-based electrodes. The current efficiencies during decomplexing and oxidation of EDTA and NTA were very high (> 90%) whereas the current efficiencies for electrochemical surfactant removal were low (5-12%). The latter was due to the low surfactant concentrations used in the study, causing mass transfer limitations of the molecules towards the anode surface.

The second and largest part of this work consisted of the exploration of novel wet oxidation technologies and a non-oxidative high temperature treatment in addition to bioconversion processes for the complete sanitation and increased energy recovery from organic waste. In the context of the life support system MELiSSA (Micro-Ecological Life Support Alternative), a total converting and biosafe anaerobic digestion system was developed for the complete reuse of dilute organic waste in space. Several pre- and post-treatments complementary with anaerobic digestion were investigated, of which a high temperature (310-350°C) and high pressure (240 bar) hydrothermal treatment resulted in the highest total biogas yield. Overall, up to 90-95% of the biochemical energy contained in the dilute organic substrate could be recovered under the form of energy rich biogas. The hydrothermal treatment could provide complete sanitation of the waste, largely liquefy the residual recalcitrant organic matter and increase its anaerobic biodegradability with approximately 20%.

In a next phase, the alkaline wet oxidation (AWO) process was investigated for increased sanitation and biofuel production from organic biowaste. Carbohydrate-rich organic wastes such as food waste and yard waste were subjected to AWO and their bio-ethanol potential was subsequently evaluated by means of enzyme assays and simultaneous saccharification and fermentation with yeast. The most optimal AWO conditions were a temperature of 180-190°C, a treatment time of 10-15 minutes, an O_2 pressure of 12 bars (1.2 Mpa) and an alkalinity of about 3 g Na_2CO_3 per 100 g of DM waste. The study showed that on average 65-70% of the cellulose contained in the wastes could be converted into ethanol at a DM content of 10%, corresponding to 20-25 g/L of ethanol. Furthermore, the lignin fraction of both wastes, known to be rate-limiting in anaerobic fermentation processes, could be largely degraded during AWO into biodegradable fragments such as carboxylic acids.

In a final phase of this work, the AWO process was applied to raw organic waste (food waste, yard waste) and to digested biowaste already treated in a full-scale anaerobic digestion (AD) plant (DRANCO, Belgium) to enhance the anaerobic biodegradability and methane yields of the wastes. The specific methane yield could be doubled for the yard waste (from 345 to 685 mL CH_4/g of VSS) by using AWO as a pretreatment before anaerobic digestion whereas the methane yield of the food waste could only be increased with 7% (from 536 to 571 mL CH_4/g of VSS). This finding supported the idea that the lignin content and the characteristics of the wastes are very important for their biodegradability after AWO treatment. In addition, it was shown that for the digested biowaste, the specific methane yield could be further increased with 35-40% (from 0.25 to 0.34 L CH_4/g of VSS) by applying AWO followed by a second digestion. This showed that there is still a considerable amount of methane that can be harvested from anaerobically digested biowaste.

An economical analysis for the EAOP and AWO process demonstrated that the application of both processes would be impaired by high costs in case they would be positioned as stand-alone processes. However, this work showed that the EAOP process has an affordable total cost (1-3 €/kg COD removed) for difficult waste streams, particularly when it would be coupled to biological treatment. The process is amenable for automation and shows high potential to detoxify recalcitrant waste streams such as metal plating and textile effluents. The total costs involved in the AWO process are largely determined by the oxygen consumption (1-5 €/ton waste) and the investment cost (2-3 €/ton waste). It was concluded that for mixed

biowaste, the benefits made in terms of extra green energy production by applying AWO and a second digestion can potentially cover the total cost of the AWO process (5-11 €/ton waste). Moreover, the composting costs proportionally decrease with the gain in methane yield and heat can be recovered from the exothermic AWO process. At the end, the overall economic balance of the AWO process in combination with anaerobic digestion provides good indications that an overall profit on the total costs of 1-10 €/ton input biowaste can be reached.

This work demonstrated that wet oxidation technologies can considerably improve the performance of biological processes for wastewater and solid waste recycling and reuse. This can lead to reduced handling of waste end-products, lower emissions to the environment and higher green energy profits.

SAMENVATTING

In het jaar 2000 produceerde elke Europeaan gemiddeld 330 kg biodegradeerbaar huishoudelijk afval (BHA). Dit komt overeen met een totale jaarlijkse productie van 107 miljoen ton biodegradeerbaar afval in Europa, een enorme hoeveelheid waarvan verwacht wordt dat ze in de toekomst met 2% per jaar zal stijgen.

Het merendeel van dit afval wordt in Europa nog steeds gestort (66%) of verbrand terwijl slechts een kleine fractie (< 15%) wordt gerecycleerd door biologische behandeling. Doordat stortplaatsen een ernstige bedreiging vormen voor het milieu (verzuring, eutrofiëring, klimaatsverandering en vervuiling), stelt de EU in de stortplaatsrichtlijn van 1999 (1999/31/EC) dat het gestorte BHA moet gereduceerd worden tot 75% tegen 2006, tot 50% tegen 2009 en tot 35% tegen 2016, gebaseerd op de productie anno 1995. Bovendien vergt verbranding van BHA veel energie door het hoge vochtgehalte ervan en dus is de netto-energieopbrengst laag.

Tot dusver is aerobe kompostering of een combinatie van anaerobe vergisting (15-20 dagen) gevolgd door een korte kompostering één van de goedkoopste en dus een vaak toegepaste biologische behandeling voor BHA. De laatste benadering (vergisting + kompostering) is momenteel de meest duurzame, omdat de nutriënten (N, P en K) en de biochemisch gebonden energie in het afval worden opgewerkt in gecontroleerde biologische systemen tot respectievelijk kompost en energierijk methaangas. De vergistingsefficiëntie van BHA is echter beperkt tot een methaanrendement van typisch 50-60% door de trage en onvolledige vertering van bepaalde afvalfracties (bv. lignocellulose vezels). Bovendien hebben toxische verbindingen in het afval (bv. xenobiotica) een inactiverende werking op de microorganismen en in het geval deze verbindingen toch kunnen worden afgebroken gebeurt dit meestal over een langere tijdsspanne dan de verblijftijden toegepast in biologische behandeling. Tot slot kan de bioveiligheid van het biologisch behandeld afval bestemd voor hergebruik niet 100% gegarandeerd worden.

De natte oxidatietechnologie werd in de jaren '80 ontwikkeld als een einde-van-de-pijp technologie voor de komplete destructie en oxidatie van problematische afvalstromen (bv. spuislib). Op een gelijkaardige wijze werden geavanceerde oxidatieprocessen (AOP's)

geexploreerd voor de volledige oxidatie en verwijdering van problematische polluenten in afvalwater. De hoge kosten die beide processen met zich meebrachten verhinderden echter een wijdverspreide toepassing.

De benadering van dit werk bestond uit de exploratie van natte oxidatietechnologieën en een niet-oxidatieve thermische behandeling gekoppeld aan biologische behandeling voor de recyclage van BHA. Vanuit een geïntegreerd afvalbeheersperspectief werd deze koppeling onderzocht op technisch, milieukundig en economisch vlak.
In een eerste deel werd de anodische elektrochemische oxidatie van vaak voorkomende polluenten in huishoudelijk en industrieel afval onderzocht aan nieuw ontwikkelde boor-gedopeerde diamant (BDD) elektrodes. Meer specifiek werd de deactivatie en oxidatie van kationische (hexadecyltrimethyl ammoniumchloride) en anionische (natrium dodecyl-benzeensulfonaat) surfactanten alsook de decomplexatie en oxidatie van chelaatvormende agentia (EDTA en NTA) bestudeerd in wat later het EAOP proces werd genoemd (elektrochemisch geavanceerd oxidatieproces). In beide studies vertoonden de BDD elektrodes een hogere stabiliteit in de onderzochte oplossingen in vergelijking met andere koolstof-gebaseerde elektrodes (bv. grafiet) en een hogere oxidatie- en deactivatiesnelheid van de doelmolecules. De stroomefficiënties gedurende decomplexatie en oxidatie van EDTA en NTA waren zeer hoog (> 90%) terwijl de stroomefficiënties voor elektrochemische surfactantverwijdering laag waren (5-12%). Dit laatste was te wijten aan massa transfer beperkingen van de molecules naar het anode-oppervlak door de lagere surfactant concentraties gebruikt in de studie.

Het tweede en grootste deel van dit werk was de exploratie van nieuwe natte oxidatietechnologieën en een niet-oxidatieve hoge temperatuursbehandeling ter aanvulling van bioconversieprocessen voor de komplete sanitatie en verhoogde energierecuperatie van organisch afval. Binnen de context van een levensondersteunend systeem genaamd MELiSSA (Micro-Ecologisch Levensondersteunend Alternatief) werd een totaal converterend en bioveilig anaeroob vergistingssysteem ontwikkeld voor volledig hergebruik van verdund organisch afval in de ruimte. Verscheidene voor- en nabehandelingen complementair met anaerobe vergisting werden onderzocht waarvan een hydrothermale behandeling onder hoge temperatuur (310-350°C) en hoge druk (240 bar) resulteerde in het hoogste totale biogasrendement. In totaal kon 90-95% van de biochemische energie vervat in het verdund

organisch substraat worden gerecupereerd onder de vorm van energierijk biogas. De hydrothermische behandeling kon volledige sterilisatie van het afval bewerkstelligen, het overblijvend organisch materiaal grotendeels oplossen in de vloeistoffase en de anaerobe biodegradeerbaarheid met ongeveer 20% doen stijgen.

In een volgende fase werd het alkalisch natte oxidatieproces (AWO) bestudeerd voor verhoogde sanitatie en bio-brandstofproductie van organisch bio-afval. Organisch afval rijk aan carbohydraten zoals voedselafval en tuinafval werden onderworpen aan AWO en hun bio-ethanolpotentieel werd vervolgens geëvalueerd d.m.v. enzymatische essays en gelijktijdige saccharificatie en fermentatie met gist. De meest optimale AWO condities waren een temperatuur van 180-190°C, een behandelingstijd van 10-15 minuten, een zuurstofdruk van 12 bar (1,2 Mpa) en een alkaliniteit van 3 g Na_2CO_3 per 100 g droge stof afval. De studie toonde aan dat gemiddeld 65-70% van de cellulose in het afval omgezet kon worden in ethanol bij een droge stof gehalte van 10%, overeenkomstig met 20-25 g/L ethanol. De ligninefractie van beide afvalstromen, welke snelheidslimiterend is in anaerobe fermentatieprocessen, kon tijdens AWO grotendeels afgebroken worden tot biodegradeerbare fragmenten zoals carboxylzuren.

In een laatste fase van dit werk werd het AWO proces toegepast op onbehandeld organisch afval (voedsel- en tuinafval) en op vergist bio-afval reeds behandeld in een volwaardige vergistingsinstallatie (DRANCO, België) om de anaerobe biodegradeerbaarheid en het methaanrendement van het afval te verhogen. Door AWO te gebruiken als een voorbehandeling van anaerobe vergisting kon het specifieke methaanrendement worden verdubbeld voor het tuinafval (van 345 tot 685 mL CH_4/g VSS) terwijl het methaanrendement van het voedselafval slechts met 7% verhoogde (van 536 tot 571 mL CH_4/g VSS). Deze bevinding bevestigde dat het ligninegehalte en de karakteristieken van het afval zeer belangrijk zijn voor de biodegradeerbaarheid na AWO behandeling. Voor het vergiste bio-afval kon het specifiek methaanrendement verder verhoogd worden met 35-40% (van 0,25 tot 0,34 L CH_4/g VSS) door AWO toe te passen gevolgd door een tweede vergisting. Dit toonde aan dat er uit anaeroob vergist afval nog een grote hoeveelheid methaangas kan gerecupereerd worden.

Een economische analyse van het EAOP- en AWO proces leidde tot de conclusie dat de toepassing van beide processen hoge kosten met zich meebrengen indien ze als alleenstaande technologieën worden ingezet. Uit dit werk kan worden afgeleid dat het EAOP proces een aanvaardbare kostprijs heeft voor problematische afvalstromen, vooral indien het gekoppeld zou worden aan een biologische behandeling. Het proces is eenvoudig te automatiseren en is geschikt om toxische of recalcitrante afvalstromen te ontgiftigen zoals afvalwaters uit de metallurgie- en textielnijverheid. De totale kostprijs van het AWO proces wordt grotendeels bepaald door het zuurstofverbruik (1-5 €/ton afval) en door de investeringskost (2-3 €/ton afval). Uit dit werk kon worden geconcludeerd dat de winst in groene energie productie als gevolg van AWO behandeling en een tweede vergisting tenminste de totale kost van het AWO proces (5-11 €/ton afval) kunnen compenseren. Bovendien daalt de kost voor kompostering proportioneel met de winst in methaanrendement en zou warmte van het exotherme AWO proces kunnen gerecupereerd worden. Dit kan uiteindelijk resulteren in een netto-winst van 1-10 €/ton bio-afval.

Dit werk toonde aan dat natte oxidatietechnologieën de performantie van biologische processen voor afvalwater- en vaste afvalbehandeling gevoelig kunnen verbeteren. Dit kan leiden tot een verminderde omgang met eindproducten van afvalbehandeling, lagere emissies naar het milieu en hogere groene energierendementen.

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Education

2000-2004	**Doctoral exam** in Agricultural and Applied Biological Sciences, foreseen for May 2004, Ghent University, Belgium Promotion on the subject *Wet oxidation technologies for the integrated bioconversion of organic wastes.* Promotor : Prof. Willy Verstraete.
2001-2004	Doctoral education in the Applied Biological Sciences
1995-2000	**Bio-engineer Chemistry** (Industrial Microbiology) at the KULeuven (Belgium), great distinction. Diploma thesis : *Quantitative analysis of aromatic alcohols in beer by means of stable isotope dilution analysis.* Promotor : Prof. F Delvaux, Prof. JP Dufour Experienced with flavour chemistry in the brewing field by means of chromatograpy and degustation panels. Educational training (July-November 1999) at the Otago University (New-Zealand) for diploma thesis
1989-1995	Highschool: Sciences-Mathematics at the Sint-Albertus College, Haasrode

Additional education

2001-2002	Spanish (Volkshogeschool, Gent). Diploma second year
1998-1999	Student Exchange Programm at the Georg-August University in Göttingen (Germany). Training in German language

International symposia, congresses and scientific awards

2001	Participation at the EURO Summer School «Closed Industrial Cycles » at Wageningen University (26-31 August 2001), poster contribution

2001	9th World Congress on Anaerobic Digestion, 2-6 September 2001, Antwerp, Belgium
2001	Scientec Matrix 2001, International Symposium on Catalytic Water Treatment, Antwerp, November 25-27
2001	15th Forum for Applied Biotechnology (FAB), Gent, September 24-25
2003	17th Forum for Applied Biotechnology (FAB), Gent, September 24-25
2004	Winner of Poster Award on the B-IWA happy hour (Belgian International Water Association) at Procter & Gamble, 23 March 2004, Brussels
2004	Oral presentation at the European Symposium on Environmental Biotechnology, April 25-28, 2004, Oostende, Belgium
2004	Oral presentation at the 10th World Congress on Anaerobic Digestion, 29 August-2 September 2004, Montreal, Canada

Professional experience

2000-2004 Doctoral research at the Laboratory for Microbial Ecology and Technology (Ghent University) :

Participation at several national and **international conferences**. Coordination and writing of scientific projects

Writing of **scientific papers** : see publication list. Tutor of 4 thesis students (bio-engineer and industrial engineer), practical exercises, teaching

Training period (February-July 2003) at the Biocentrum at the Technical University of Denmark (DTU) and at Risø National Lab financed by a FWO-travel fund. Training in sugar analysis via HPLC, follow-up and analysis of fermentation reactors. Bio-ethanol production from organic waste by simultaneous saccharafication and fermentation

Management of a European research project (ESA). Writing of scientific reports. Follow-up of internal lab responsibilities

Collaborator of research projects commissioned by DSM, Janssen Pharmaceuticals and Milliken

Publications (peer reviewed)

Dufour JP, Wierda R, Leus M, Lissens G, Delvaux F, Derdelinckx G & Larsen D (2002). Quantitative analysis of beer aromatic alcohols using stable isotope dilution assay. *Journal of the American Society of Brewing Chemists* 60 (2): 88-96.

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