Anaerobic digestion of food waste:

Current status, problems and an alternative product

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EXECUTIVE SUMMARY

In recent years there has been increased interest in diverting the food waste fraction of the municipal solid waste (MSW) from landfills, due to the high decomposition potential and production of methane as a final product. Recently, anaerobic digestion (AD) has been recognized as one of the best options for treating this waste stream since it results in two valuable final products, biogas and compost that may be utilized for electricity production and as soil fertilizer respectively. Also, the wastewater utilities have shown increased interest for identifying an alternative supplemental carbon source to the use of methanol for enhancing the process of denitrification and meeting regulatory nitrogen standards.

The objectives of this thesis were threefold:

- 1. Identifying the best available AD technology by analysis of the number of existing plants, operating capacity, process efficiency, feedstock flexibility, and the experience of plant managers of the foremost technologies in North America (Toronto, Canada), and in Europe (Barcelona, Spain).
- 2. On the basis of the above information, determine the challenges and problems associated with the application of AD technology as part of the integrated solid waste management systems.
- 3. Conduct an experimental investigation of the possibility of using the products of the anaerobic acidogenesis of food waste as supplemental carbon source for the process of denitrification in wastewater treatment plants (WWTP).

The literature analysis and the field trips showed that the best available AD technology is the Valorga high-solid content process with 19 existing plants and current operating capacity of about 2.2 million tons of waste per year. This technology has demonstrated high flexibility in term of feedstock quality and high efficiency in biogas production per ton of waste processed.

This study also showed that the main problems of the AD plants are feedstock purity, compost quality and odor emissions. The biggest challenge of the AD technology is the economic feasibility in terms of capital investment, operating costs, and revenues from biogas and compost product. It was observed that the capital cost per ton of AD capacity is in the range of the mass- burn waste-to-energy (WTE) plants while the electricity production per ton of processed material is about one fifth that of WTE.

The experimental study carried out as the second part of this project has shown that the anaerobic acetogenesis of food waste is a feasible alternative to biogas generation. The volatile fatty acids (VFA) produced from food waste in a biochemical reactor can be used as a suitable supplemental carbon source for enhancing the denitrification rate in WWTP, in place of the currently used methanol. This finding is of special importance because this carbon source can lower the operating costs of denitrification, decrease the capital and operating costs of the anaerobic digestion of source-separated food waste, and reduce the greenhouse gas emissions of both processes. These results have contributed to a Patent Disclosure for such a process, filed with Columbia Technology Ventures.

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1. INTRODUCTION

Anaerobic digestion (AD) is historically one of the oldest processing technologies used by mankind. Until the 1970s, it was commonly used only in the wastewater treatment plants waste management (Palmisano at al. 1996). The amount of generated solid waste continuously increases and due to the large environmental impacts of its improper treatment, its management has become an environmental and social concern. Food waste comprises 12.4 % of the total municipal solid waste (MSW), according to U.S. EPA estimates. This corresponds to over 40 million tons, according to the 2006 State of Garbage survey of BioCycle and Columbia University (Arsova et al. 2008). Also, EPA has estimated that less than a million tons are co-composted aerobically with yard wastes (EPA 2007).

Rapid biodegradation of the organic fraction of the MSW is of key importance to identify environmental more responsible way to process it rather than landfilling or composting it. Anaerobic digestion has the advantage of biogas production and can lead to efficient resource recovery and contribution to the conservation of non-renewable energy sources. Furthermore, anaerobic digestion is closed and controlled process and based on fugitive emissions is more preferable than landfilling and aerobic composting (Levis et al. 2010).

Even though proven to be effective for treating organics, anaerobic digestion plants are facing difficulties in obtaining fairly clean feedstock that results in technical difficulties with the equipment and poor compost quality. Furthermore, the economic feasibility of these plants has been questioned due to the high investment and operation costs. Also there are more than 40 different AD technologies available on the market and it is challenging to identify the best one (Kelleher 2007).

In this study we have reviewed the anaerobic digestion reactions and examined the AD technologies that are available on the market, in order to identify the most efficient one. Having in mind the difficulties AD plants are facing in practice and the increased interest in finding a sustainable supplemental carbon source for denitrification in the wastewater treatment plants (WWTP), we have also tested the possibility to link these two processes by means of laboratory. This experimental study investigated the possibility to use the volatile fatty acids (VFA), naturally produced in the process of anaerobic acidogenesis from the food waste, as supplemental carbon source for denitrification in the waste water treatment plants (WWTP). This experimental study was conducted over a period of ten months and we examined the possibility to stop the AD reaction before the methanogenesis and instead of methane to produce VFAs. Furthermore we tested the product of this experiment as a supplemental carbon source for denitrification of wastewater. The methods, materials and detailed results are elaborated in this study. All tons reported in this study refer to metric tons.

2. ANAEROBIC DIGESTION PROCESS

Anaerobic digestion (AD) is a microbial decomposition of organic matter into methane, carbon dioxide, inorganic nutrients and compost in oxygen depleted environment and presence of the hydrogen gas. This process, also known as bio-methanogenesis, occurs naturally in wetlands, rice fields, intestines of animals, manures and aquatic sediments, and is responsible for the carbon cycle in the ecosystems.

Natural and anthropogenic sources account for 30 and 70 %, respectively, of the total methane released in the atmosphere every year. Major natural sources of methane are the wetlands and animal guts (mainly insects and ruminants) while the main anthropogenic sources have been identified in the fossil fuel processing industries, rice fields and landfills. Biological activity has been identified to be the cause for more than 80% of the flux of the atmospheric methane (Palmisano et al. 1996).

In general there are three different methanogenic ecosystems in the nature (Figure 1) : (a) in lacustrine and marine sediments, marshes, swamps, rice soils, sludge and digesters where the organic matter is completely degraded; (b) in ruminants and intestinal tracts of almost all living creatures (e.g. humans, insects, termites), where the process of mineralization is incomplete and most of the intermediate products (e.g. volatile fatty acids) are absorbed into the bloodstream; (c) in absence of organic matter (e.g. hot springs) where methanogenesis occurs only from geochemical hydrogen formed as part of the geological process (Garcia et al. 2000).



Figure 1 Schematic diagram of three different methanogenic ecosystems in nature (Garcia et al. 2000)

In Figure 1, the solid arrows show the reactions that occur and the dashed arrows show the reactions that do not occur in the specific ecosystem.

Humans have harnessed bio-methanogenesis for rapid and controlled decomposition of organic wastes and biomass feedstock to methane, carbon dioxide and stabilized residue. In the generalized scheme of the anaerobic digestion, the feedstock is harvested or collected, coarsely shredded and placed into a reactor with active inoculums of methanogenic microorganisms. Since the methane is a significant greenhouse gas, anaerobic digestion has higher control over the methane production and contributes to lower the carbon footprint of the food waste management in the way that the fugitive emissions are lower than then the emissions in the cases of the landfilling and aerobic composting (Levis et al. 2010).

Generally three main reactions occur during the entire process of the anaerobic digestion to methane: hydrolysis, acid forming and methanogenesis. Although AD can be considered to take place in three stages all reactions occur simultaneously and are interdependent. In the experimental study to be described later, we shortened the AD process at the end of the acid forming stage, because the goal was to produce volatile fatty acids and avoid methane production. Methanogenesis was not important in our experimental study but is described below in order to provide the complete picture of the AD process.

2.1 Hydrolysis

Hydrolysis is a reaction that breaks down the complex organic molecules into soluble monomers (constituents), Figure 2, Stage 1. This reaction is catalyzed by enzymes excreted from the hydrolytic and fermentative bacteria (cellulase, protease and lipase). End products of this reaction are soluble sugars, amino acids; glycerol and long- chain carboxylic acids (Ralph & Dong 2010).

Approximate chemical formula for the organic fraction of the municipal solid waste (MSW) is $C_6H_{10}O_4$ (Shefali & Themelis 2002).

Hydrolysis reaction of the organic fraction of the MSW can be represented by the following reaction:

 $C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2$ (Ostrem & Themelis 2004)

2.2 Acid-forming stage

This stage is facilitated by microorganisms known as acid formers that transform the products of the hydrolysis into simple organic acids such as acetic, propionic and butyric acid as well as ethanol, carbon dioxide and hydrogen. (Figure 2, Stage 2)

Acid forming stage comprises two reactions, fermentation and the acetogenesis reactions. During the fermentation the soluble organic products of the hydrolysis are transformed into simple organic compounds, mostly volatile (short chain) fatty acids such as propionic, formic, butyric, valeric etc, ketones and alcohols.

Typical reactions occurring at this stage are the following:

- Conversion of the glucose to ethanol:
- Conversion of the glucose to propionate:

(Ostrem & Themelis 2004)

The acetogenesis is completed through carbohydrate fermentation and results in acetate, CO_2 and H_2 , compounds that can be utilized by the methanogens. The presence of hydrogen is of critical importance in acetogenesis of compounds such as propionic and butyric acid. These reactions can only proceed if the concentration of H_2 is very low (Ralph & Dong 2010). Thus the presence of hydrogen scavenging bacteria is essential to ensure the thermodynamic feasibility of this reaction (Ostrem & Themelis 2004).



Figure 2 Anaerobic Digestion process reactions (DOE 2008)

Important reactions during the acetogenesis stage are as follow (Ostrem & Themelis 2004):

- Conversion of glucose to acetate:
- Conversion of ethanol to acetate:
- Conversion of propionate to acetate:
- Conversion of bicarbonate to acetate:

2.3 Methanogenesis

Methanogenesis is a reaction facilitated by the methanogenic microorganisms that convert soluble mater into methane. Two thirds of the total methane produced is derived converting the acetic acid or by fermentation of alcohol formed in the second stage, such as methanol. The other one third of the produced methane is a result of the reduction of the carbon dioxide by hydrogen. Considering that the methane has high climate change potential the goal is to find an alternative in order to lower the environmental foot print of the organic waste treatment. Therefore in the experimental part we avoided this stage and instead of methane we targeted the production of volatile fatty acids.

The reactions that occur during this stage are as follows (Ostrem & Themelis 2004):

Acetate conversion:

 $2CH_3CH_2OH + CO_2 \leftrightarrow 2CH_3COOH + CH_4$ Followed by: $CH_3COOH \leftrightarrow CH_4 + CO_2$

- Methanol conversion

 $CH_3OH + H_2 \leftrightarrow CH_4 + H_2O$

- Carbon dioxide reduction by hydrogen

 $CO_2 + 4H_2 \leftrightarrow CH_4 + H_2O$

The amount of methane that can be expected to be produced can be calculated as (Parkin & Owen 1986):

$$C_{n}H_{a}O_{b}N_{c} + \left[n - \frac{a}{4} - \frac{b}{2} + 3\left(\frac{c}{4}\right)\right]H_{2}O \rightarrow \left[\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + 3\left(\frac{c}{8}\right)\right]CO_{2} + \left[\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - 3\left(\frac{c}{8}\right)\right]CH_{4} + cNH_{3}$$

In the case of the organic fraction of the MSW this reaction would be as follows: $C_6H_{10}O_4 + 1.5H_2O \rightarrow 0.75CO_2 + 3.25CH_4$

3. BIOCHEMICAL REACTIONS IN ANAEROBIC DIGESTION

The conversion of complex organic matter to methane and carbon dioxide is possible only by the common action of at least four different groups of microorganisms (MO). The essential microbial complex is comprised of hydrolytic bacteria, fermenting bacteria, acetogenic bacteria and methanogenic *Archaea*. These groups of MO have established syntrophic relationships where the later members of the food chain depend on the previous for their substrates, but also they may have significant influence on the earlier members in the chain by removing the metabolic products (Garcia et al. 2000).

The first group of MO consist the hydrolytic bacteria. These organisms catalyze the hydrolysis reaction through the extracellular hydrolytic enzymes they excrete. The resulting monomers from this reaction undergo fermentation directly to acetate, or through the pathway of the volatile fatty acids and alcohols facilitated by the so-called secondary fermenters or obligate proton reducers (Ralph & Dong 2010). These bacteria convert their substrates to acetate, carbon dioxide, hydrogen, and perhaps formate, which are subsequently used by the methanogens (Schink 1997).

3.1. Hydrolytic bacteria

Biodegradable polymers found in the MSW include lignocelluloses, proteins, lipids and starch. Specialized microbial population of hydrolytic bacteria is responsible for depolymerization of these organic polymers towards their building compounds, monomers. Usually this is found to be the slowest and the rate limiting step in the overall anaerobic digestion process. Furthermore, the ultimate methane yield is directly dependent on the efficiency of this reaction (Palmisano & Barlaz 1996).

Extracellular microbial enzymes catalyzing this reaction are known as hydrolyses or lyses. Depending on the type of the reaction they catalyze, these hydrolyses can be esterase (enzymes that hydrolyze ester bonds), glycosidase (enzymes that hydrolyze glycosides bonds), or peptidase (enzymes that hydrolyze peptide bonds). For example, lipases hydrolyze the ester bonds of lipids to produce fatty acids and glycerol. Lyses, on the other side, catalyze the non-hydrolytic removal of groups from substrates (Palmisano & Barlaz 1996).

Lignocellulose refers to the three major components of the plant tissue: cellulose, hemicelluloses and lignin. The cellulose and hemicelluloses are biodegradable and make up over 90% of the biochemical methane potential of the MSW, while the phenolic groups in lignin are even inhibitory to the enzymes. Cellulose is degraded by hydrolyses to yield a soluble disaccharide, cellobiose, which on further hydrolysis results in D-glucose. The cellulolytic enzyme system is composed of endoglucanases, exoglucanases, and glucosidases. The main anaerobic bacteria degrading cellulose include *Bacterioides succinogenes, Clostridium lochhadii, Clostridium cellobioporus, Ruminococcus flavefaciens, Ruminococcus albus, Butyrivibrio fibrosolvens, Clostridium thermocellum, Clostridium stercorarium and Micromonospora bispora* (Palmisano & Barlaz 1996).



Figure 3 Overall process of anaerobic decomposition after Madigan et al., 2003

Hemicelluloses are simpler structured and more readily degradable then cellulose by anaerobic microbes. Despite that, its depolymerization requires complex enzyme system due to the various monomers comprising it. The predominant bacteria found to degrade the hemicelluloses in the rumen are *Bacterioides ruminicola*. *B. fibrisolvens*, *R. flavenfaciens*, and *R. albus* (Palmisano & Barlaz 1996). Pectin represents an important group of hemicelluloses in young plant tissues, berries and fruit. Several *Clostridium* species have been identified as pectinolytic as well as rumen bacteria like *Bacteroides rumenicola*, and *Streptococcus bovis* (Palmisano & Barlaz 1996). Lignin is highly branched, aromatic polymer whose depolymeryzation leads to monomers that can be used by the anaerobic bacteria in several anaerobic energy-yielding processes such as anoxygenic photosynthesis, denitrification, sulfate reduction, fermentation and methanogenesis. However, it is still doubtful whether lignin can be depolymerized to its monomers under AD conditions (Palmisano & Barlaz 1996).

In anaerobic digesters, proteins serve as a source of carbon and energy for bacteria growth and a source of nitrogen. Proteins are hydrolyzed by proteolytic enzymes to peptides, amino acids, ammonia, and carbon dioxide. It has been shown that a specialized groups of anaerobic bacteria such as the proteolytic clostridia (e.g. *Clostridium perfringens, C. bifermentans, C. histolyticum*, and *C. sporogenes*) are responsible for protein degradation in digesters (Palmisano & Barlaz 1996). In addition to these organisms, numerous other species of anaerobic bacteria such as *Bacterioides, Butyrivibrio, Fusobacterium, Slelnomonas Peptococcus, Campylobacter* and *Streptococcus* are capable for depolymerization of the proteins to amino acids and further to simple fatty acids such as acetic, propionic and butyric acid as referenced in Archives of Env. Protection,(Palmisano & Barlaz 1996), (Rozej et al. 2008).

Hydrolysis of the lipids is catalyzed by enzymes called esterase and leads to saturated and unsaturated long chain fatty acids and glycerol. Glycerol is easily assimilated and metabolized by the bacteria while the long chain fatty acids undergo an intracellular beta-oxydation mediated by a variety of enzymes, resulting in short chain fatty acids (e.g. acetic and propionic acid) and hydrogen. Anaerobic microorganisms capable to decompose lipids usually found in MSW anaerobic digesters are *Anaerovibrio lipotyca* and *Syntrophomonas wolfei* (Palmisano & Barlaz 1996). Also, various species of *Clostridium* and *Micrococcus* are able to degrade lipids to Acetyl-coA as referenced in Archives of Env. Protection.

Starch from the food waste is readily biodegradable but requires multiple enzymes to complete its hydrolysis. Three main types of enzymes that act synergistically are: alpha-amylases, beta-amylases, gluco-amylases. Some of the microbes found in anaerobic digesters capable of degrading starch are *Streptococcus bovis, Bacteriodes amylophilus, Selenomonas ruminatium, Succinomonas amylolytica, B. ruminocola,* and a number of *Lactobacillus species* (Palmisano & Barlaz 1996).

3.2 Acetogenic bacteria/hydrogen-producing acetogens (OHPA)

Acetogenesis is the stage when the products of the hydrolysis are processed to hydrogen, carbon dioxide, formate and acetate. This pathway occurs naturally in well balanced methanogenic systems. However, in practice, there are cases of electron or hydrogen accumulation (e.g. when methanogenesis is inhibited) when numerous other fermentation products may be formed (e.g. propionate, butyrate, lactate, succinate, and alcohols) as a mechanism to remove the excess electrons or hydrogen. Organisms that convert these fermentation products to acetate, generally exhibit obligate proton- reducing metabolism and are obligatory dependent on the hydrogen removal as referenced in Archives of Env. Protection. Because of this the acetogenic bacteria are also called obligatory hydrogen-producing acetogens (OHPAs).

Despite the significant importance of synthrophs, the knowledge of their taxonomic position, diversity and physiology is insufficient, mainly because of the difficulties in isolating them. Several important proton-reducing syntrophic bacteria such as butyrateoxidizers, propionate- oxidizers and even acetate-oxidizers have been successfully isolated and cultured from methanogenic communities in recent years as referenced in Archives of Env. Protection. Thermophilic acetate-oxydizing syntroph, Thermacetogenium phaetum, was isolated and characterized by Hattori et al. (2000). The first described syntrophic propionate-oxidizing bacterium is Syntrophobacter wolinii, followed by two other Syntrophobacter species. Syntrophus aciditrophicus, isolated by Jackson et al. (1999), is a universal syntroph oxidizing fatty acids and benzoate. *Smithella propionica*, which was isolated by Liu et al. (1999) is an organism that produces much less acetate from propionate than the Syntrophobacter strains, and besides acetate it produces small amount of butyrate. Thermophilic propionate- oxidizing bacteria have also been described, and two of these have been obtained in pure culture so far: *Pelotomaculum thermopropionicum* strain SI, and Desulfotomaculum thermobenzoicum, subsp. Thermosintrophicum. Finally, Sekiguchi et al. (2000) isolated a thermophilic butyrate-oxydizer capable of oxidizing saturated fatty acids with four to ten carbon atoms.

3.3 Methanogenic microorganisms;

The main route of methane production is through a syntrophic relationship between acetate-oxidizing bacteria and hydrogen-utilizing methanogenic *Archea*. The acetoclastic and hydrogenotrophic methanogens contribute 70% and 30%, respectively, to the methane production in industrial wastewater treatment.

Numerous methanogens have been isolated and described so far, but the studies, mainly based on 16S rDNA cloning analyses, suggest that the most commonly found methanogens genera, in the biogas reactors, are *Methanobacterium*, *Methanothermobacter* (formerly *Methanobacterium*), *Methanobrevibacter*, *Methanosarcina*, and *Methanosaeta* (formerly *Methanotrix*) as referenced in Archives of Env. Protection.

Among the acetoclastic methanogenic organisms, *Methanosarcina* and *Methanosaeta* species has been reported to be dominated in large-scale mesophilic and thermophilic digesters treating wastewater and sewage sludge. Its dominance comes mainly due to its wide tolerance for environmental factors such as nutrients and temperature (Palmisano & Barlaz 1996).

3.4 Interactions between different microbial consortia in the AD reactors

As mentioned previously the anaerobic methanogenesis is a process that evolves at least four different groups of anaerobic microorganisms. Each group contains diverse microorganisms responsible for different metabolic tasks. Distinguishing characteristic of this anaerobic consortium is that different species of anaerobic microorganisms degrade one organic compound interactively, sharing energy and carbon sources from the compound (Sekiguchi et al. 2001).

These organisms have developed specific kind of interdependent relationship called syntrophy, special kind of symbiotic cooperation of mutual dependence of the partner bacteria with respect to energy limitation where neither partner can exist without the other and together they exhibit a metabolic activity that neither one could accomplish on its own. In this unique cooperation between two metabolically different types of microorganisms they depend on each other for degradation of a certain substrate for energetic reasons (Schink 1997).

This unique cooperation between the MOs involved in the methanogenesis has evolved due to the need to utilize the energy obtained from the electron donor substrate more efficiently. The overall reaction anaerobic degradation is a reaction with very low energy yield comparing to the aerobic degradation. The main reason is that the electron acceptor in this case is the carbon dioxide and not oxygen like in the aerobic degradation. Carbon in the carbon dioxide is in the most highly oxidized state with a COD: C ratio of zero. Since the energy available depends on the oxidation state of the substrate and indicates the electrons available for removal as it is oxidized, with carbon dioxide as electron acceptor the amount of free energy available is very low. As shown in the case of the glucose, anaerobic degradation yields around 15 % the energy that would be released through aerobic degradation:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$
 Free energy kJ/mol glucose -2,880
 $C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$ Free energy kJ/mol glucose -428

The syntrophic association between fatty-acid-oxidizing microbes, hydrogen-consuming methanogens, and acetate-consuming methanogens represents one syntrophic example in the methanogenic community. Fatty acids are converted by syntrophic oxidizers to acetate and hydrogen/CO₂, and these products are subsequently utilized by the two types of methanogens to form methane. Without this food chain, the degradation of fatty acids cannot occur unless coupled with the hydrogen- and acetate-consuming reactions, because the first step of the reaction is endergonic (Schink 1997).

Reactions that occur are as follows as referenced in the Environmental Microbiology (Ralph & Dong 2010):

- Conversion of propionate to acetate: $CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$ free energy value: +76.1 kJ
- Conversion of butyrate to acetate: $CH_3(CH_2)_2COO^- + 2H_2O \leftrightarrow 2CH_3COO^- + H^+ + 2H_2$ free energy value: +48.3 kJ

Both reactions have unfavorable thermodynamics and unless in syntrophy with the hydrogen consuming bacteria and methanogens these organisms cannot exist. In particular, hydrogen is the most important intermediate and the hydrogen-scavenging reaction makes the whole reaction energetically feasible. The following reactions occur as referenced in the Environmental Microbiology (Ralph & Dong 2010):

- Acetogenic reactions
- $2HCO_3^- + 4H_2 + H^+ \leftrightarrow CH_3COO^- + 4H_2O$ free energy value: -104.6 kJ
- Methanogenic reactions

 $CH_3COO^- + H_2O \leftrightarrow CH_4 + HCO_3^-$ free energy value: -31.0 kJ

$$4H_2 + HCO_3^- + H^+ \leftrightarrow CH_4 + 3H_2O$$
 free energy value: -135.6 kJ

From this point of view, hydrogen consuming methanogens make an essential contribution not only to the production of methane but also in driving the initial step of oxidation of the organic matter to be degraded by heterotrophic microbes in the reactors. Of the intermediates produced during anaerobic degradation in reactors, butyrate, propionate and acetate are the most important in addition to hydrogen. These substrates (especially propionate and butyrate) are also oxidized by the syntrophic association of fatty-acidoxidizers and hydrogen-consuming methanogens (Sekiguchi et al. 2001).

The energy that the MOs obtain from the electron- donor substrate is used for both, cell maintenance and cell synthesis. Biomass growth yield depends on the fraction of the energy that is available for cell synthesis. In the cases of the methanogens the fraction of the energy available for cell synthesis is fs^0 = 0.05 for acetate methanogens and fs^0 =0.08 for hydrogen utilizing methanogens. This small amount of energy available leads to microbial growth yield of Y=0.035 gVSS/gBODI and Y= 0.45gVSS/g H₂ respectively for the acetate and hydrogen utilizing methanogens, and categorize these organisms into slow growing organisms. Therefore the methanogenesis is the rate limiting step in the anaerobic digestion reaction and requires retention time of at least 15- 20 days for a steady state system as referenced in the Environmental Biotechnology: Principles and Applications.

Since the methane produced in the AD systems is 70% produced from acetate oxidation of special interest for the experimental part of this study was its minimum limiting retention time, $[\theta_x^{min}]_{lim,}$, of 4 d. This allowed us to design the reactor and secure washout of the methanogens in order to avoid methane production. On the other side the hydrolysis and acidification occur readily and the concentration of the volatile acids increases from the retention time of 3 to 5 days as referenced in the. From here the designed retention time in the experimental set up for acidogenesis was decided to be 4 days.

4. PARAMETERS AFFECTING THE ANAEROBIC DIGESTION OF FOOD WASTE

4.1. pH value

The pH value of the reacting material is a pivotal factor in the AD of food waste. The importance of the pH is due to the fact that methanogenic bacteria are very sensitive to acidic conditions and their growth and methane production are inhibited in acidic environment. In batch reactors pH value is closer dependent of the retention time and loading rate, as will be described later.

Different stages of the AD process have different optimal pH values. Also the pH value changes in response to the biological transformations during different stages of AD process. Production of organic acids during the acetogenesis can lower the pH below 5 what is lethal for methanogens and cause decrease in the methanogens population. Consequently this would lead to acid accumulation, since the methanogens are responsible for the consumption of the formed acids, and digester failure. On the other side excess proliferation of methanogens can lead to higher concentration of ammonia, increasing the pH above 8, what is inhibitory to the acidogenesis (Lusk 1999).

Constant pH is crucial in the start-up phase because fresh waste has to go first thru the stage of hydrolisys and acidogenesis before any methane can be formed, which will lower the pH. In order to keep the value of pH on the equilibrium buffer has to be added into the system, such as calcium carbonate or lime.

Although it has been proven that the optimal range of pH for obtaining maximal biogas yield in anaerobic digestion is 6.5–7.5, the range is relatively wide in the plants and the optimal value of pH varies with substrate and digestion technique (Liu et al. 2007). The pH value is a function of volatile fatty acid (VFA) concentration, bicarbonate concentration, and alkalinity of the system as well as the fraction of CO_2 in digester gas. In order to fix constant pH value it is crucial to adjust the relationship between the VFA and bicarbonate concentrations (Liu et al. 2007).

In 2007 Cun-fang Liu a, Xing-zhong Yuan a, Guang-ming Zeng a, Wen-wei Li and Jing Li b developed a mathematical model to describe the relationship between the pH and methane production for anaerobic digestion of organic fraction of the municipal solid waste (MSW) in a batch process. The maximum energy recovery of MSW can be obtained by using optimization control of pH. This model includes all three processes occurring in the AD system and is described as a set of algebraic equations that have been formulated based on mass balances for substrates, products and microbial components, and physic-chemical equilibrium relationships among ionized/unionized species.

The expression of relationship between pH and methane yield is:

$$\frac{d\mathrm{CH}_4}{dt} = \left(\mathrm{Vm}_{\max}\mathrm{Xm}\frac{\mathrm{Ac}^{-1}\mathrm{x}10^{-\mathrm{pH}}}{\mathrm{Ac}^{-1}\mathrm{x}10^{-\mathrm{pH}} + \mathrm{Ka}\mathrm{Km}}\right) X \left(\frac{\mathrm{Kim}\mathrm{Ka}}{\mathrm{Kim}\mathrm{Ka} + \mathrm{Ac}^{-1}\mathrm{x}10^{-\mathrm{pH}}}\right)$$

where Vm_{max} is the maximal yield rate of methane (in volume at 0°C and 1 atm pressure) per gram of methanogenic bacteria per day (L/g d); X_m- methanogenic biomass (g/L); K_m,

saturation constant of methane yield (g/L); K_{im} , inhibition constant of acetate on methane yield (g/L), K_a , the dissociation constant for acetate (1.728 \cdot 10⁻⁵) and A_c is ionized acetate concentration (g/L) (Liu et al. 2007);

This model is valid for prediction of the cumulative methane production, and the calculation of the optimal value of pH in different conditions. Also, this model can be used to predict the maximum methane production on the optimal pH value. Therefore a maximum generation rate of methane can be obtained and a great efficiency of anaerobic digestion can be achieved in the operation of anaerobic digestion of MSW (Liu et al. 2007).

4.2 Composition of the food waste

The composition of food waste is variable depending on the time of the year, cultural habits, region etc. It is important to know the composition of the food waste in order to be able to predict both the bio- methanization potential and the most efficient AD facility design.

The bio-methanization potential of the waste depends on the concentration of the four main components: proteins, lipids, carbohydrates, and cellulose. This is due to the different bio-chemical characteristics of these components (Neves et al. 2007).

The highest methane yields have systems with excess of lipids but with the longest retention time. The methanization is fastest in systems with excess of proteins followed by the reactors with excess of cellulose and carbohydrates respectively. However there are also inhibitory effects observed in the assays with excess of lipids and excess of proteins due to the VFA accumulation and ammonium nitrogen respectively. The lowest rates of the hydrolysis are the assays with an excess of lipids and cellulose, indicating that when these components are in excess, a slower hydrolysis is induced (Neves et al. 2007).

4.3 Loading rate

Organic loading rate is a measure of the biological conversion capacity of the AD system. It determines the amount of volatile solids feasible as an input in the AD system. Overloading of the system can results in low biogas yield. This happens due to accumulation of inhibiting substances such as fatty acids in the digester slurry (Vandevivere et al. 1999).



Figure 4 Effect of the loading rate above the sustainable

The events that would occur in the case of overloading the system are shown in the Figure 4. It would cause proliferation of the acidogenic bacteria further decreasing the pH in the system and disturbing the population of the methanogenic bacteria. Also there is a definite

relationship between the biogas yield and the loading rate. This is the concept that we used in the design of the experimental part of this study. The loading rate was at the point in favor of the acidogenesis avoiding the methane production and maximizing the VFA production in it.

Loading rate can be calculated using the following equation:

Loading rate
$$\left(\frac{mg\ COD}{m^3 * day}\right) = \frac{Organic\ mater\ \left(\frac{mg\ COD}{m^3}\right) * Flow\ rate\ \left(\frac{m^3}{day}\right)}{Operating\ volume\ (m^3)}$$

4.4 Retention time

Retention time (residence time), in the AD reactors, refers to the time that feedstock stays in the digester. It can be calculated using the following equation:

Retantion time
$$\boldsymbol{\theta}$$
 (days) = $\frac{\text{Operating volume } \boldsymbol{V}(m^3)}{\text{Flow rate } \boldsymbol{Q}(\frac{m^3}{dav})}$

It is determined by the average time needed for decomposition of the organic material, as measured by the chemical oxygen demand (COD) and the biological oxygen demand (BOD) of the influent and the effluent material. The longer the substrate is kept under proper reaction conditions, the more complete its degradation will be. However, the rate of the reaction decreases with longer residence time, indicating that there is an optimal retention time that will achieve the benefits of digestion in a cost effective way (Viswanath et al. 1991). The appropriate time depends on the type of feedstock, environmental conditions and intended use of the digested material (Ostrem & Themelis 2004)

Furthermore retention time in the AD system depends on process temperature and total solid content. Mesophilic digesters have longer retention time (10-40 days) then thermophilic digesters. Also the high solid content systems ("dry" processes) have longer retention time then low solid content systems ("wet" processes). Commonly used method for shortening the residence time in AD reactors is mixing the digester. Usually it is done by recirculation of the produced biogas back in the reactor.

Also the residence time affects the microbial communities in the digester. Different microbial communities develop in digesters operating on different retention times. This was one of the crucial parameters in the designing the acidogenesis experimental reactor. The retention time we used was determined according to the kinetics of the different MOs involved as described previously to be 4 days. In our case we wanted to secure washout of the methanogens and proliferation of the acidogens what was achieved and will be described in details later in this study.

4.5 Operating temperature

Operating temperature is the most important factor determining the performances of the AD reactors because it is an essential condition for the survival and optimum thriving of the microbial consortia. Despite the fact that they can survive a wide range of temperatures, bacteria have two optimum ranges of temperature, defined as mesophilic and thermophilic temperature optimum. Mesophilic digesters have an operating temperature in the range of 25- 40 °C and thermophilic digesters have operating temperature in the range of 50- 65 °C. The rate of AD process shown in Figure 5 is measured by gas production rates, bacteria growth rates, and substrate degradation.

According to the reported experimental results as well as the operating performances of commercial scale AD plants, mesophilic and thermophilic reactors have different advantages and disadvantages.



Figure 5 Rate of AD Process vs. Temperature (Ostrem & Themelis 2004)

Thermophilic digesters allow higher loading rate and yield higher methane production, substrate degradation and pathogen destruction. Also, the higher temperature shortens the required retention time because it speeds up the reactions of degradation of the organic material. However, the thermophilic anaerobic bacteria are very sensitive to toxins and small environmental changes. Furthermore, these bacteria need more time (over a month) to develop redox population. These systems are harder to maintain and are less attractive for commercial application because they require additional energy input for self heating.

Mesophilic AD reactors operate with robust microbial consortia that tolerate greater changes in the environment and are more stable and easier to maintain. Another advantage is that usually these systems do not need any additional energy input for heating the system. On the other hand, the disadvantages of the mesophilic AD systems are longer

retention time and lower biogas production. However due to the fact that they are easier to operate and maintain, as well as the lower investment cost, they are more attractive for commercial scale plants.

4.6 Classification of the AD systems:

There are many different technologies on the market that are used for AD treatment of the organic fraction of the MSW. These systems differ based on the design of the reactor and the operating parameters.

The design of the reactor depends on the feedstock that is going to be processed and varies from very simple and easy to maintain AD digesters used in rural China and India to very complex and automatic systems used lately in the developed world for treatment of the organic fraction of the solid waste (OFMSW). The feedstock also determines the need and type of pretreatment. In the case of OFMSW the pretreatment is usually big part of the AD plant and is necessary in order to clean up the feedstock to the required level as well as to separate as much as possible recyclable materials.

The design of the digester also depends on the amount of the available feedstock that determines the capacity of the reactor. The bigger systems have been proven to be reliable and economic, so the trend is to build bigger plants as will be shown later in this study (Ostrem & Themelis 2004).

Characterization of the AD systems based on the operating parameters is done by the following criteria:

- 1. <u>Loading rate in total solids content</u>:
- <u>Low-solids</u> content (<15%Total Solids) sometimes also called "wet digestion";
- <u>High-solids</u> content (25-30 % TS) also known as "dry digestion".

When the feedstock used is the organic fraction of the MSW both systems apply and have been proven successful. In both cases water needs to be added in order to lower the content of total solids. The "dry digestion" requires smaller and therefore less costly digesters on one side but more costly additional equipment for mixing and material flow on the other side (Ostrem & Themelis 2004)".

- 2. <u>Operating temperature</u>:
- <u>Thermophilic</u> AD processes operate in the temperature range of 50°C-65°C ;
- <u>Mesophilic</u> AD processes operate at about 37°C.

Anaerobic digestion of the OFMSW is possible in both temperature ranges. Thermophilic AD digesters have been shown to be more efficient in biogas production, faster rate of decomposition but with higher maintenance costs.

3. <u>Number of reactors used in series:</u>

- <u>Single stage digester</u>: All reactions take place in one reactor and environmental conditions are maintained at levels that suit all types of bacteria. Therefore, operating conditions for a particular stage are not optimal.
- <u>Multi-stage digesters</u> have physically separated biochemical reactions of hydrolysis and acidogenesis in different reactor vessels. Each vessel maintains the optimal environmental conditions for the microorganisms that facilitate the specific reaction that is happening inside. Therefore these systems can be more efficient.

Both types of AD systems are used in processing the OFMSW and further in this study specific cases will be described.

- 4. <u>Method of introducing the feed into the reactor</u>:
- <u>Continuous flow reactors</u> have feed and discharge flows in continuous or semicontinuous manner. This is the most common form of industrial scale reactors.
- <u>Batch reactors</u> are loaded and allowed to react for a certain period (usually two weeks).

Digestion of the OFMSW is possible in both types of systems although there are advantages and disadvantages in both cases. For example the batch reactors need to be bigger in volume due to the long retention time while in the case of the continuous flow reactor the effluent is a mixture of partly and completely digested material (Ostrem & Themelis 2004).

5 FEEDSTOCK MATERIALS USED IN ANAEROBIC DIGESTION

The most suitable feedstock for Anaerobic Digestion is:

- Animal waste and biowaste from wastewater treatment plants
- Food and kitchen wastes from restaurants, canteens, food markets, and municipal source- separated food wastes.
- Organic waste from food processing industry, slaughter houses, etc.

As in the case of aerobic composting, there have been attempts to physically separate the organic fraction from the <u>mixed</u> MSW stream and subject it to AD (DiStefano & Belenky, 2009). However, experience with such operations around the world has, generally, not been satisfactory. E.g., the compost product of a \$60 million modern recycling plant near Athens that processes mixed MSW has proven to be unsuitable as soil conditioner because of impurities, such as small pieces of plastics and metals. As a result, six years after start up, most of the compost product is landfilled. Although most of the AD plants are now operating with source separated organics (SSO) they are still facing problems due to the impurities in the feedstock. This is the case in the visited plants in Toronto and Barcelona as will be described later in this study.

5.1 Food waste in US and its characteristics

Food waste includes leftovers from residential food preparation and consumption as well as from commercial (or industrial) sources such as deli markets, restaurants etc. According to U.S. EPA estimates, food wastes comprise about 12.4% of the U.S. MSW in 2006 (Figure 6); this would correspond to over 40 million tons, according the 2006 State of Garbage survey of BioCycle and Columbia University (Arsova et al. 2008). EPA has estimated that less than a million tons are co-composted aerobically with yard wastes (EPA 2007).



Figure 6 Total MSW generation (by Material). 2006 EPA

The composition of the organic fraction of municipal solid waste depends on various factors, including climate, collection frequency, season and cultural practices.

The biodegradable fraction of MSW contains anywhere from 15%-70% water (Miller & N. L. Clesceri 2003). Food waste is characterized by high percentages of moisture (> 70%) and Volatile Solids (> 95%) and has a very high biodegradability.

6 APPLICATION OF THE ANAEROBIC DIGESTION AROUND THE WORLD

Over the centuries, AD has been applied in several ways in different parts of the world. In China and India, it has been extensively used to recover energy from farm waste, such as manure. Most of these facilities are farm or village-scale and the biogas is used for heating, cooking and lighting. In North America, AD is used both on large farms for manure treatment and at wastewater treatment plants (Palmisano & Barlaz 1996) (Ostrem & Themelis 2004). European nations have gone further in the application of this technology

by establishing commercial plants for the treatment of source separated organics from the municipal solid waste. Recently application of the AD as sustainable solution for treatment of the organic fraction of the municipal solid waste has been recognized worldwide and the number of this kind of plants has increased dramatically over the last decade (IEA 2008).

6.1 Current application of AD technology on an industrial scale

Currently there are nearly 240 AD facilities around the world operating of capacity over 2,500 metric tons of organic waste per year. The total installed capacity of these plants is over 11 million metric tons per year (IEA 2008). This plants process not only the organic fraction of the municipal solid waste but also organic waste from the food industries and animal manure.

As shown in Figure 7, the installed AD capacity has increased substantially since 1995. The total AD capacity has increased five-fold worldwide, from about 2 million metric tons in 1995 to over 11 million by 2008 (IEA 2008).



Figure 7 Increase of installed global AD capacity

Europe leads in number of AD plants and total installed capacity. Most of the AD plants were built there principally due to the EU Landfill Directive 1999/31/EC that requires from the member states to reduce the amount of landfilled organics for 65% relative to the 1995 amount by 2016. There are more than 120 plants processing the organic fraction of MSW in Europe, with total operating capacity of about 4.6 million tons per year (IEA 2008). The number and total capacity of AD plants treating organic municipal solid waste (MSW) in Europe are shown in the

Table **1**.

Country	Number of plants	Country capacity (t/y)
Germany	55	1,250,000
Spain	23	1,800,000
Switzerland	13	130,000
France	6	400,000
Netherlands	5	300,000
Belgium	5	200,000
Italy	5	160,000
Austria	4	70,000
Sweden	3	35,000
Portugal	3	100,000
United Kingdom	2	100,000
Denmark	2	40,000
Poland	1	20,000
Total	127	4,605,000

Table 1 European countries with facilities processing MSW in anaerobic digesters in 2006
(Levis et al. 2010)

The size of individual AD plants has also increased over the years, as shown in Figure 8. While in 1985 the biggest plant had capacity of 25,000 tons/year, the biggest plant built lately has 500,000 tons/year of capacity. Regarding operating conditions, the development of AD technologies has evolved with time from low-solids content ("wet") to high-solids ("dry") and from mesophilic to thermophilic. By 1995, high-solids content processes accounted for 9% of the number of plants and 20% of the operating capacity. High-solids content plants built since 1995 account for 30% of the operating capacity. High-solid processes are usually thermophilic. This entails shorter retention time and lower reactor costs, higher biogas yield, and higher operating costs. Nevertheless, currently mesophilic, low-solids AD plants are the most common.



2008 (IEA 2008)

6.2 Most commonly used AD technologies worldwide

The principal technologies used around the world are Kompogas, Valorga, RosRoca, BTA, Dranco, Cites and Linde (IEA 2008). The total installed capacity worldwide today of each of these technologies is shown in Table 2.

	Table 2 Installed	capacity of the	principal AD	technologies
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AD	Number of	Total capacity,
technology	plants	tons/year

Kompogas	26	533,500
Valorga	19	2,197,000
Ros Roca	17	541,000
BTA	17	300,500
DRANCO	15	627,000
Citec	13	469,500
Linde	11	459,000
Sum total	118	5,127,500

Most of the feedstock to these plants is provided by municipalities that offer sourceseparated collection of the organic fraction. The retention time, biogas production rate and total annual biogas production of various AD processes are shown in Table 3 (Ostrem & Themelis 2004).

Table 3 Operating conditions, biogas production rate and total capacity of the mostcommon used AD processes

AD technology	Retention time, days	Biogas production Nm ³ /Mg of feed	Total annual biogas production Nm ³
Kompogas	15-20	100	53,350,000
Valorga	18-25	80-160	263,640,000
BTA	12 to 17	85-95	27,045,000
Dranco	20	100-200	94,050,000

Based on this analysis, the Valorga technology appears to be the most successful, on the basis of installed capacity and biogas production per ton. The average biogas production is at $113 \text{ Nm}^3/\text{t}$ of feed material.

A study was made using the Multi-Criteria Decision-Making (MCDA) method, based on the following criteria: (a) GHG emissions, (b) energy recovery, (c) material recovered and (d) operating costs. This study showed the Valorga technology to be 2nd best, right after Dranco technology (Karagiannidis et al. 2008). The Dranco technology was found to combine the

advantages of low-cost and high energy recovery. However, Dranco is a thermophilic process and therefore not as attractive as Valorga; there has been only one new plant since 2000. Also, the Valorga technology offers both mesophilic and thermophilic operation

6.3 Brief description of principal AD processes

6.3.1 Kompogas

This technology was started in Switzerland at the end of the 1980's. The first plant started the trial phase in 1991 in Rumlang, Switzerland. There are 26 operating plants now, with total installed capacity of 533,500 tons (Table 2). Most of these plants process source separated organics. Kompogas is a thermophilic process operating at 23-28% total solids without gas recirculation. The reactor is a horizontal cylinder and the slurry moves in plug-flow with retention time of 15-20 days. There is a slowly rotating intermittent propeller in the digester to push the organic material, homogenize and degasify the pulp and to keep the heavy particles in the suspension. Due to the mechanical requirements of the system, the size of the reactor is limited and the need for bigger capacity is satisfied by installing a number of reactors in parallel. This modular design reduces capital construction costs as well as allowing for a wide range of facility sizes, from 5,000 to 100,000 tons per year (Ostrem & Themelis 2004).

Prior to the AD, the feedstock is treated mechanically for separation of the inorganic contaminants and size-reduction. In between the mechanical treatment and the AD reactor organic material is stored in a buffer tank to secure continuous feeding of the reactor. Also in this tank thickening occurs in order to reach final concentration of 23- 28% of TS in the AD system. On its way from the buffer tank to the methanizer the organic material flows through the heat exchanger for preheating of the substrate. The digesting chamber is fully enclosed and heated to eliminate the undesirable germs and weed seeds (Hyder Consulting 2005). The fermented material is dewatered for separation of the solid material from the liquid for further process in the composting units.

The schematic diagram of a Kompogas AD facility is shown in Figure 9.



Figure 9 Schematic diagram of Kompogas AD facility

6.3.2 Valorga

This process was developed in France in 1981 and was initially designed to treat organic fraction of MSW and later adapted to treating mixed MSW (Shefali & Themelis 2002), (de Laclos et al. 1997). The very first pilot plant was installed 1982 in Montpellier, France. First industrial scale plant, of 50.000 t/y, was opened August 1988 in Amiens, France, as the very first AD plant for treatment of the MSW with the high content of total solids in the world.

Prior to the AD reactor the substrate passes through pretreatment consisted of automatic separation of non biodegradable contaminants such as plastic bags, glass from the desired organic material. After the pretreatment the waste is mixed into a thick sludge with concentration of 25- 32 % of TS and introduced in the AD reactor from the bottom.

The Valorga reactor is a vertical, plug-flow cylinder separated into two compartments by a vertical partition. This wall extends 2/3 of the diameter and in full height of the reactor. The design of the reactor ensures that the material moves up and around the partition. Biogas is re-circulated through the bottom of the reactor to provide mixing and suspension of the solids as the slurry moves through the reactor (de Laclos et al. 1997).

Typically, the Valorga process is operated at high solids concentration (25-32%), and can be operated on both mesophilic and thermophilic operating temperature.

The digested material is dewatered and the solid cake is treated aerobically to completely stabilized compost. The biogas produced on these plants is used for production of heat, electricity or is purified to a quality of natural gas and sold like a fuel.



Figure 10 Valorga AD reactor

6.3.3 Biotechnische Abfallverwertung GmbH (BTA) process

This process was developed in the 1980s in Germany, as multistage low-solids system for treating mixed MSW or source separated organic waste (food and garden waste) on mesophilic temperatures. BTA includes waste pre-treatment and separation stages in fully enclosed and highly automated facilities, whose capacity ranges from 2,000 to 150,000 tons/year (Shefali & Themelis 2002)

A research and development facility is located in Baden, Germany but BTA is available around the globe through official licensed companies like Canada Composting Inc. for Canada and USA.

This technology is available in both, single stage plant design as well as two stages process. The unique patented part of this technology is the wet mechanical pretreatment of the waste consisted of the hydropulper and hydrocyclon.

The hydropulper is a unit where by means of buoyancy and shear forces the floating as well as the heavy non-biodegradable materials is separated from the organic fraction. Organics leave the hydropulper in a form of suspension that is easier for degradation later. Second unique step of the BTA pretreatment is the hydrocyclon, or grit-removal system, part following the hydropulper. Here the small pieces of heavy material and glass as well as sand are removed.



Figure 11 BTA anaerobic digestion process scheme (BTA International)

6.3.4 Dranco

The Dry Anaerobic Composting (DRANCO) process was developed in 1983 in Belgium and commercialized by the company Organic Waste Systems in 1988. This is a single-stage thermophilic process (50–58°C), with high-solid content, and without biogas recirculation. Operating plants have capacities in the range of 10,000–120,000 metric tons/yr. (Shefali & Themelis 2002). This is a process for treatment of the organic fraction of the MSW (IEA 2008)



Figure 12 Dranco anaerobic digester

The feed is introduced continuously through the top of the reactor and digested material is continuously removed from the bottom. There is no mixing in the reactor apart from the downward plug flow of the waste due to gravity. The digested material is first de-watered in a screw press and the filter cake is cured for two weeks to final compost product. The filtrate obtained from de-watering is re-circulated in the system and used to adjust the solids concentration of incoming waste. The retention time of this technology is usually 20 days.

7 CASE STUDIES OF ANAEROBIC DIGESTION PLANTS IN NORTH AMERICA AND EUROPE

In this section the findings from the visits of the anaerobic digestion plants in North America and Barcelona, Spain, are presented. All the data were collected during the site visits of these plants conducted by the author (Arsova 2009b) (Arsova 2009c) (Arsova 2009d). The Canadian plants are the only industrial scale AD facilities in North America processing organic fraction of the MSW. The Barcelona plants were selected as a good example of how AD plants can be successfully integrated in an advanced integrated waste management system. Furthermore, there are three AD plants serving for the metropolitan area of Barcelona and one of them is the largest AD facility in Europe.

7.1 Anaerobic digestion of source-separated organic wastes in North America

Despite the wide application of AD in waste water treatment, agriculture, and industry, there are only three industrial size AD facilities operating in North America and treating the organic fraction of the MSW. One plant is located in the U.S. and two are in Canada.

7.1.1 Anaerobic Digestion in the US: East Bay Municipal Utility District-Oakland, California

The East Bay Municipal Utility District (EBMUD) is principally a wastewater treatment facility in Oakland, CA. They process source separated food waste from a food waste processing facility in San Francisco together with the biosolids from the waste water treatment. After some additional grinding to form slurry, they add it to their anaerobic sludge digesters. EBMUD has excess capacity in their digesters due to the closing of some industries that were supplying material for anaerobic treatment. The process of co-digestion of the SSO and the biosolids is performed in two mesophilic and two thermophilic reactors without any noticeable difference in their performances. Due to the location in an industrial zone, the fact that this is a large WWTP and the manner in which the SSO is received, no specific odor control is necessary (Barlaz et al. 2008)

In 2008, they processed 90 metric tons/day of food waste five days a week, i.e. about 22,000 tons/yr (Neves et al. 2007). The amount of electricity produced is enough to cover only 90% of the onsite electricity usage. This is due the restriction to operate only two of their three 2MW generators at a time in compliance with the air quality regulations. The excess amount of the biogas is flared and the solid residuals are used as landfill daily cover (Barlaz et al. 2008).

7.1.2 Anaerobic digestion of source separated organic waste in Canada

Both AD plants in Canada are located in Ontario and serve the city of Toronto and the surrounding communities. Both of them have BTA patented technology installed. The plant in Dufferin has the single-stage BTA configuration while the plant in Newmarket uses the two-stage process configuration (Arsova 2009b) (Arsova 2009c). Main feedstock for both plants is the Source-Separated Organic fraction (SSO) from the Toronto's residential Green Bin and the commercial Yellow bag collection program. The city of Toronto now collects over 110,000 metric tons of food waste and has plans for expanding the program to include "multi-family" dwellings (apartment buildings, etc.) (Arsova 2009b).

Dufferin Organic Processing Facility, Toronto, Ontario

The Dufferin Organic Processing Facility (DOPF) started operations in 2002 and was designed as a demonstration plant with nominal capacity of 25,000 tons/year. It utilizes patented BTA process that includes wet pretreatment and single-stage low-solids, mesophilic anaerobic digester. A trommel screen and material recovery system were installed prior to the BTA anaerobic digestion to open plastic bags and sort out the contaminants.



Figure 13 Anaerobic digester on the Dufferin AD plant

Currently this system is not used because there is only a small amount of non-organic material in the SSO (Arsova 2009b).



Figure 14 Commercial Yellow Bag collection program in the city of Toronto (photo by L. Arsova)
The hydro-mechanical (wet) pretreatment system is comprised of a hydropulper followed by a hydrocyclone. This is a batch process with a dual objective, to separate contaminants from the organic waste and to transform the SSO into organic pulp. Contaminants are separated in two stages: first the floating materials (textile, plastic, foils etc), and the heavy fraction (bones, glass, stones, coins, etc), Figure 17, are removed in the hydro-pulper; second, the grit fraction (small pieces of heavy material such as glass are removed in the hydro-cyclone, Figure 16.



)w chart

Typically, contaminants comprise 23%, by weight, of the proceed SSO, (<20% light fraction, 1.5% heavy fraction, 1.5% grit fraction). Pulped organics with a solids content of 8-9% are fed into a digester with a liquid capacity of 3,600 m³ and designed retention time of 17-24 days. It should be noted that current retention time is 7 days because the City of Toronto needs to process more SSO due to an increase of the SSO collection. This results in a higher concentration of volatile fatty acids in the residue and lower specific gas production. The sludge coming out of the digester is filtered to separate the solids cake from the liquid fraction. About 0.33 tons of digested solids are produced per ton of SSO feedstock to the plant and further processed to final compost. On the average, 30-60 tons per day of this material are transported to off-site aerobic composting facilities. The liquid fraction is recirculated into the hydro-pulper.



Figure 16 Grit fraction at Dufferin AD plant (photo by L. Arsova)

As noted earlier, the nominal capacity of this plant was 25,000 metric tons of SSO/year. Since May 2008, after some changes in the equipment and operating procedures, the plant is now operating at about 190% of the nominal capacity, i.e. 42,500 tons/year. On average, 185-200 tons/day are processed in summer and 135 tons/day in winter (Arsova 2009b).

Current biogas production is 100-120 m³/metric ton of SSO (residence time of 20-23 days). Since this plant was primary designed as a demonstration plant, it does not have an energy conversion system and all biogas is combusted in an open flare. It has been estimated that if the DOPF were to use the biogas to run a gas engine, out of 35,000 metric tons of SSO processed in 2007, it would have generated 4,500 MWh of electricity, i.e. about 130 kWh per ton of SSO processed (Arsova 2009b). This amount corresponds to about one fourth of the electricity generated per ton of MSW combusted in U.S. WTE facilities (550 kWh/ ton MSW).



Figure 17 Floating and heavy fractions separated at Dufferin AD facility

(photo by L. Arsova)

Newmarket Organic Processing Facility, Newmarket, Ontario

The Newmarket anaerobic digestion plant was built in July 2000 by Canada Composting Inc. and has been operated by Halton Recycling LTD. since 2003 (Arsova 2009c). The original design of this facility was for a two-stage Anaerobic Digestion process, with separate tanks for hydrolysis and methanogenesis. Due to financial difficulties the hydrolysis tank was not built and the facility is now operating as a single stage AD plant with methanizer tank designed for two stages AD process (Arsova 2009a).



Figure 18 Anaerobic digester and aerobic VCU at the Newmarket plant

The incoming feedstock is pretreated in two phases, mechanically and hydro-mechanically. Mechanical separation removes large contaminants and recyclables. It consists of a bag breaker, trommel screen for separation of medium and large size materials, and magnetic and eddy current separators, for separation of ferrous metals and aluminum cans. The hydro-mechanical treatment comprises three hydropulpers in parallel, followed by a hydrocyclon. The floating, heavy, and grid fraction of contaminants are removed here, as at the Dufferin facility. The feedstock is of lower quality than at Dufferin and the amount of non-compostable residue that goes to the landfill is 25-30% of the feedstock.

The organic pulp leaving the hydropulper is stored in a pulp buffer tank to ensure continuous feeding of the AD reactor. From the buffer tank and on its way to the digester, the pulp passes through screw presses, for separation of the solids from the liquid, and then through a 50 micron filter. Thus, significant fraction of the organics is separated at the screw press and is then treated aerobically in the composting units described later. This is a design problem of this facility, because the Up-flow Anaerobic Sludge Blanket (UASB) reactor installed as a methanizer is suitable only for solubilized organic material. Because of these limitations of the reactor and without the hydrolysis tank significant part of the organics are "lost" on the screw presses that affect the biogas production. The retention time in the digester now is 15 days.



Figure 19 Flowsheet of the Newmarket AD facility

The filter cake separated at the screw press is subjected to composting for 13 days. The composting process starts in the Vertical Composting Units (VCU), in-vessel aerobic composting units where temperatures are sufficient to kill pathogens. After seven days in the VCU, the final compost product is cured in the maturing tanks. The amount of compost produced is 0.29 t per ton of the processed feedstock (Arsova 2009c)

The average specific biogas production is 105 m^3 /ton of processed feedstock with an average methane content of 60% and is used for production of electricity (Arsova 2009c).

The Nemarket facility has designed capacity of 150,000 tons of organic waste per year. Due to odor emission problems, under court order, the facility processed only 17,000 tons of SSO in 2008 (Arsova 2009c).



Figure 20 Biofilter on the Newmarket facility installed as part of the Remediation Plan in 2007 (photo by L. Arsova)

In 2006, Halton Recycling put into effect a Remediation Plan to meet environmental requirements and reduce the odor emissions. This plan included installation of two biofilters, three wet scrubbers and eight activated carbon filter units during 2007. Additional retrofitting of the basic BTA equipment took place in 2008. Communications of the author with the management of this facility have indicated that technical problems with the odor emissions have been solved and it is planned to increase the operating capacity to 70,000 tons of SSO by 2013 (Arsova 2009c).

7.2 Anaerobic digestion as part of the integrated waste management in the Metropolitan Area of Barcelona, Spain

Integrated waste management in the metropolitan area of Barcelona is a great example of successful integration of the anaerobic digestion into the general solid waste management plan. During the study visit all the data was collected from the officials of the Environmental Authority of the Metropolitan Area of Barcelona and the management of the visited plants. There are three AD plants serving the metropolitan area of Barcelona and the AD plant in the Ekopark II is the biggest facility of its kind in Europe. These plants are processing the source separated fraction of the MSW and have three different technologies installed, Valorga, RosRoca and BTA.

7.2.1 Integrated waste management system in the Metropolitan Area of Barcelona, Spain.

The Environmental Authority of the Metropolitan Area of Barcelona (EMMA from the title in Spanish) is a local government body serving 33 municipalities in the Metropolitan Area of Barcelona covering geographic area of 583 km². It provides services to a population of 3.12 million people. It is responsible for waste water and solid waste management. In

2007, 1.66 million tons of MSW were generated that is 1.46 kg/day or 0.54 metric tons per capita. The municipal solid waste in the Metropolitan Area of Barcelona is collected in five separate fractions as follows: glass, paper and cardboard, light packaging (plastic and metal), source separated organics (SSO) and "all other". Out of the total amount of collected MSW 154,103 tons are source separated organics that is 0.05 tons per capita.



Figure 21 Entity of the Environment of the Metropolitan Area of Barcelona and locations of the Ecoparks and the Waste-to-energy facilities

Source separated fractions of paper and cardboard, glass and light packaging go either directly to private recycling companies or, in the case of the light packaging fraction, first to material recovery facility for separation and then to private recycling companies. The SSO fraction is processed exclusively in the AD plants at the Ekoparks while the "all other" fraction is processed either in the aerobic composting facilities at the Ekoparks or in the Waste- to- Energy plant.

7.2.2 Ecoparks

Ecoparks are specially constructed sites for treatment of the organic fraction of the MSW. Usually these sites have both, anaerobic digestion and aerobic composting facilities, installed. The two fractions treated on these sites are:

- Source Separated Organics comprised of food waste, paper napkins, used kitchen paper as well as green waste.
- "All other" fraction is the waste that remains after the recyclable and compostable materials are separated at the source by the citizens. This fraction may contain between 30- 40% of organic matter.

Reported numbers in 2007 clearly show an increase in the amount of separately collected organic fraction and decrease in the amount of the "all other" fraction (Figure 22Figure 23).



Figure 22 Evolution of the amount of separately collected organic fraction of the MSW (source EMMA)



Figure 23 Evolution of the amount of the collected "all other" fraction of the MSW (source EMMA)

Currently, the metropolitan area of Barcelona has three operating Ecoparks and one under construction expected to start operating during 2010:

- 1. The Ecopark 1- Barcelona;
- 2. The Ecopark 2- Montcada i Reixac;
- 3. The Ecopark 3- Sant Adria de Besos (Ecoparc del Mediterrani)
- 4. The Ecopark 4 Hostalets Pierola (under construction)

All Ecoparks are owned by the Environmental Entity (EMMA), but operated by the companies that built them and have the concession rights over the plants for 15 years. Ecopark 1 is under management of the UTE Ecoparc, Ekopark 2 is managed by the company Ebeso and the Ecopark 3, is under concession of CESPA the company.

In the table bellow summary of the Ecoparks performance and characteristics are given. Further in this thesis detailed descriptions and explanations are given for each AD plant in the Metropolitan Area of Balcelona.

Table 4 Summary of the carachteristics of the AD plants of the Ecoparks in theMetropolitan area of Barcelona

	Plant	AD Technolog y	AD capacity (t/year)	Waste fraction processed	Final products	Refuse managemen t
1	Ecopark 1	BTA	50 000	SSO	Compost &	Landfill

					electricity	
2	Ecopark 2	Valorga	120 000	SSO & green waste	Compost & electricity	Landfill
3	Ecopark 3	Ros Roca	90 000	"all other"	Digestate & electricity	WTE plant

Ecopark 1- Barcelona

The Ecopark 1- Barcelona treats SSO and the "all other" fraction from the city of Barcelona and the following municipalities: Hospitalet de Llobregat, El Prat de Llobregat and Viladecans.

The plant, which entered into operation in 2001, was the first facility for treatment of municipal waste in the metropolitan area and is currently being remodeled.

The original plant had the Linden AD technology installed consisted of dry mechanical pretreatment with sieving drum (>120mm), wet-mechanical pre-treatment of suspensors and sieving drum, and low solid content anaerobic digestion. From the very beginning this technology was not providing sufficient cleaning of the feedstock what resulted in problems in the AD process.

The reported main problems of the original design were:

• Insufficient elimination of contaminants

- Constantly clogged pipes
- Floating layers and massive sediments in the digester
- Inefficient mixing of the material in the digester
- High loss of organics in the separation resulting in low biogas yield
- Unacceptable quality of the separated residues
- Big amount of rejected waste for landfilling

According to Mr. Trullols, director of the department for solid waste management of the Environmental Authority of the Metropolitan Area of Barcelona, one of the reactors on this facility exploded in 2006. Explosion was caused by a pressure build up under very thick and solidified layer of the material in the reactor. This layer was built of the contaminants that ended up in the reactor due to the bad quality of the feedstock and the inefficient separation of contaminants. At that time the "all other" fraction was treated in all AD digesters on the site.

Because of the problems, the operator of this plant, UTE Ecoparc, decided to remove the existing pre-treatment and also to refurbish the digester itself. Thus, BTA via its licensee BIOTEC was assigned to integrate a complete new BTA® Hydromechanical Pre-treatment, re-engineer one 6,000 m3 digester and equip it with the BTA® Gas Mixing System. Also, the BTA® Process Control System was installed. The BTA® Hydromechanical Pre-treatment consists of 3 x 32 m3 BTA® Waste Pulpers (hydropulpers), corresponding light fraction presses and four BTA® Grit Removal Systems (hydrocyclones). Ecopark 1 has a total installed capacity of 85,000 t/y of SSO, in Anaerobic Digestion and 160,000 t/y of "all other"

fraction in aerobic composting tunnels, i.e. a total capacity of 245,000 tons of waste per year.



Figure 24 The author in front of Ecopark 1

Pretreatment:

The pretreatment and the treatment of SSO and the "all other" fractions, entering the facility, are performed in two separate processing lines.

The pre-treatment of the SSO is very complex and consists of a series of process units:

- 1. Tromell with 400 mm sieve
- 2. Double trommel with 150 mm in the first part and 60 mm sieve in the second part.
- 3. Magnetic separation of the ferrous metals
- 4. Flocculate separation for Al
- 5. Ballistic separation,
- 6. Optic separator of plastics
- 7. Aspiration of plastic film
- 8. Manual separation

The pre-treatment of the "all other" fraction is simpler because the aerobic composting does not require high purity of the feedstock as the AD and comrises:

- 1. Trommel for separation of the voluminous matters with blades inside
- 2. Trommel of 45 mm for separation of the organics that go directly to the compost tunnels
- 3. Ballistic separation
- 4. Magnetic separator
- 5. Flocculate separation for Al
- 6. Aspiration of plastic film
- 7. Manual separation

This pretreatment separates the recyclables such as: paper, packaging materials (tetra pack), and different types of plastics (PET, PEAD and PE).

Anaerobic digestion:



Figure 25 Material and energy flows at the Ecopark 1 AD plant

After the mechanical pretreatment and separation of the contaminants from the SSO, the organic material goes to three hydropulpers in parallel, followed by four hydrocyclones, as unique part of the BTA AD technology. After this, the material is collected and stored in one buffer tank to be used for continual feeding of the four methanizing tanks (each of 6000 m³) with fresh organics. Retention time in the methanizers is 15 days. Produced biogas is collected and after desulfurization is burned in five co-generation engines, each with capacity of 1MW.

The sludge coming out of the digester is centrifuged to separate the liquid and solid fractions. The solids are then treated aerobically in 38 composting tunnels and the filtrate solution is re-circulated back to the system and mixed with incoming fresh waste material. Odor control and waste water treatment:

The whole facility is under negative pressure and the odorous air is treated through 4 biofilters, 2 organic and 2 inorganic. During the visit the odor at the plant was unbearable and detailed tour of the facility was impossible. According to the management of the facility, at that point they were experiencing problems with one of the biofilters what required short shut down of the odor control system for maintenance.

Also they have waste water treatment facility where the waste water is treated prior to relieving it in the public sewage system.

The author was not allowed to take pictures but the equipment was very similar to that used at the Dufferin, Ontario facility in Canada.

Ecopark 2- Montcada i Reixac

The Ecopark 2- Montcada i Reixac is located in the Industrial zone of the town of Can Salvatella Andis, 9.5 miles away from the center of the city of Barcelona. It serves all municipalities comprising the metropolitan Area of Barcelona except for the City of Barcelona. Although it is a metropolitan facility, it also serves few municipalities out of the metropolitan area of Barcelona.

This plant started operating in 2003 and has both, anaerobic digestion and aerobic composting facilities, installed on the site and processes the SSO and "all other" fractions as well as green waste from pruning and cleaning of municipal parks and gardens. Anaerobic digestion technology installed is Valorga and the aerobic treatment is tunnel composting. From the opening until 2006 both, SSO and "all other", fractions were processed in the AD reactors when problems occurred in the reactors treating "all other" fraction. During routine service of the reactor damage on the inner separation wall were discovered. Since then only the SSO fraction is processed in the anaerobic digestion reactors and the "all other" fraction is processed only in the aerobic composting. Total installed capacity on this plant is 240.000 t/year of organic waste. Out of this amount 120.000 t/ year is the capacity in the anaerobic digestion and aerobic composting of the SSO and only aerobic composting of the "all other" fraction. The green waste is mixed with the digested material from the anaerobic digestion prior to its introducing to the aerobic composting tunnels.



Figure 26 Ecopark 2

Pretreatment

The pretreatment prepare the "all other" fraction for aerobic composting and the SSO fraction for anaerobic digestion, separating the recyclables and the refuse materials.

Pretreatment of the two fractions is performed in two separated lines. The pretreatment of the SSO fraction is a single separation line with capacity of 30 t/ h. The separation of the recyclables and the impurities from the "all other" fraction is performed on two lines, each with capacity of 45 t/h. Pretreatment of the SSO starts in a sorting cabin with manual separation of the voluminous recyclables such as cardboard, plastics and glass. After the sorting cabin the material goes through the following pretreatment units:

- Bag breaker
- Trommel with sieve size of 80 mm
- Electromagnetic separator of the ferrous materials

Mechanical pretreatment of the "all other" fraction comprises the following process units:

- Sorting cabin for manual separation of recyclables such as cardboard, plastics and glass.
- Trommel with 60 mm sieves and knifes.
- Trommel with two different sieve sizes, 150mm in the first part followed by 60mm.
- Second sorting cabin for separation of non- ferrous metals.

Refused material from both pretreatment lines is pressed, packed and sent for disposal on a controlled sanitary landfill.



Figure 27 Sorting cabin, bag breaker and tromell at the beginning of the pretreatment of the SSO fraction (photo by L. Arsova)

Anaerobic Digestion:

Anaerobic digestion technology installed on this site is Valorga (high solid content, TS 40-45 %). Three anaerobic digesters are installed on the site, each with capacity of 4500 m³. The AD reactor is operated on mesophilic temperature of 35° C and retention time of 25 days. The input material is a mixture of the digested material from the reactor (25%), fresh organic material (50-60 %) and water. Constant temperature in the reactor is maintained by heating with steam and the mixing of the material in the reactor is secured by recirculation of the produced biogas as part of the original design of the Valorga AD reactor.



Figure 28 Anaerobic digestion reators, gas tank and the gas stack on the site of Ecopark 2 (photo by L. Arsova)

The produced biogas is collected from the top of the AD reactors and contains on average 55% of methane. It is first desulfurized and then stored under pressure in gas storage tank. Any possible surpluses are burned in a gas stack. There are four generators, each with capacity of 1 MW, for utilization of the biogas and production of electricity and steam. The steam is used for heating of the AD reactors and the electricity is used on the site (59%) and the rest (41%) is sold to the grid. In total 20.2 GWh of electricity was produced in 2008. The digested sludge coming out of the digesters undergoes a dehydration process. The resultant solid material is mixed in 3:1 ration with green waste and then treated for 2 weeks in composting tunnels. The liquid is purified and recirculated in the system.

(Note: the material balance for this plant could not be constructed due to insufficient data.)

Aerobic composting:

The organic material separated from the "all other" fraction in the pretreatment is treated under controlled conditions in aerobic composting tunnels. There are 17 tunnels dimensions of 5x5x34m where the material is kept under controlled humidity, air and temperature for 3 weeks. After this period it is disinfected on temperature of 65°C and kept for maturation additional 4 weeks. At the end of the maturing period the material is refined through 10mm trommel and vibrating table.

The final compost produced here does not meet the required quality to be used in agriculture and they have problems selling it. Usually it is used for sides of the roads, parks and other public green areas. However they are giving it for free and they do not gain any revenues from it.

Odor control system and waste water treatment:

The entire facility, including the pretreatment halls and composting tunnels, are under negative pressure and the collected air is treated first though acidic scrubber, water scrubber, and at the end trough inorganic biofilters.

Composting leachate and digester effluents are purified WWTP installed on the site before releasing it into the public sewage system.



Figure 29 Rejected material pressed and packed for disposal on controlled landfill (photo by L. Arsova)

Ecopark 3- Ecopark del Mediterrani

Ecopark 3 is located in the district of Sant Adria de Besos, 4.1 mile away from the city center. It processes only the "all other" fraction of the municipal solid waste from the municipalities of Badalona, Sant Adria de Besos, Santa Coloma de Gramenet and the city of Barcelona. Due to the exceptional location of this facility, next to the sea and one of the most beautiful beaches in Barcelona, they have made a great effort from the architectural point of view to minimize the visual impact of the facility. The facility is surrounded with glass facade and has a green roof. Unique characteristic of this plant is that its vertical organization, meaning that different units of the plant are one above the other, due to the limited area available. Unfortunately at the moment of the visit the plant was not in operation due to an accident that happened in March 2009 and was under reconstruction. The crash was still under investigation and the reason for it was unknown at that point. The crash happened when one of the pipes transferring the digested material from the reactor broke and the entire plant was flooded what seriously damaged most of the equipment at the facility due to the vertical organization of the process units. This plant has total designed capacity of 260,000 t/y of MSW and AD capacity of 90,000 t/y.

Pretreatment

Waste entering the plant undergoes mechanical pretreatment at the beginning for separation of the recyclable materials from the organic matter. This is performed in two, semi-automatic separation lines each having the following process units in series:

- Primary manual sorting cabin
- Trommel,
- Ballistic screen,
- Magnetic separator (ferrous material),
- Film separator,
- Secondary manual sorting cabin,
- Automatic sorter of PET and PEAD, and
- Inductive separator (non-ferrous material).

Cleaned organic fraction then passes through a ballistic belt, vibrating screen, magnetic separator and film suction for additional clean up of the contaminants.

The rejected waste that contains material that cannot be used in AD process nor can be recycled is sent directly to the pit in the Waste- to – Energy plant, located next to the Ecopark 3, by a belt installed in an underground passageway.



Figure 30 Ecopark 3 del Mediterrani (photo by L. Arsova)

Anaerobic Digestion:

The organic fraction once cleaned of the contaminants undergoes wet pretreatment. This pretreatment is performed in three pulpers each of 20 m³ capacity. Here the organics are mixed with water and the solution is homogenized by continuous mixing of the material. The resulting suspension goes through a sand trap for final extraction of the heavy and floating impurities. This kind of pretreatment is highly effective in extraction of unsuitable materials (>90%). Subsequently clarified organic suspension is introduced into two digesters each with a volume of 5,700 m³ where the reactions of AD of organics take place. AD technology installed is RosRoca, low solid content process operating on mesophilic temperature of 37°C and retention time of 14-16 days. The biogas produced is extracted from the top of digesters, partly compressed and reintroduced into the tank so as to ensure constant agitation and prevent the precipitation of materials in the tank.



Figure 31 Inside of the one of the AD reactors

(pipes for reintroducing the biogas), (photo by L. Arsova)

Digested sludge, product of the methanization, is dehydrated using centrifuges separating the solids from the liquid fraction. Solid material is shipped to external composting facilities and the liquids are treated on the site. Produced biogas is used for electricity production in three generators each with capacity of 1.4 KW. They have reported 20.5 GWh/y of electricity in 2008, half of it used on the site and the other half sold to the grid.



Figure 32 Material balance at the AD plant in the Ecopark 3

Odor control system and waste water treatment:

In order to control the odor on the site the entire facility is continuously maintained under negative pressure. The airflow collected is treated in two regenerative thermal oxidation units (750- 800°C).

Waste water is treated on the site before releasing in the recipient. First stage is biological trough nitrification- denitrification and second stage is physical- chemical stage that uses H_2O_2 as reducing agent.

Ecopark 4

Ecopark 4 is scheduled to become operational in 2010 and will have a treatment capacity of 300,000 tons of waste per year. This plant is primarily aimed to treat the "all other" fraction (260,000 -300,000 tons / year), but separately collected organic material will be treated (up to 40.000 t/any) according to the needs. This facility is going to be the biggest aerobic composting facility in Europe and will not have any anaerobic digestion.

8 IMPORTANT ISSUES RELATED TO THE ANAEROBIC DIGESTION PLANTS

Although anaerobic digestion as a technology has been applied in the treatment of organic material for some time now there are problems and difficulties that are associated to them. Hereby the most important issues that are concerning the managers of the existing and the potential investors in the future AD plants for treatment of the organic fraction of the MSW were looked into.

As a result of this research and in the correspondence with the officials of the plants visited the following have been identified as the biggest challenges:

- Economic feasibility
- Feedstock quality
- Efficiency of the AD technology
- Quality of the final compost product
- Air emissions control

In the following sections these issues have been discussed in details and specific examples from the visits of the AD plants in Toronto and Barcelona are given.

8.1 Economics of the anaerobic digestion plants

Economic feasibility of the anaerobic digestion plants has been questioned due to the fact that the investment as well as the operating costs of these facilities is in the range of the mass- burn Waste-to- Energy facilities. The reported numbers state that the operating costs for anaerobic digestion facilities are between \$77 and \$140 per metric ton of capacity, whereas mass burn WTE facilities cost between \$77 and \$190 per metric ton (Levis et al. 2010). Same is true for the investment costs as will be described later.

8.1.1 Costs at the AD plants in Canada

The most reliable source of actual costs in at this time is the Dufferin Organics Processing Facility that was built for \$10 million in 2000 (Arsova 2009b). This number corresponds to only \$400 per annual ton of capacity and is relatively low to other AD plants because Dufferin was built as a demonstration prototype, does not have installed equipment for mechanical pretreatment for generating electricity from the biogas produced, and for curing the product of the AD reactor.

The estimated capital charges, operating costs, and revenues (biogas, compost, gate fees of the Dufferin facility are shown in

Table 5.

	Costs	\$/ton
1	Amortization of the capital costs	50
2	Operating costs	110
3	Landfilling of the inorganic residue	25
	Total costs	185

 Table 5 Estimated costs at the Dufferin AD facility (Kelleher 2007)

In communication with the management of the AD facility in Newmarket the researcher have been given the breakdown of the costs and revenues but due to the confidentiality agreement cannot be published here. However we can just report that the number of the operational cost fall in the range of the reported numbers for the AD plants (Levis et al. 2010). Also the officials of the Newmarket plant claim that their plant is operating profitably with the revenues covering the cost and gaining additional income.

Communication of the authors with the waste management of Toronto has indicated that, following the satisfactory results of the Green Bin collection program and operation of the Dufferin AD facility, the City Council of Toronto has decided to construct two new AD plants using the Dufferin model and with total capacity of 110,000 tons/year. Preliminary estimated capital costs for these two AD facilities are \$ 69 million, corresponding to about \$630 per ton of annual capacity (Goldstein 2008). It is interesting to note that this number is in the same range as the reported costs of waste-to-energy facilities (\$600 to \$750 per annual ton of capacity, i.e. capital charges of \$60-75 per ton of MSW processed) (Themelis 2009). The estimated capital charges, operating costs and revenues for these two plants are shown in Table 6.

	Costs/revenues	\$/ton
1	Amortization of the capital costs	63
2	Operating costs	80
3	Revenues at \$0.10/kWh	-13
	TOTAL COSTS	130

Table 6 Estimated costs of the new AD plants in Canada (Goldstein 2008)

8.1.2 Costs of the Ecoparks in Barcelona

The Environmental Agency of Barcelona is the owner of all facilities but they are given under concession of the private companies that built them for a period of 15 years. During this period the Environmental Agency is paying $100 \in (\$130)$ per ton of waste processed in any of the plants. Out of this amount $15 \in$ are to cover the investment costs and $85 \in$ are operating costs (Arsova 2009d).

Revenues from the compost and the electricity go to the managing companies and are not available to the public. The investment costs of the plants are shown in the Table 7.

	AD facility	Technology	Opening year	AD capacity (t/year)	Capital cost (million \$)	Capital cost per annual ton of capacity (\$/ton)
1	ECOPARK 1	BTA	2001 (2006)	50 000	130.2	531
2	ECOPARK 2	Valorga	2004	120 000	68.4	285
3	ECOPARK 3	RosRoca	2006	90 000	58.8	226

Table 7 Investment costs of the AD plants in Barcelona

Table 7 shows that the cost per annual ton of installed capacity at Ekopark 1 is almost double that of the other two plants. This difference is due to the additional costs for the refurbishment of the original equipment and installation of the new BTA technology.

Also, the AD plants installed in Barcelona have investment cost per annual ton of capacity that is one half that of the plants that are planned to be built in Canada. This is due to the operating capacity of the plants; the AD plants in Barcelona are almost twice as large as those in Canada and that significantly decreases the investment cost per ton. However, the operating costs at all plants are in the same range comparable to the WTE plants.

The high capital cost of AD facilities and the limited revenue from the biogas and compost products indicate that the gate fee, to be paid by the citizens or local government, should be in the order of \$100-150 per ton of waste delivered at the plant. Considering that landfill gate fees in the U.S. on average are 42\$ per ton indicates that AD facilities must be subsidized (Arsova et al. 2008) (Gebrezgabher et al. 2010). Therefore, it can be concluded from the economic analysis that the investment as well as the operating costs of different technologies are in the same range and are not the overriding factor for process selection.

8.2 Feedstock quality

Purity of the feedstock is essential condition for the success of an AD plant. There are three important issues directly related to the feedstock quality as follows:

- the size and the investment cost of the pretreatment
- quality of the final compost product
- overall performance of the AD system

Cleaner feedstock needs less intense pretreatment for separation of the impurities. This is obvious comparing the plants in Barcelona with the plants in Canada. The prior have a mechanical separation part of the plant noticeable bigger than the plants in Canada. This is to expect having in mind that the plants in Barcelona were originally designed to process the SSO and "all the rest" fraction and the plants in Canada were exclusively designed for treatment of SSO. The intensive pretreatment leads to higher investment and operating costs contributing to the high prize of the AD treatment.

Production of the marketable compost is of a great importance since it is a source of revenue. However it has to meet quality requirements prior it can be used as soil conditioner on agricultural land and it is ultimately related to the feedstock purity. The AD plants in Barcelona produce compost from the SSO and "all other" fraction with noticeable difference in its quality. The compost produced from the "all other" fraction does not meet the quality requirements. On the other side AD plants in Canada does not have a problem with the quality of the compost what is due to the fact that they process much cleaner feedstock, 23- 30% of contaminants comparing to 40-70% of impurities in the feedstock in the plants in Barcelona (Arsova 2009b; Arsova 2009c; Arsova 2009d) .

Very important to emphasize is that the bad feedstock can cause a technical problems and disturb the overall performance of the AD plant, as seen in the AD plants in Barcelona. According to the officials in Barcelona the plants perform much better and have fewer problems since they are processing only SSO fraction in the AD (Arsova 2009d).

One of the solutions for the problem with the quality of the feedstock is to educate the waste generators. It is of great importance to have citizens aware of the significance the AD of the organic waste and well informed about the proper source separation of this fraction. Also cleaner feedstock can be collected from fresh markets, deli markets, restaurants etc. However, getting fairly clean feedstock has shown to be very problematic even in well informed and highly environmentally sensible societies such as Toronto, Barcelona, and Wien. The contaminants at the plant of Biogas Wien amounts to 30% of the feedstock what confirms the difficulties experienced in Toronto and Barcelona with collecting pure organic waste stream (Themelis 2009).

8.3 Quality of the final compost product

There are numerous possibilities of application of the compost in the horticulture. It has been used the most by landscapers, lawn care companies, golf courses, nurseries, and retail garden centers, while its use in commercial growing is not very common (Levis et al. 2010). Also the lower quality compost can be successfully used on the road side projects what is the case with the compost from the AD plants in Barcelona (Arsova 2009d). Erosion control is another growing market for this product (Barlaz et al. 2008). The main reasons for using compost are: to increase water penetration and retention, improve drought resistance, improve soil tillage properties, build humus content, improve plant health, suppress weeds, and use fewer chemicals (Levis et al. 2010).

Ensuring the quality of the compost and the availability of compost markets is of crucial importance in ensuring revenues from this product. There are two sources of concern related to the quality of the compost. First the compost produced from low quality feedstock does not meet the quality requirements to be used in agriculture and second the compost that meets the criteria has shown inconsistence in the quality.

According to the general manager of the Newmarket AD plant the compost they produce meets the quality requirements for agricultural use and that they have no problems selling it on the market. Even more he said that they can sell additional amounts if they were to produce more compost. The situation in Barcelona is totally opposite. First the compost produced from "all other" fraction is not of the required quality and second even they produce good compost from the SSO the demand on the market is very low. Even though the Barcelona area is agricultural there is still public resistance to use compost produced from waste as soil conditioner. In this situation the officials in Barcelona are constantly conduction public campaigns and giving the compost for free.

8.4 Efficiency of the technologies installed

Overall efficiency of the AD technologies installed in Toronto and Barcelona in term of the production of biogas, compost and electricity for each plant are given in the table 7.

From the reported numbers Valorga technology seems to be the most efficient one. This goes along with the fact that Valorga is the most favorable technology around the globe, as explained earlier. According to the officials in Barcelona and based on their experience with different AD technologies, Valorga is also the most flexible technology when it comes to the quality of the feedstock. It is robust technology easy to maintain and much flexible to the quality of the feedstock them the others (Arsova 2009d).

Facility	Technology	AD capacity (t/year)	Biogas/t of organics (Nm³)	Compost/t of organics (t)
1 Ecopark 1	ВТА	50 000	90	0.13
2 Ecopark 2	Valorga	120 000	150	N/A
3 Ecopark 3	Ros Roca	90 000	120	0.35
4 Dufferin	ВТА	25 000	100-120	0.33
5 Newmarket	ВТА	150 000	105	0.29

Table 8 Efficiency of the installed AD technologies in the Ecoparks of Barcelona

8.5 Air emissions control

Odors emitted from the AD plants are one problem that urges the public against these plants. Main sources of the odors are the pretreatment and the aerobic composting. Even though all the plants are maintained under negative pressure this problems still remains open in almost all visited facilities. The two plants without any problems caused by the odor are the Dufferin and Ecopark 3 in Barcelona, and the common thing is that these facilities do not have the aerobic composting facilities on their sites. Also AD plants located in industrial zones (e.g. Dufferin, Ekopark 1, 2) do not recognize the odor as a problem because their surroundings do not complain about it. On the other side the AD plant in Newmarket due to the complains from the neighboring residential settlements is operating under court order with much smaller capacity then the installed and was required to make big changes in the odor monitoring and control system.

Also the air emissions of these plants include certain percentage of produced methane. Since it is impossible to collect 100% of the produced biogas certain amount ends in the atmosphere increasing the carbon footprint of these plants. These fugitive emissions are of specific interest because not just it leads to air pollution but also are a sink of organic material that can be otherwise utilized if the biogas was to collected in perfectly controlled manner. The fugitive emissions from the AD plants of MSW have been reported as 1% of the total production of the methane on the site (Thomas D. DiStefano & Belenky 2009).

9 ANAEROBIC ACIDOGENESIS OF FOOD WASTE AND POTENTIAL USE OF ITS PRODUCTS AS A SUPPLEMENTAL CARBON SOURCE FOR BIOLOGICAL NITROGEN REMOVAL (BNR) FROM WASTEWATER

9.1 Motivation and objectives

Anaerobic digestion has been recognized as the best option for the treatment of the organic fraction of the MSW and superior to the landfilling and aerobic composting (Morton A Barlaz et al. 2008). Therefore, as described previously, there have been numerous plants designed and built for this purpose. However despite the success stories of many AD plants and the production of "green" energy and compost, this technology is also some problems. As an alternative to methane generation, food waste can be bioreacted to yield volatile fatty acids (VFA); these acids may be used to promote denitrification in carbon limited wastewater streams, in place of using supplemental carbon sources such as methanol. Typically, the wastewater treatment utilities add external organic electron donors to enhance the denitrification rates (Grady et al. 1999). Most commonly used among the external electron donors is methanol, mainly due to its lower cost as compared to ethanol and acetate (Louzeiro et al. 2003).

The anaerobic acidogenesis process comprises the reactions of hydrolysis, fermentation and acetogenesis. These reactions precede the methanogenesis step in the anaerobic digestion (AD) process. This study examined whether the effluent VFA from the anaerobic acidogenesis of the food waste can be used as an external carbon source for the denitrification in WWTP.

When compared to anaerobic digestion (AD), acidogenesis leading to VFA offers the advantages of lower capital and operating costs. This is due to the shorter residence time required. Furthermore, this process is amenable to easier control of fugitive emissions.. Also, VFA produced in this manner could be more cost-effective and sustainable than the use of methanol.

The specific objectives of this experimental study were to:

- 1. Demonstrate the potential of recovering volatile fatty acids by means of acidogenesis of food waste in bench-scale experiments.
- 2. Quantify the biokinetics of denitrification bymeans of VFA contained in the effluent of acidogenesis, under laboratory conditions.

9.2 Materials and methods

9.2.1 Anaerobic acidogenesis of the food waste

A bench scale experimental study was conducted in a 6-liters glass reactor equipped with a water jacket for maintaining a constant temperature of 37°C (mesophilic bacteria reaction). The pH was continuously controlled and maintained at pH=6.5, by injection of a buffer solution of 1 M sodium bicarbonate and 1 M sodium hydroxide. A Teflon stirrer blade

provided continuous mixing of the material in the reactor. The reactor was operated in batch mode for four weeks (results are not shown here) and in chemostat mode for three months (November 2009- January 2010). Retention time (RT) during the chemostat mode was 4 days. The seed biomass was provided by Halton Recycling Inc. (Newmarket, Ontario, Canada) and originated from their AD plant treating organic waste.

The feedstock to the reactor was food waste from the campus restaurant, consisting of mixed cooked and fresh food leftovers. Fresh feed material was prepared once a week and was stored at 4°C. The preparation included homogenization in a kitchen blender, diluting with water and sampling for further analyses. The average organic loading rate was 13000 mg total COD/l/day and 3200 mg soluble COD/l/day of food waste. Both, the feed material and the digestate from the reactor, were sampled three times per week for measuring the parameters shown in Table 9.

Table 9 Monitored parameters

PARAMETERS

- **1.** Total Chemical Oxygen Demand- tCOD (mg COD/l)
- **2.** Soluble Chemical Oxygen Demand- sCOD (mg COD/l)
- **3.** Total Kjeldahl Nitrogen- TKN (mg/l)
- **4.** Soluble Kjeldahl Nitrogen- sKN (mg/l)
- 5. Ammonia (mg/l)
- **6.** Total Volatile Fatty Acids COD- VFA COD (mgCOD/l)
- **7.** Volatile Fatty Acids speciation

All laboratory analyses were conducted according to Standard Methods for Examination of Water and Waste water (Eaton et al. 2005). Volatile Fatty Acid speciation and the concentration were analyzed in a Metrohm 861 Advanced Compact Ion Chromatographer. Samples for testing the soluble COD were filtered through 0.45 µm filter paper.

9.2.2 Biokinetics of the denitrification

Denitrification biokinetics were determined via "extant" batch assays (Chandran & Smets, 2001) using nitrate as electron acceptor. Denitrification rates were determined via influent

and effluent nitrate (ion-selective electrode, Accumet) and influent total COD measurements. Also, the pH and ORP values were measured.

The methanol and ethanol microbial consortia were cultivated in sequenced batch reactor (SBR) as reported by Bayshtok et al., 2009. These denitrification consortia were tested for their affinity to use VFA from the food waste digester as supplemental carbon source instead methanol/ethanol. For these denitrification rate assays the biomass was withdrawn from the SBR just prior to the start of the "settle" phase and washed by centrifugation at 10,000 rpm for 5 min at room temperature and resuspended in COD and nitrate free feed medium bubbled with N₂ gas. The digestate from the food waste reactor was centrifuged at 10,000 rpm for 10 min at room temperature and filtered through 0.45 μ m filter paper, in order to remove any biomass, prior to being used as carbon source for specific denitrification rate test (sDNR).

Initial carbon source and nitrate concentrations in the batch biokinetics assays were 250 mg COD/l and 100 mg NO_3^- -N/l respectively. This initial COD: N ratio of 2.5:1, lower than based on stochiometric COD: N requirements of 5:1 for nitrate, rendered the organic carbon as limiting nutrient (Grady ate al., 1999). The sDNR was computed by linear regression of the nitrate depletion profiles normalized to the tCOD of the batch test beaker (Bayshtok et al. 2009).

9.3 Results

9.3.1 Anaerobic acidogenesis of food waste:

The concentration of the fermentate was between 43,000 mg COD/l and 111,000 mg COD/l consisted on average of 50% of sCOD. The average concentration of the volatile fatty acids (VFAs) in the sCOD was 17.5 %. Results of the measurements performed on the key parameters are given in Table 10.

	Parameter (mg/l)	min	max	Average	SD
1.	tCOD	42,872.92	111,182.50	61,610.43	14,491.76
2.	sCOD	20,981.46	46,116.88	30,389.81	7,030.42
3.	TKN	563.08	2,775.93	1,410.77	516.22
4.	sKN	0.56	1,388.24	548.26	375.28
5.	NH4	9.69	523.08	179.31	160.75

Table 10 Values of the monitored parameters in the fermentate

Measured parameters were used to calculate the performance ratios of the anaerobic acidogenesis. Following ratios were monitored: sCOD/ NH₄⁺, sCOD/sKN and sKN/ NH₄⁺ and the results are shown in Table 11.

	Ratio	min	max	Average	SD
1.	sCOD/NH4+	65.14	2,733.24	567.84	656.73
2.	sCOD/sKN	27.29	1,224.49	157.39	279.09
3.	sKN/ NH ₄ +	0.03	1.14	0.33	0.22

Table 11 Performance Ratios

The conversion rates were calculated based on the direct measurement of the total feed COD ($tCOD_f$), the soluble and VFA COD in the feed material ($sCOD_f$, VFA COD_f) and the digestate ($sCOD_d$, VFA COD_d). The conversion rates were calculated using the following equations:

$$Feed \ tCOD - to - digestate \ sCOD \ conversion \ rate = \frac{(sCODd - sCODf)}{tCODf}$$

$$Feed \ tCOD - to - digestate \ VFA \ COD \ conversion \ rate = \frac{(VFA \ CODd - \ VFA \ CODf)}{tCODf}$$

The minimum, maximum as well as the average and the standard deviation of the results for these conversion rates are provided in the Table 12.

	Conversion rate (%)	min	max	Average	SD
1.	Feed tCOD to fermentate sCOD	7.22	65.10	34.75	17.70
2.	Feed tCOD to feremntate VFA COD	2.25	13.05	8.93	2.92

Table 12 Conversion rate	S
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The VFA concentration in mg COD/l in the fermentate was in the range between 3,300 mg COD/l and 6,560 mgCOD/l. The most common volatile fatty acids in the sCOD were acetic, propionic, n-butiric and valeric acid. The n-butiric acid had the highest concentration in mgCOD/l followed by the propionic and acetic acid, while the valeric acid had the lowest concentration. The concentration of different species of the VFAs changed with time and the evolution of each of them is ilustrated in the Figure 33.

From the figures it can be noticed that the concentration of the acetic and valeric acid were stable over the time. Oposite to the these, the propionic and n-butyric acid showed high variability in the concentration, especially the n-butyric acid.



Figure 33 Evolution of the concentrations of the VFAs in the fermented material

During the operating time of the reactor there was production of small amounts of gas. This happened occasionally and there was no continuous production. In total during the operation of the reactor there were ten samples of gas. In eight samples methane was found in average concentration of 0.6%, seven of the samples contained nitrogen in concentration of 2.2% on average, and in all ten samples the concentration of the CO_2 was on average 26.5%. Therefore, selective acidogenesis with almost complete elimination of methanogenesis of food waste was successfully demonstrated.

9.3.2 Specific denitrification rate tests (SDNR)

The SDNR tests showed that the ethanol cultivated biomass was more successful in using the effluent of the food waste digestion as carbon source than methanol cultivated biomass. The results of these tests are shown in Table 13.

Table 13 Results of the specific denitrification rate tests

Specific Denitrification Rate tests (mg NO₃-N/ mg VSS-d)

	Methanol biomass	Ethanol biomass
1.	0.13	0.44
2.	0.07	0.56
3.	0.23	0.66
4.	0.19	0.37
avg	0.15	0.51
sd	0.07	0.13

There was a slight difference in the concentration of different VFAs in the carbon source illustrated in the Figure 34.



Figure 34 SDNR results and VFA speciation in the supplemental carbon source

9.4 Discussion of experimental part of thesis

9.4.1 Anaerobic acidogenesis of the food waste;

Many researchers have studied the suitability of the VFAs for denitrification. Among the others Gerber et al. 1987 has reported that the denitrification rates for acetate, propionate and butyrate were as much as four times higher than for methanol and ethanol. Also Tam et

al. 1992 has reported acetate as being more efficient as carbon source for nutrient removal compared to methanol or glucose.

Achieved conversion rate of the feed tCOD to digestate sCOD in our reactor was higher than reported for biomass destruction, 22% on average (Ezenekwe et al. 2002). Also the concentration of the sCOD in the tCOD of the digested material was higher than reported 17% for mesophilic plug-flow anaerobic fermenter using mechanically-sorted organic waste (Sans et al. 1995). However the acetogenesis rate was not that successful and the concentration of VFA in the sCOD was lower than previously reported 85-90% for primary sludge fermentate (P. Elefsiniotis & G. D. Wareham 2006), around 50% for effluent from anaerobicaly treated 1:1 mixture of starch- rich industrial and municipal wastewater (Katehis et al. 2003), and 80% reported for anaerobic acidogenesis of food waste (Llabres et al. 1999; S.-J. Lim et al. 2008). These numbers are not directly comparable because the experimental conditions differ but can give an overall idea of range of results that have been reported. Main reasons for the big difference between previously reported and the results from our experiment may be due to different retention time or the composition of the feed material.

The performance ratios sCOD/NH3, sCOD/sKN, sKN/NH3 obtained in our reactor were much better than average reported values of 65, 9 and 0.7 respectively (Ezenekwe et al. 2002).

Among the analysed volatile fatty acids, the acetic had the most constant concentration while the biggest fluctuations were noticed in the concentration of the n-butyric acid. It can also be noticed that after the 50th day of operation the trends of the concentration of the VFA were constant, except for the n-butyric acid, and at the very end the concentrations had very similar values. Unfortunately, we were unable to determine any relation between the concentration of the different VFA in the carbon source and the SDNR results.

9.4.2 Specific denitrification rates

The results of the SDNR tests performed with the fermentate from our reactor showed that the VFA naturally produced in the anaerobic acidogenesis of food waste are suitable supplemental carbon source for denitrification. The biomass cultivated on ethanol showed higher SDNR that the biomass cultivated on methanol.

However the SDNR results for both, ethanol and methanol cultivated biomass, were comparable to the previously reported denitrification rates achieved using VFA produced from different organic materials. Reported SDNR values are shown in Table 13. The SDNR results of our experiment, average of 0.15 an 0.51 mg N/mg VSS-d for methanol and ethanol cultivated biomass respectively, are better than previously reported values.

	Specific denitrification		
Carbon source	rate (mg N/mg VSS-d)	Reference	
	0.12-0.28	(Katehis et al. 2003)	
-	0.0111	(P Elefsiniotis et al. 2004)	
- Effluent VFA	0.28	(Pavan et al. 1998)	
	0.054	(Llabres et al. 1999)	
-	0.048	(Min et al. 2002)	
-	0.08	(Ezenekwe et al. 2002)	

Table 14 SDNR results reported in previous studies

Compared to the results of the same sDNR tests conducted with methanol as carbon source and methanol cultivated biomass the results with our carbon source were lower (Bayshtok et al. 2009). The reason for this might be the acclimatization period that bacteria used for conducting the sDNR tests need to get used to new carbon source (P Elefsiniotis et al. 2004). In our case the methylotrophic bacteria showed lower affinity to the new carbon source then the ethanol degrading bacteria.

10 DISCUSSION

This study has elaborated the anaerobic digestion technology, its application in the treatment of the organic fraction of the MSW as well as the difficulties and the challenges that the AD plants management and the technology developers are facing.

Anaerobic digestion has technically been proven to be successful in treating the organic wastes and resulting in biogas and compost as final products, both marketable and produced this way are contribute to increasing the sustainability of the waste management. As a result of the long experience with the application of the AD technology in treating farm manure and sewage sludge at the WWTP few decades ago this technology was applied for the first time in treating the organic fraction of the MSW. Most of these plants were built and are still operating in the EU and were result of the European legislation to divert all organic waste from the landfills.

Although the treating the organic fraction in anaerobic reactors showed success and more than 120 AD plants for treatment of the SSO fraction are operating in Europe there are still problems and challenges that this technology needs to overcome. As discussed earlier, the economics of these plants are still not positive. According to all the analysis previously showed this is still very expensive technology, both the investment and operation costs are in the range of the WTE plants and need to be subsidized in order to be affordable for the citizens.

Another challenge is the collection of clean feedstock what has been seen as one major problem even in places consider highly sensitive to environmental issues and educated about waste separation. As we have shown previously this has been identified as a problem in Toronto, Barcelona and Wien. The quality of the feedstock determines the size and the price of the pretreatment of the material as well as the efficiency of the anaerobic digestion process in the quality of the compost final product. The quality of the feedstock is strongly related to the overall economics of these plants since it determines the marketability of the compost product as well as the amount of the biogas that can be produced and used for electricity production.

Furthermore from the environmental point the airborne emissions of these plants have been identified as a burden. AD plants that have aerobic composting installed on the site for production of final compost product are facing difficulties with odor causing emissions that have led to closing and limiting of the operating capacity of some of the plants. Also together with odor causing emissions there is a certain amount of methane emitted in the air, reported as fugitive emission. This amount in certain cases can be significant and contribute to increasing the carbon footprint of this otherwise considered green plants.

Also in some cases the technology vendors and the design of the AD plants have failed and problems like explosions and inefficient organic decomposition are occurring. For example at the Newmarket plant in Canada due to financial difficulties the hydrolysis tank was not built what is now resulting in less efficient decomposition of the organics and having high concentration of organic material that ends strait in the aerobic composting instead of going through the AD first and contribute to higher production of methane.

Beside the challenges related to the AD of the organic fraction of the MSW there is another important existing problem on the WWTP and related to the denitrification stage of the wastewater. This stage of the WWTP requires addition of carbon source in order to be completed. Most of the WWTP are now using methanol as the cheapest form of the supplemental carbon source although shown to be not the most efficient one. As presented earlier, many studies have proven that the denitrification is more efficient with acetate and ethanol as a supplemental carbon source but their application on commercial WWTP is not feasible due to the high costs.

Having the AD treatment and the challenges coupled with it on one side and the denitrification as a problem on the WWTP on the other side the idea of connecting them and making them both more efficient came along. As described through experimental study we perform anaerobic acidogenesis from food waste and then we tested the acidic product as a supplemental carbon source for denitrification. The results confirmed the hypothesis that this is possible and that further research needs to be done towards its application in the commercial WWTP.

Shifting from methanol to VFAs in the denitrification of the wastewater would have many advantages. Many of the existing WWTP have already installed anaerobic digesters for treatment of the sewage sludge that can be used for acidogenesis and production of VFAs. This can be performed in co-digestion with food waste and can further improve both, the solid waste and the wastewater management.

In order to see what might be the benefits of the shifting from methanol to VFAs for the purpose of this study, additional calculations were made, based on the experimental results and the stoichiometry of the denitrification process with methanol and VFA. The purpose was to see how much of methanol would be replaced by VFAs and what are the potential benefits of that (Arsova 2010). Here are the findings:

		g biomass	
	g SCS*	produced	
Methanol	2.44		0.49
Acetic acid	3.73		0.68
Propionic acid	2.62		0.68
n-Butyric acid	2.08		0.68
Valeric acid	2.11		0.68
Experimental			
mixture	2.55		0.69

Table 15 Comparison of the methanol and VFA mixture based on stochiometry

*supplemental carbon source, values are given per gN-NO₃ removed.

These results show that the amount of VFA mixture needed to remove 1 g $N-NO_3$ is about the same as for methanol. However the amount of biomass produced during denitrification with VFA mixture is larger than in the case of denitrification with methanol. This is important from the point that more biomass leads to higher denitrification rate and more efficient denitrification. This corresponds to the experimental results reported by previous studies that observed that denitrifiers prefer acetate over methanol and these results in higher denitrification rates.

Also, although the same amount is needed, the VFA mixture is less costly because it can be produced on the WWTP site using the existing AD reactors. In this case, the VFA mixture can be produced from the WWTP sludge or even in co-digestion with the food waste from the MSW.

It is important to emphasize that these results were obtained on the basis of stoichiometric calculations and may not be the perfect representation of what may occur in actual tests and on the field.

11 CONCLUSIONS

Anaerobic digestion is a proven technology for processing source-separated organic wastes and has experienced significant growth during the last 15 years. This technology is superior to the landfiling and also the aerobic composting of the SSO. The most successful AD processes at this time are high-solids, thermophilic processes that can produce up to 125 standard cubic meters of biogas per ton of feedstock, at 50-60% methane concentration. Among the available technologies worldwide, Valorga has been proven to be the most widely used, with the largest number of plants and highest installed capacity. Furthermore Valorga plants have reported the highest biogas yield and are most flexible with regard to feedstock quality.
Despite the fact that the AD technology has been widely applied in Europe there are only two AD plants in North America, specifically designed for food waste processing and both of them are serving the population of metropolitan Toronto in Canada. In addition, there is one WWTP co-digesting food waste and biosolids. In Europe AD has become part of the integrated solid waste management systems, as seen in the case of Barcelona.

Even though AD is effective, there are problems associated with the application of this technology in diverting organics from the landfills and composting facilities. Modern AD plants are fairly costly with investment cost up to about \$600 per annual ton of capacity. This number was based on the projections for the new AD plants planned to be built in Toronto and is corroborated by the new AD plant built for the City of Vienna next to the Pfafeneau WTE plant. Also, the operating costs of these plants are fairly high in the range of \$100-150 per ton of waste delivered at the plant which is comparable to the gate fees at Waste-to- Energy plants and much higher than the average landfill gate fee in the U.S. of \$42 per ton. These high costs as well as the experiences with Dufferin and Barcelona AD plants suggest that AD facilities need to be subsidized by the government.

Additional difficulties in the operation of AD plants are due to the problem of getting fairly clean feedstock what on the other side is crucial factor for the compost quality and the overall efficiency of the AD process. Most of these plants are supplied by SSO material from the separate waste collection systems. Even so, they still generate residue amounting from 25% at the plants in Toronto, 30% in Wien to up to 40% and higher in Barcelona. It is therefore, very important for communities served by AD to exercise the discipline required to minimize contamination of source-separated organic wastes and for the AD process to include extensive pretreatment for contaminant separation.

As demonstrated at the Newmarket facility, control of odor emissions is of the utmost importance. This entails fully enclosed facilities, including the feedstock deliver bay, the curing stage of the process, and collection and treatment of the plant air in complex air treatment system.

The experimental study carried out as the second part of this project has shown that the anaerobic acetogenesis of food waste is a feasible alternative to biogas generation. The volatile fatty acids (VFA) produced from food waste in a biochemical reactor can be used as a suitable supplemental carbon source for enhancing the denitrification rate in WWTP, in place of the currently used methanol. This finding is of special importance because this carbon source can lower the operating costs of denitrification, decrease the capital and operating costs of the anaerobic digestion of source-separated food waste, and reduce the greenhouse gas emissions of both processes. These results have contributed to a Patent Disclosure for such a process, filed with Columbia Technology Ventures.

12 SUGGESTED FURTHER RESEARCH

Further research is necessary to collect additional data on the use of the organic acids produced from the anaerobic digestion of food waste as supplemental carbon source for

the denitrification of WWTP effluents. Also, further experiments should be performed for identifying the optimum operating parameters for producing higher concentrations of VFAs in the liquid product of an acetogenesis reactor. In addition, technical and economic feasibility studies of the environmental and economic aspects of the industrial application of this process alternative should be carried out.

REFERENCES

- Arsova, L., 2010. Denitrification in the WWTP, Volatile Fatty Acids Vs. Methanol.
- Arsova, L., 2009a. Private Communication with Mr. Kevin Matthews, President of Canada Composting.
- Arsova, L., 2009b. Visit of Dufferin facility and private communication, Mr. Doug Beattie, Plant Manager, Toronto, Canada.
- Arsova, L., 2009c. Visit of Newmarket facility and private communication, Mr. Noel Moya, General Manager, Newmarket AD plant, Ontario, Canada.
- Arsova, L., 2009d. Visit of the Environmental Authority of the Metropolitan Area of Barcelona, Ecoparks 1, 2 and 3 and private communication with their officials.
- Arsova, L. et al., 2008. "The State Of Garbage In America". *Biocycle*, 49(12), p.22.
- Barlaz, Morton A et al., 2008. "An Assessment of the State-of-the-Practice of Food Waste Composting in North America",
- Bayshtok, V. et al., 2009. "Impact of varying electron donors on the molecular microbial ecology and biokinetics of methylotrophic denitrifying bacteria". *Biotechnology and bioengineering*, 102(6), pp.1527-36. Available at: http://www.ncbi.nlm.nih.gov/pubmed/19097144.
- Chandran, K & Smets, B.F., 2001. "Estimating biomass yield coefficients for autotrophic ammonia and nitrite oxidation from batch respirograms". *Water research*, 35(13), pp.3153-6. Available at: http://www.ncbi.nlm.nih.gov/pubmed/11487112.
- DiStefano, Thimas D. & Belenky, L.G., 2009. "Life- Cycle Analysis of Energy and Greenhouse Gas Emissions from Anaerobic Biodegradation of Municipal Solid Waste". *Journal of Environmental Engineering*, 135(11).
- DiStefano, Thomas D. & Belenky, L.G., 2009. "Life-Cycle Analysis of Energy and Greenhouse Gas Emissions from Anaerobic Biodegradation of Municipal Solid Waste". *Journal of*

Environmental Engineering, 135(11), p.1097. Available at: http://link.aip.org/link/JOEEDU/v135/i11/p1097/s1&Agg=doi.

- DOE, U., 2008. Department of Energy, Energy Efficiency and Renewable Energy. www.eere.energy.gov. Available at: http://www1.eere.energy.gov/tribalenergy/guide/images/illust_anaerobic_digestion. gif.
- Eaton, A., Clesceri, L. & Greenberg, A. eds., 2005. "*Standard methods for the examination of water and wastewater* 21st ed"., Washington, DC: APHA, AWWA and WEF.
- Elefsiniotis, P, Wareham, D.G. & Smith, M.O., 2004. "Use of volatile fatty acids from an acidphase digester for denitrification". *Journal of biotechnology*, 114(3), pp.289-97. Available at: http://www.ncbi.nlm.nih.gov/pubmed/15522438.
- Elefsiniotis, P. & Wareham, G.D., 2006. "Utilization Patterns of Volatile Fatty Acids in the Denitrification Reaction". *Enzyme and Microbial Technology*, 41(2007), pp.92-97.
- EPA, U.E.P.A., 2007. "Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2006",
- Ezenekwe, I. et al., 2002. WEFTEC 2002. In "A Novel Application of Acid-phase Digestion for Concurrent Filament Destruction and Soluble COD Recovery from Froth".
- Garcia, J.-L., Patel, B.K.C. & Ollivier, B., 2000. "Taxonomic, Phylogenetic, and Ecological Diversity of Methanogenic Archaea". *Anaerobe*, 6, pp.205-226.
- Gebrezgabher, S. a et al., 2010. "Economic analysis of anaerobic digestion—A case of Green power biogas plant in The Netherlands". *NJAS - Wageningen Journal of Life Sciences*, 57(2), pp.109-115. Available at: http://linkinghub.elsevier.com/retrieve/pii/S1573521409000049.
- Goldstein, N., 2008. "Toronto moves forward with anaerobic digestion of residential SSO". *BioCYcle*, 49(9), p.44.
- Grady, C., Daigger, G. & Lim, H., 1999. "*Biological wastewater treatmen*"t, New York: Marcel Dekker.

Hyder Consulting, 2005. "Independent Review of the KOMPOGAS technology", Final report,

- IEA, 2008. *IEA Bioenergy Task 37 Plant list 2008*, Available at: http://www.iea-biogas.net/anlagelisten/Plantlist_08.pdf.
- International, B., BTA International. Available at: http://btainternational.de/home.html?&lang=3.

- Karagiannidis, A., Perkoulidis, G. & Tjandra, S., 2008. "Multicriteria facility location model for municipal solid waste management system in North Greece". *European Journal of Operational Research*, (187), pp.1402-1421.
- Katehis, D. et al., 2003. WEFTEC 2003. In "Viability and Application of Primary Sludge Fermentate as a BNR Supplemental Carbon Source".
- Kelleher, M., 2007. Anaerobic Digestion Outlook for MSW Streams. *BioCycle*, 48(8), p.51.
- Laclos, F. de, Desbois, H.S. & Saint-Joly, C., 1997. "Anaerobic digestion of Municipal Solid Organic Waste: Valorga full-scale plant in Tilburg, NL". *Water, Science Technology*, 36(6-7), pp.457-462.
- Levis, J.W. et al., 2010. "Assessment of the state of food waste treatment in the United States and Canada". *Waste management (New York, N.Y.)*, 30(8-9), pp.1486-94. Available at: http://www.ncbi.nlm.nih.gov/pubmed/20171867.
- Lim, S.-J. et al., 2008. "Anaerobic organic acid production of food waste in once-a-day feeding and drawing-off bioreactor". *Bioresource Technology*, 99, pp.7866-7874.
- Liu, C.-fang et al., 2007. "Prediction of methane yield at optimum pH for anaerobic digestion of organic fraction of municipal solid waste". *Bioresource Technology*, 99, pp.882-888.
- Llabres, P. et al., 1999. "The Use of Organic Fraction of Municipal Solid Waste Hydrolysis Products for Biological Butrient Removal in Wastewater Treatment Plants". *Water Resources*, 33(1), pp.214-222.
- Louzeiro, N. et al., 2003. "Process control and design considerations for methanol-induced denitrification in a sequencing batch reactor". *Environmental Technology*, 24(2), p.161–169.
- Lusk, P., 1999. "Latest Progress in Anaerobic Digestion". *Biocycle*, 40.
- Miller, P.A. & Clesceri, N.L., 2003. "Waste sites as Biological reactors", LEWIS PUBLISHERS.
- Min, K. et al., 2002. "Acidigenic fermentation: utilization of wasted sludge as a carbon source in the denitrification process". *Environ Technology*, (23), pp.293-230.
- Neves, L. et al., 2007. "Influence of composition on the biomethanation potencial of restaurant waste at mesophilic temperatures". *Waste management*, 28, pp.965-97.
- Ostrem, K. & Themelis, Nickolas J., 2004. "*GREENING WASTE : ANAEROBIC DIGESTION FOR TREATING THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTES*". Available at: http://www.seas.columbia.edu/earth/wtert/sofos/Ostrem_Thesis_final.pdf.

Palmisano, A.C. & Barlaz, Morton A., 1996. "Microbiology of solid waste,"

- Parkin, G.F. & Owen, W.F., 1986. "Fundamentals of Anaerobic Digestion of Wastewater Sludge. *Journal of Environmental Engineering*", 112(5), pp.867-920. Available at: http://cedb.asce.org/cgi/WWWdisplay.cgi?49921.
- Pavan, P. et al., 1998. "Effect of addition of anaerobic fermented OFMSW on BNR process: Preliminary results". *Water Science and Technology*, 39(1), pp.327-334.
- Ralph, M. & Dong, G.J.-, 2010. "*Environmental Microbiology* Second.", A JOHN WILEY & SONS, INC., PUBLICATION.
- Rozej, A., Montusiewicz, A. & Lebiocka, M., 2008. No Title. *Archives of Env. Protection*, 34(3), pp.299-304.
- Sans, C. et al., 1995. "Volatile Fatty Acids Production by Mesophilic Fermentation of Mechanically- Sorted Urban Organic waste in a Plug- Flow Reactor." *Bioresource Technology*, 51, pp.89-96.
- Schink, B., 1997. "Energetics of syntrophic cooperation in methanogenic degradation". *Microbiol Mol Biol Rev*, 61, pp.262-280.
- Sekiguchi, Y., Kamagata, Y. & Harada, H., 2001. "Current opinion in Biotechnology". *Current Opinion in Biotechnology*, 12, p.277–282.
- Shefali, V. & Themelis, Nickolas J., 2002. "ANAEROBIC DIGESTION OF BIODEGRADABLE ORGANICS IN MUNICIPAL SOLID WASTE". Available at: http://www.seas.columbia.edu/earth/vermathesis.pdf.
- Themelis, Nickolas J., 2009. Visit of Pfaffenau and Wien Biogas Facilities. Available at: http://www.wien.gv.at/umwelt/ma48/service/publikationen/pdf/da-sein-fuer-wienen.pdf.
- Themelis, Nickolas J. & Reshadi, S., 2009. NAWTEC 17. Chantilly, VA. In "*Potential for reducing the capital costs of WTE facilities*".

Vandevivere, P., De Baere, L. & Verstraete, W., 1999. Unpublished manuscript.

Viswanath, P., Sumithra Devi, S. & Nand, K., 1991. "Anaerobic Digestion of Fruit and Vegetable Processing Wastes for Biogas Production. *Bioresource Technology*, 40, pp.43-48.