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ТЕХНОЛОГИЧНИ ПАРАМЕТРИ НА АНАЕРОБНАТА ФЕРМЕНТАЦИЯ ПРИ БИОРАЗГРАДИМИ ОРГАНИКИ В ТВЪРДИ БИТОВИ ОТПАДЪЦИ

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TECHNOLOGICAL PARAMETERS OF ANAEROBIC DIGESTION OF BIODEGRADABLE ORGANICS IN MUNICIPAL SOLID WASTES

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Abstract

This study examined in depth the current status of the anaerobic digestion technologies for the treatment of the organic fraction of municipal solid wastes (MSW). Anaerobic digestion (AD) consists of the degradation of organic material in the absence of oxygen. It produces mainly 55 % methane and 45 % carbon dioxide gas and a compost product suitable as a soil conditioner.

A review of systems in operation worldwide was made, including types of process design and their engineering and environmental performance. The study also provided information on the trend in installed capacity and size of plants, which indicated that in the late 90's there was a notable rise in size of new plants.

The AD systems for MSW digestion are widely used throughout the world. Commercially available digesters range from 70 m^3 to 5000 m^3 reactor capacity. The smaller digesters make use of the generated biogas (i.e. mixture of CH_4 and CO_2) for heating the digester while larger units generate up to 2 MW of electricity.

Key words: compost, methane digestion, anaerobic digestion, digestors, organic wastes

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1. INTRODUCTION

Municipal solid waste (MSW) is the waste generated in a community with the exception of industrial and agricultural wastes [9]. Hence MSW includes residential waste (e.g., households), commercial (e.g., from stores, markets, shops, hotels etc), and institutional waste (e.g., schools, hospitals etc). Paper, paperboard, garden and food waste can be classified in a broad category known as organic or biodegradable waste.

The organic compound fraction of MSW in the US represents 70% of the waste composition and consists of paper, garden waste, food waste and other organic waste including plastics. The biodegradable fraction (paper, garden and food waste) accounts for 53% of waste composition [3]. Therefore, treatment of these wastes is an important component of an integrated solid waste management strategy and reduces both the toxicity and volume of the MSW requiring final disposal in

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a landfill. This study explores the anaerobic digestion technology (AD), i.e. in the absence of oxygen, as one of the main options for processing the biodegradable organic materials in MSW. The biodegradable fraction of MSW contains anywhere from 15%-70% water. This thesis examines in depth anaerobic digestion (AD) technologies in order to determine their economic and environmental competitiveness, as one of the options for processing the biodegradable organic materials in MSW.

2. DEVELOPMENT AND PRESENT STATUS OF AD TECHNOLOGY

2.1 Historical Background

Historical evidence indicates that the AD process is one of the oldest technologies. Biogas was used for heating bath water in Assyria during the 10th century BC and in Persia during the 16th century [11]. AD advanced with scientific research and, in the 17 th century, Jan Baptista Van Helmont established that flammable gases evolved from decaying organic matter. Also, Count Alessandro Volta in 1776 showed that there was a relationship between the amount of decaying organic matter and the amount of flammable gas produced. In 1808, Sir Humphry Davy demonstrated the production of methane production by the anaerobic digestion of cattle manure [5].

The industrialization of AD began in 1859 with the first digestion plant in Bombay, India. By 1895, AD had made inroads into England where biogas was recovered from a well-designed sewage treatment facility and fueled street lamps in Exeter. Further AD advances were due to the development of microbiology. Research led by Buswell and others [5] in the 1930s identified anaerobic bacteria and the conditions that promote methane production.

Prior to 1920, most of the AD took place in anaerobic ponds. As the understanding of AD process control and its benefits improved, more sophisticated equipment and operational techniques emerged. The result was the use of closed tanks and heating and mixing equipment to optimize AD. The primary aim of waste stabilization in due course led to the basic municipal sludge digester. This design then spread throughout the world. However, methane production suffered a setback as low-cost coal and petroleum became abundant. AD systems made a comeback during WWII with fuel shortages hitting Europe but after the war AD was once again forgotten. Another factor that led to declining interest in AD was increased interest in aerobic digestion systems.

While the developed world shunned AD except as a wastewater sludge digestion technique, developing countries such as India and China embraced this technology. These countries saw gradual increase in small-scale AD systems used mostly for energy generation and sanitation purpose. In the developed countries, industrial expansion and urbanization coupled with low-cost electricity resulted in aerobic composting and landfilling to become the choice technologies for waste treatment, until recent times. The energy crisis in 1973 and again in 1979 triggered renewed interest in development of simple AD systems for methane production as an energy source. India, China and Southeast Asia responded to the crisis with marked expansion of AD. Most of the AD systems were small digesters using combined human, animal and kitchen wastes. Many community digesters were installed to produce large volumes of biogas for village electrification. Also, Europe, North America and the Soviet Union became involved with research in AD for methane production from animal manure. The U.S. established renewable energy programs, emphasizing the AD of biomass for energy production.

The rush for deployment of AD systems to meet energy needs also led to many foreign-aid projects. Unfortunately, the knowledge on AD was still in a fledgling state and there were numerous failures. China, India and Thailand reported 50% failure rates. Failures of farm digesters in the U.S. approached 80%. Europe and Russia also experienced high farm digester failure rates [5]. Nevertheless, those designs that succeeded furthered the interest in research and development of AD. Apart from biogas production, AD found wider acceptance as an inexpensive technology for waste stabilization, nutrient recovery, reduction in biological oxygen demand (BOD), and sludge treatment. The dominant application of AD technology has been in farm-based facilities. About six to eight



million family-sized, low-technology digesters are used to provide biogas for cooking and lighting fuels with varying degrees of success.

China and India have now adopted a trend towards larger, more sophisticated farm-based systems with better process control to generate electricity. With time, AD systems are becoming more complex and not limited to agriculture or animal waste treatment. The technology is now being applied for municipal waste treatment as well as industrial waste. Taiwan flares most biogas from waste treatment and has cut down river pollution, caused by direct discharge from the animal production industry, by simply using standard AD systems that serve 5,000 farms [4].

In recent times, Europe came under pressure to explore AD market because of two significant reasons: High energy prices and stringent environmental regulations, especially controls on organic matter going to landfills as well as further expansion of landfills (Table 1).

Country	
Austria	Aims to ban landfilling of more than 5% organics by 2004
Belgium	Soon to ban direct landfilling of combustible MSW
Denmark	Banning and landfilling of combustible MSW
Finland	Policies to encourage co-combustion of MSW with other fuels
France	Banning landfilling of combustibles by 2002.Landfill levy of 20FF/tonne
Germany	Restricting landfilling of waste with more than 5% organic carbon content by 2005.
Netherlands	Landfilling of combustibles banned.Direct landfilling of other MSW banned by 2000.
Sweden	Decrease in reliance on landfill by increasing recycling rates and WTE rates.
UK	Recycling target of 25% by 2000. Lanfill tax of 7 pounds/tonne since 1996.
Ireland	Considering imposition of landfill tax.

Table 1. Current and Planned Waste Legislation in Europe

Because of environmental pressures, many nations have implemented or are considering methods to reduce the environmental impacts of waste disposal. Both Germany and Denmark have pledged to double their biogas production by the year 2000 and triple it by the year 2005 [4]. The incentive comes from the "Green-Pricing" initiative of government that allows biogas-generated electricity to be sold at a premium. Also, the co-generated "waste" steam and hot water is used in district heating systems, thereby earning additional revenue for project developers. In Europe, AD facilities generally have had a good record in treating a wide spectrum of waste streams like farm, industrial, and municipal wastes. Some AD facilities in Europe have been in operation for over 20 years. More than 600 farm-based digesters operate in Europe, where the key factor is their design simplicity. Around 250 of these systems have been installed in Germany alone in the past five years. In addition to farm digesters, Europe leads in large centralized AD systems. Between 1987-95, there were more than 150 new AD plants constructed in Europe [11]. In Europe, there are 30 large centralized digesters of which 15 are in Denmark alone and 30 more are under construction. The Danish facilities co-digest manure, clean organic industrial wastes, and source-separated municipal solid waste.

The AD technology is also used for treating industrial wastewater. The treatment of high-organic industrial wastewater is less costly by AD then by aerobic composting. There are now more than 1000 vendor-supplied systems in operation or under construction throughout the world. According to [4], European plants comprise 44% of the installed systems, with only 14% of the systems located in North



America. A large number of plants are located in Brazil treating vinasse from sugar cane-based for ethanol production. Over 35 industries have been identified using AD. They include chemicals processing, fiber, food, waste meat and milk, and pharmaceuticals. In many cases, AD is used as a pretreatment step to lower sludge disposal costs and odors, thus reducing the costs of final treatment onsite or at a municipal wastewater treatment.

Both AD and aerobic composting offer a biological route for the recovery of nutrients from the organic fraction of MSW. However, aerobic composting is energy consuming, requiring 50-75 kWh of electricity per ton of MSW input. In contrast, AD is an energy producer, with around 75-150 kWh of electricity generated per ton of MSW input [11]. Using the data of Table 3 and applying the usual 31% efficiency of U.S. power plants using fossil fuels, the electricity generated from methane per ton of MSW processed by AD is calculated to be in the range of 48-104 kWh.

3. THE ANAEROBIC DIGESTION PROCESS

Anaerobic biodegradation of organic material proceeds in the absence of oxygen and the presence of anaerobic microorganisms. AD is the consequence of a series of metabolic interactions among various groups of microorganisms. It occurs in three stages, hydrolysis/liquefaction, acidogenesis and methanogenesis. The first group of microorganism secretes enzymes, which hydrolyses polymeric materials to monomers such as glucose and amino acids. These are subsequently converted by second group i.e. acetogenic bacteria to higher volatile fatty acids, H_2 and acetic acid. Finally, the third group of bacteria, methanogenic, convert H_2 , CO_2 , and acetate, to CH_4 . The AD is carried out in large digesters that are maintained at temperatures ranging from 30 °C – 65 °C.

3.1 Hydrolysis / liquefaction

In the first stage of hydrolysis, or liquefaction, fermentative bacteria convert the insoluble complex organic matter, such as cellulose, into soluble molecules such as sugars, amino acids and fatty acids. The complex polymeric matter is hydrolyzed to monomer, e.g., cellulose to sugars or alcohols and proteins to peptides or amino acids, by hydrolytic enzymes, (lipases, proteases, cellulases, amylases, etc.) by microbes. The hydrolytic activity is of significant importance in high organic waste and may become rate limiting. Some industrial operations overcome this limitation by the use of chemical reagents to enhance hydrolysis. The application of chemicals to enhance the first step has been found to result in a shorter digestion time and provide a higher methane yield [8].

Hydrolysis / Liquefaction reactions

Lipids → Fatty Acids

Polysaccharides → Monosaccharides

Protein → Amino Acids

Nucleic Acids → Purines & Pyrimidines

3.2 Acetogenesis

In the second stage, acetogenic bacteria, also known as acid formers, convert the products of the first phase to simple organic acids, carbon dioxide and hydrogen. The principal acids produced are acetic acid (CH₃COOH), propionic acid (CH₃CH₂COOH), butyric acid (CH₃CH₂CH₂COOH), and ethanol (C₂H₃OH). The products formed during acetogenesis are due to a number of different microbes, e.g., syntrophobacter wolinii, a propionate decomposer and sytrophomonos wolfei, a butyrate decomposer. Other acid formers are clostridium spp., peptococcus anerobus, lactobacillus, and actinomyces [11]. An acetogenesis reaction is shown below:

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

3.3 Methanogenesis



Finally, in the third stage methane is produced by bacteria called methane formers (also known as methanogens) in two ways: either by means of cleavage of acetic acid molecules to generate carbon dioxide and methane, or by reduction of carbon dioxide with hydrogen. Methane production is higher from reduction of carbon dioxide but limited hydrogen concentration in digesters results in that the acetate reaction is the primary producer of methane [7]. The methanogenic bacteria include *methanobacterium, methanobacillus, methanococcus and methanosarcina*. Methanogens can also be divided into two groups: acetate and H₂/CO₂ consumers. Methanosarcina spp. and methanothrix spp. (also, methanosaeta) are considered to be important in AD both as acetate and H₂/CO₂ consumers. The methanogenesis reactions can be expressed as follows:

$$\begin{array}{lll} CH_3COOH \rightarrow & CH_4 + & CO_2 \\ (acetic acid) & (methane) & (carbon dioxide) \\ 2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \\ (ethanol) & \\ CO2 + & 4H_2 \rightarrow CH_4 + & 2H_2O \\ & & (hydrogen) & (water) \\ \end{array}$$

3.4 General Process Description

Generally the overall AD process can be divided into four stages: Pretreatment, waste digestion, gas recovery and residue treatment. Most digestion systems require pre-treatment of waste to obtain homogeneous feedstock. The preprocessing involves separation of non-digestible materials and shredding. The waste received by AD digester is usually source separated or mechanically sorted. The separation ensures removal of undesirable or recyclable materials such as glass, metals, stones etc. In source separation, recyclables are removed from the organic wastes at the source. Mechanical separation can be employed if source separation is not available. However, the resultant fraction is then more contaminated leading to lower compost quality [8]. The waste is shredded before it is fed into the digester.

Inside the digester, the feed is diluted to achieve desired solids content and remains in the digester for a designated retention time. For dilution, a varying range of water sources can be used such as clean water, sewage sludge, or recirculated liquid from the digester effluent. A heat exchanger is usually required to maintain temperature in the digesting vessel. The biogas obtained in AD is scrubbed to obtain pipeline quality gas. In case of residue treatment, the effluent from the digester is de-watered, and the liquid recycled for use in the dilution of incoming feed. The biosolids are aerobically cured to obtain a compost product.

3.5 Various AD systems

AD processes can be classified according to the total solids (TS) content of the slurry in the digester reactor. Low solids systems (LS) contain less than 10 % TS, medium solids (MS) contain about 15%-20%, and high solids (HS) processes range from 22% to 40% [9]. AD processes can be categorized further on the basis of number of reactors used, into single-stage and multi-stage. In single stage processes, the three stages of anaerobic process occur in one reactor and are separated in time (i.e., one stage after the other) while multi-stage processes make use of two or more reactors that separate the acetogenesis and methanogenesis stages in space. Batch reactors are used where the reactor is loaded with feedstock at the beginning of the reaction and products are discharged at the end of a cycle. The other type of reactor used, mostly for low solids slurries, is continuous flow where the feedstock is continuously charged and discharged. As noted earlier, the AD systems treat various types of wastestreams and in some plants MSW is mixed with sewage sludge or other type of waste. These types of processes will be discussed in more detail later.

4. IMPORTANT OPERATING PARAMETERS IN AD PROCESS

The rate at which the microorganisms grow is of paramount importance in the AD process. The operating parameters of the digester must be controlled so as to enhance the microbial activity and thus increase the anaerobic degradation efficiency of the system. Some of these parameters are discussed in the following section.

4.1 Waste composition / Volatile Solids (VS)

The wastes treated by AD may comprise a biodegradable organic fraction, a combustible and an inert fraction. The biodegradable organic fraction includes kitchen scraps, food residue, and grass and tree cuttings. The combustible fraction includes slowly degrading lignocellulosic organic matter containing coarser wood, paper, and cardboard. As these lignocellulosic organic materials do not readily degrade under anaerobic conditions, they are better suited for waste-to-energy plants. Finally, the inert fraction contains stones, glass, sand, metal, etc. This fraction ideally should be removed, recycled or used as land fill. The removal of inert fraction prior to digestion is important as otherwise it increases digester volume and wear of equipment. In waste streams high in sewage and manure, the microbes thrive and hydrolyses the substrate rapidly whereas for the more resistant waste materials, such as wood, digestion is limited.

The volatile solids (VS) in organic wastes are measured as total solids minus the ash content, as obtained by complete combustion of the feed wastes. The volatile solids comprise the biodegradable volatile solids (BVS) fraction and the refractory volatile solids (RVS). Kayhanian [3] showed that knowledge of the BVS fraction of MSW helps in better estimation of the biodegradability of waste, of biogas generation, organic loading rate and C/N ratio. Lignin is a complex organic material that is not easily degraded by anaerobic bacteria and constitutes the refractory volatile solids (RVS) in organic MSW. Waste characterized by high VS and low non-biodegradable matter, or RVS, is best suited to AD treatment. The composition of wastes affects both the yield and biogas quality as well as the compost quality.

4.2 pH Level

Anaerobic bacteria, specially the methanogens, are sensitive to the acid concentration within the digester and their growth can be inhibited by acidic conditions. The acid concentration in aqueous systems is expressed by the pH value, i.e. the concentration of hydrogen ions. At neutral conditions, water contains a concentration of 10 -7 hydrogen ions and has a pH of 7. Acid solutions have a pH less than 7 while alkaline solutions are at a pH higher than 7. It has been determined [8] that an optimum pH value for AD lies between 5.5 and 8.5. During digestion, the two processes of acidification and methanogenesis require different pH levels for optimal process control. The retention time of digestate affects the pH value and in a batch reactor acetogenesis occurs at a rapid pace. Acetogenesis can lead to accumulation of large amounts of organic acids resulting in pH below 5. Excessive generation of acid can inhibit methanogens, due to their sensitivity to acid conditions. Reduction in pH can be controlled by the addition of lime or recycled filtrate obtained during residue treatment. In fact, the use of recycled filtrate can even eliminate the lime requirement.

As digestion reaches the methanogenesis stage, the concentration of ammonia increases and the pH value can increase to above 8. Once methane production is stabilized, the pH level stays between 7.2 and 8.2.

4.3 Temperature

There are mainly two temperature ranges that provide optimum digestion conditions for the production of methane – the mesophilic and thermophilic ranges. The mesophilic range is between $20^{\circ} \text{ C} - 40^{\circ} \text{ C}$ and the optimum temperature is considered to be $30^{\circ} \text{ C} - 35^{\circ} \text{ C}$. The thermophilic temperature range is between $50^{\circ} \text{ C} - 65^{\circ} \text{ C}$ [8]. It has been observed that higher temperatures in the thermophilic range reduce the required retention time [6].



4.4 Carbon to Nitrogen Ratio (C/N)

The relationship between the amount of carbon and nitrogen present in organic materials is represented by the C/N ratio. Optimum C/N ratios in anaerobic digesters are between 20-30. A high C/N ratio is an indication of rapid consumption of nitrogen by methanogens and results in lower gas production. On the other hand, a lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria. Optimum C/N ratios of the digester materials can be achieved by mixing materials of high and low C/N ratios, such as organic solid waste mixed with sewage or animal manure.

4.5 Total solids content (TS) / OrganicLoading Rate (OLR)

As discussed earlier, Low solids (LS) AD systems contain less than 10 % TS, medium solids (MS) about 15-20 % and high solids (HS) processes range from 22 % to 40 % [9]. An increase in TS in the reactor results in a corresponding decrease in reactor volume.

Organic loading rate (OLR) is a measure of the biological conversion capacity of the AD system. Feeding the system above its sustainable OLR results in low biogas yield due to accumulation of inhibiting substances such as fatty acids in the digester slurry. In such a case, the feeding rate to the system must be reduced. OLR is a particularly important control parameter in continuous systems. Many plants have reported system failures due to overloading [8]. OLR is twice in HS in comparison to LS.

4.6 Retention (or residence) Time

The required retention time for completion of the AD reactions varies with differing technologies, process temperature, and waste composition. The retention time for wastes treated in mesophilic digester range from 10 to 40 days. Lower retention times are required in digesters operated in the thermophilic range. A high solids reactor operating in the thermophilic range has a retention time of 14 days.

4.7 Mixing

The purpose of mixing in a digester is to blend the fresh material with digestate containing microbes. Furthermore, mixing prevents scum formation and avoids temperature gradients within the digester. However excessive mixing can disrupt the microbes so slow mixing is preferred. The kind of mixing equipment and amount of mixing varies with the type of reactor and the solids content in the digester.

4.8 Compost

When the digestion is complete, the residue slurry, also known as digestate, is removed, the water content is filtered out and re-circulated to the digester, and the filter cake is cured aerobically, usually in compost piles, to form compost. The compost product is screened for any undesirable materials, (such as glass shards, plastic pieces etc) and sold as soil amendment.

The quality of compost is dependent on the waste composition. Some countries have prescribed standards for compost quality. The U.S. Department of Agriculture has set standards for heavy metals in the compost (Table 2). These standards are for compost treated by the aerobic process but may also be applied to AD compost product.

Heavy Metal	Standard*
Cadmium (Cd)	10
Nickel (Ni)	200
Lead (Pb)	250
Copper (Cu)	1000
Chromium (Cr)	1000
Zinc (Zn)	2500

Standard for compost produced by aerobic process

Table 2. US Department of Agriculture Compost Heavy Metals Standards (ppm) [2]

Some of the European Union (EU) countries have set standards for the quality of compost produced by anaerobic digestion of solid wastes.

Country	Cd	Pb	Hg	Ni	Zn	Cu	Cr	As
Austria	1	150	1	60	400	100	70	-
Denmark	0.8	120	0.8	30	4000	1000	100	40
Finland	3	150	2	100	1500	600		50
France ^a	8	800	8	200			-	
Germany, class 1 ^b	1.5	150	1	50	400	100	100	
Ireland		P-9	-	ω.	tos	.,		*
Italy ^c	10	500	10	200	2500	600	10 ^d	500 d
Netherlands, "superclean compost" e	0.7	65	0.2	10	75	25	50	5
Netherlands, "clean compost"e	1	100	0.3	20	200	60	50	15
Norway, class I ^f	0.8	60	0.6	30	400	150	60	
Norway, class II ^f	2	80	3	50	800	650	100	
Spain	40	1200	25	400	4000	1750	750	**
Sweden (guidelines)	1	100	1	50	300	100	100	
Switzerland	1	120	1	30	400	100	100	
UK	-		-		-	_		_
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- a) No official legislation.
- b) Class I-compost is used for food production.
- c) Regulations for source sorted compost varies between regions.
- d) Chrome (III) 500 mg/kg ts. Chrome (VI) 10 mg/kg ts.
- e) The division into two classes was made in order to stimulate an improved compost quality. The quality is generally so good that a change to only one class is discussed.
- f) The maximum application of class I is 40 tonnes/ha during 10 years and for class II maximum 20 tonnes/ha during 10 years.

Table 3. Limits concentrations (mg/kg total solids) of heavy metals and arsenic in compost according to regulations in different countries [1, 11]



4.9 Biogas Composition

The gas obtained during AD comprises of methane, carbon dioxide, some inert gases and sulfur compounds (Table 3). Usually 100 - 200 m of total gas are produced per ton of organic MSW digested (RISE-AT, 1998).

Methane	F. CO. 0.1
IVICUITATIC	55 – 70 % by vol.
Carbon dioxide	30 – 45 % by vol
Hydrogen sulphide	200 – 4000 ppm by vol
Energy content of AD gas product	20 – 25MJ / standard m ³
Energy content of CH ₄ per ton MSW	167 – 373 MJ / Ton MSW

Table 4. Typical Biogas Composition [8]

5. CONCLUSIONS

In the last decade of the 20 th century, the use of AD technology for the processing of organic wastes has expanded appreciably. Between 1996 and 2000 the number of new AD plants increased from 2 to 7 plants per year. Europe is far ahead in AD technology and Germany and Denmark are leading in the use of AD technology.

AD technology has seen remarkable progress in reactor and process design. Earlier, long periods of time were required for complete degradation. Mesophilic temperatures (about 35° C) would require up to 30 days for digestion. The development of thermophilic ($60-65^{\circ}$ C) AD has reduced the retention time for solids in the digester to less than 15 days.

AD plants have also made much progress in their capacity to treat a wide range of waste streams. In late 70's, most of the AD plants were designed to treat sewage and were predominantly low-solids operations. However, during the last decade the number of high solids processes has increased appreciably to include organic MSW treatment. If one of the goals of new plants is energy generation, then high solids are more promising.

This study showed that multi-stage processes provide biological stability by keeping the acidogenesis and methanogenesis separately and allowing higher organic loading rate without shock to methanogenic bacteria. However, multi-stage systems are complex and the benefits do not justify high investment costs.

In future, the best practicable environmental option will be deriving energy from waste. Energy recovery technologies include combustion of waste and anaerobic digestion (AD). However, combustion of the wet stream of MSW does not provide efficient energy recovery. So the advantages offered by AD are worth exploring for the wet stream of Municipal Solid Waste (MSW) of New York City and elsewhere.

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