ANAEROBIC DIGESTION, GASIFICATION, AND PYROLYSIS

Lee G.A. Potts
Biwater Treatment, Lancashire, UK

Duncan J. Martin
University of Nottingham, UK

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Summary

Incinerators for municipal solid waste can be used for electricity generation or space heating. However, they need complex burners to handle unsorted municipal solid waste (MSW) as a very low-grade fuel and also costly cleaners for the flue gas, so they are only economic at large scales. This heightens local objections to their construction and extends haulage distances. However, there are alternative methods of utilizing MSW as an energy source, by converting the organic fractions to gaseous or liquid fuels. These may be cleaner and suitable for a wider variety of uses. They require a sorted feedstock, which is best provided by separation at source but they can be applied to an organic fraction separated from mixed wastes. Plants may also be smaller and less intrusive, especially with source separation, so better suited to smaller towns. The methods of conversion fall into two broad categories, microbial and physical/chemical. The former use anaerobic digestion, a slow process best suited to kitchen and garden wastes, which consumes little or no energy and conserves much of the complex organic matter, of potential value as a soil conditioner. The latter rely on fast thermal treatments, such as pyrolysis and gasification, which can convert all organic matter, including paper, wood, and synthetic polymers, to simple products. These processes may yield more energy but the net yield is reduced by the energy consumed in the process. Although all three processes are well established for other feedstocks, their application to MSW remains under development and few full-scale plants have accumulated a long period of operating experience.

1. Conversion of Municipal Solid Waste to Gaseous Fuels

The stabilization of MSW can be combined with the generation of energy through its partial conversion to a gaseous fuel, by such processes as anaerobic digestion, pyrolysis, or gasification. In the first of these, the organic fraction of MSW is slowly digested by microorganisms under anaerobic conditions. The products are a methane-rich biogas and a solid digestate, which can be used as a compost or soil conditioner after maturation. The alternative thermal treatments, pyrolysis and gasification, also yield fuel gases and are much faster. The liquid products can be used as chemical feedstock or as fuels, while the solid char remaining can also be used a low-grade fuel. The distinction between them is that pyrolysis takes place in the absence of air, and so requires an energy input to reach the high temperatures required, while gasification achieves a similar effect by partial combustion of MSW with a restricted supply of oxygen.

All these processes use wastes as a source of renewable energy. It may therefore be misleading to ameliorate the public image of incinerators by referring to them as "Waste to Energy" (WtE) or "Energy from Waste" (EfW) plants. "Energy Recovery Incinerator" would be a more accurate title.

2. Anaerobic Digestion

2.1. Background

The main biological treatment methods for MSW are aerobic composting and anaerobic digestion (AD). Each relies upon the action of a diverse group of microorganisms to stabilize the waste but a fundamental difference between the two processes is the presence or absence of oxygen. Aerobic composting, which is not further discussed here, produces no fuel and, as it requires active aeration to reach maximal reaction rates, it is a net energy consumer. However, it is faster than AD and breaks down more of the organic matter.

Anaerobic digestion is a natural biological decomposition process that occurs in oxygen-free conditions. It involves the conversion of organic matter by microorganisms to generate a gaseous product, known as "biogas," leaving a stabilized solid product, known as "digestate." It occurs in some natural environments, such as sediments and marshlands and also in the digestive tracts of ruminants and termites. Methane is generated from all these sources. However, suitable conditions can also be created artificially, in landfills and digestion plants. AD has been used for over 100 years in sewage treatment to stabilize waste sludges and more recently to treat selected farm and industrial wastes.

Modern landfills also develop anaerobic conditions, due to the depth and compaction of the waste, so they generate a biogas known as "landfill gas." The feedstock is usually unsorted MSW, often mixed with industrial, construction, and other wastes. Stabilization is very slow and little process control is possible. Recent experiments with leachate recycle, in the "flushing bioreactor" landfill, suggest that considerable acceleration might be feasible. Proof of this concept in long-term large-scale trials is eagerly awaited. However, the conditions in landfills differ widely from those in digesters, so this discussion will be restricted to the latter.

Anaerobic digestion first became of interest in the 1970s, as a means of stabilizing MSW and also as a renewable energy source, following the "energy crises" of this period. More recent drivers include the increasing levels of MSW generation and the problems associated with landfilling, such as biogas migration and groundwater pollution. The many years of experience developed from sewage sludge and farm waste digestion led naturally to development work on AD and it is now an established, reliable treatment for MSW. In 1999, there were more than 50 full-scale operational plants, mostly in Europe, with a combined annual treatment capacity of over one million tonnes. The first large-scale plant for AD of MSW was, however, built in Florida (USA). It was known as the "RefCoM project" (Refuse Converted to Methane) and ran intermittently from 1978 to 1985. Much operating information was determined in this pioneering work, which formed a basis for future developments. Among the major problems encountered were waste preparation and the use of mechanical stirrers. The plant was fed between 6 and 18 tonnes per day of sorted and shredded MSW mixed with sewage sludge, giving a dry solids content of 2.7–6.3%. (Feed concentrations were limited by the use of mechanical stirring.) Biogas production was 1300–3500 m^3/d, with average methane content of 53%. A residence time of 6–26 days gave a volatile solid reduction of about 75%.

This was followed by many pilot scale plant investigations in Europe. For example, research trials were conducted using the Valorga process on a 5 m^3 pilot plant in Montpellier, France. This plant utilized food waste from MSW. A larger pilot plant in La Buisse (France), treated around 8000 tonnes per year. The waste entering this facility was initially crushed and screened to remove some of the nonbiodegradable materials, which also created a particle size more suitable for degradation. Instead of slurried feed, this process was fed with moist solids, giving a solids content of around 30%. It operated in the mesophilic temperature range. The biogas production was 4.4–5.0 m^3/day per cubic meter of reactor volume. Another early European pilot plant using the DrAnCo process (Dry Anaerobic Composting) operated in Ghent (Belgium), from 1984. This process also used high-solids digestion but in the thermophilic temperature regime. These trials exemplify the two major strands in AD process development. "Wet" (or low solids) processes are similar to the AD systems utilized in wastewater treatment and need a slurried feed, with a total solids content of up to 10%. "Dry" (or high solids) processes such as DrAnCo and Valorga, use a feed of moist solids at 30–40% TS. All can achieve waste stabilization within 20 days.

The advantages of AD over incineration include:

(a) lower emissions of carbon dioxide (because some complex compounds are not digested)
(b) conservation of these complex organics as a potential soil conditioner
(c) easy treatment of the "wet" fraction of MSW (which is problematical in incineration)
(d) elimination of odors (AD plants are fully enclosed)
(e) no production of such toxic products as dioxins

It is also important to recognize that, when biogas is utilized as a renewable fuel, the combustion of its methane content makes no net addition to carbon dioxide emissions. This is because the combustion of the fossil fuel it replaces would generate at least as much carbon dioxide.

Compared with landfill, its advantages include process acceleration and the elimination of biogas emissions and leachate escapes. Compared with composting, it uses much less land and energy and does not generate smells and fungal spores.

However, AD has some disadvantages:

(a) It is slow, so it needs large, costly digesters (capital costs for composting are much lower)
(b) Material handling and preparation problems can arise
(c) Wastewater treatment can be costly

(d) The need for separate treatment of the nonbiodegradable materials imposes additional costs
(e) The digestate is often of poor quality, unsuitable for sale as a compost

2.2. Principles

In an oxygen-free environment, a consortium of microorganisms convert most organic materials to biogas, a carbon dioxide and methane mixture, containing 55–70% methane. Bacteria conduct the majority of the biochemical processes in AD. Four successive phases can be identified: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, each being generally conducted by a different group of bacteria. Some of the microorganisms have a symbiotic dependence on others for metabolic intermediates, so the relationships between these groups are very complex. Acidogenesis is a relatively fast reaction but all the other three steps can be very slow. The conditions and the composition of the waste may determine which of them is rate controlling: different authorities have proposed all three.

In hydrolysis, extracellular microbial enzymes convert the insoluble polymeric materials in the waste (polysaccharides, proteins, and lipids) into simple sugars, amino acids, and fatty acids. These soluble products can be transported into the microbial cells as substrates, so the remaining steps are intracellular. Hydrolysis may be the rate-limiting step in the overall process for some wastes and its rate depends upon such factors as temperature, pH, inhibition, substrate availability, and bacterial population.

Acidogenesis converts these simple molecules to a mixture of volatile fatty acids plus carbon dioxide and hydrogen. The proportion of the different substrates generated by acidogenesis depends upon conditions, which also affects which bacterial species are dominant. Most of the acids formed cannot be utilized as substrates by the methanogenic bacteria, the only exceptions being formic and acetic acids. This highly exothermic step yields the energy utilized in the endothermic steps of hydrolysis and acetogenesis.

Acetogenesis then converts the larger volatile fatty acids (for example, propionic, butyric, and valeric acids) to acetic acid, carbon dioxide, and hydrogen, all of which can be utilized in methanogenesis. The acetogenic phase is energetically coupled to the following methanogenic phase.
The methanogenic bacteria are obligate anaerobes, severely inhibited by traces of oxygen. They are not closely related to the more familiar kinds of microorganisms and are believed to be survivors of the earliest living organisms. They evolved before photosynthesis created the atmosphere we have today, which is toxic to them, so they can thrive only in anaerobic environments, such as the depths of boggy soils and marshes, in the sediments at the bottoms of lakes, and in the guts of animals. However, within these ecological niches, they are common.

They can utilize only a few substrates, which include formic and acetic acids, carbon monoxide, carbon dioxide, hydrogen, and methylamine. About 70% of the methane produced is formed by "acetoclastic" bacteria, which simply split the acetic acid molecule. Most of the rest is produced by "hydrogentrophic" methanogens, which combine hydrogen with carbon dioxide. Neither reaction is highly exothermic, so the energy yield is low and growth is very slow. These major reactions can be written as:

$$CH_3COOH = CH_4 + CO_2 \quad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad (2)$$

The AD environment is extremely complex and competitive. Other bacterial groups are also involved and a balance between them is essential. The sulfate-reducing bacteria may for example compete with the methanogenic bacteria for substrates. Under most conditions, natural processes commonly establish a viable balance but AD is consequently sensitive to any rapid changes which might upset this equilibrium.

2.3. Conditions

Successful AD requires the careful control of conditions in the digester.

2.3.1. Moisture Content

Moisture content is considered to be one of the most important factors affecting waste stabilization. Moisture may aid digestion by:

- controlling cell turgidity;
- reacting, in polymer hydrolysis;
- solubilizing and transporting nutrients, intermediates, products, inhibitors, enzymes and microorganisms;
- by modifying the shapes of enzymes and other macromolecules; and
- by exposing more of the waste surface to microbial attack.

The moisture content of raw MSW varies with waste composition, climatic conditions, and collection methods but is usually 20–30%, too low for efficient AD. Raising the moisture content of an anaerobic digester increases generation of methane. Studies have shown that the minimum moisture content is 36% for a mechanically mixed, mesophilic digester fed with the putrescible fraction of MSW. Water must therefore be added, usually in the form of recycled leachate or an aqueous waste, such as sewage sludge. However, the addition of excess water can lead to greater capital and operating costs due to the larger digester volume required and may complicate handling of the waste and digestate.

2.3.2. Temperature

AD can proceed in three temperature ranges:

- cryophilic, less than 20 °C (very slow, so rarely used for digestion of MSW);
- mesophilic, 20–45 °C (35 °C is generally used for mesophilic operation); and
- thermophilic, above 45 °C (55 °C is generally used for thermophilic operation)

Although digestion is faster in the thermophilic range, much of the biogas is used to heat the digester. The process is also less stable, as the microbial population is less diverse. Mesophilic operation is therefore most common. The exact optimum temperature might vary with waste composition and digester design but the temperatures must be kept constant to maintain constant biogas production. External heating is usual in wet digestion. A proportion of the digester contents may be recycled and mixed with the feedstock, then passed through an external heat exchanger for heating to digester temperature.

Some recent AD processes include a pasteurization step, in response to tighter standards for pathogen levels in composts. National standards vary but may specify permissible thermal regimes, as well as maximum counts of key species in the finished compost. Generally, there are three design approaches. The first involves pasteurizing the waste prior to digestion, so it might enter the digester at 70 °C or above, eliminating the need for heating. The second relies on thermophilic digestion, which can achieve pasteurization at 55 °C if the retention time is long enough. In each of these methods, additional fuel may be needed to supplement the biogas generated by the process. The third method uses aerobic composting of the digestate. Aerobic biological processes are highly exothermic, so can achieve temperatures high enough to kill pathogens, while also stabilizing and sweetening the digestate.

2.3.3. pH

The three parameters alkalinity, acidity, and pH are closely related so will be considered together. They combine to indicate the state of the in AD process, so it is important to check them regularly. If methanogenesis fails to utilize the volatile fatty acids (VFAs) as they are formed, a biochemical imbalance develops. VFAs then accumulate and progressively inhibit methanogenesis, until it stops completely.

The VFA concentration is thus an important indication of stability, as high levels can indicate such an imbalance. A low pH usually occurs with high VFA levels but if there is enough alkalinity available the acids may be buffered. Buffering agents, such as calcium carbonate, may be added. However, buffering can be provided by the reaction of ammonium ions with bicarbonate ions to form ammonium bicarbonate, so much of the buffering capacity is due to the high solubility of the ammonia and carbon dioxide generated by the process. An alkalinity of greater than 500 mg/l is an indication of good buffering capacity.

High VFA levels can occur for many reasons, such as: overloading, inhibition, poor mixing, nutrient shortage, variations of temperature, or other conditions, or an excessive loss of bacteria in the discharge. A VFA level above 500 mg/l is detrimental. The optimum pH level is different for each bacterial group in AD, but the methanogenic bacteria are the most susceptible to the acidic conditions that tend to arise. A narrow range of 6.8–7.5 is optimal for methanogenesis and there is little reaction below 6.4.

2.3.4. Waste Composition

Only the biodegradable fraction of MSW can be stabilized in AD. MSW typically contains 40–50% cellulose, 10–15% lignin, 5–12% hemicellulose, 4–5% lipids, and 2% protein. Kitchen waste is readily biodegradable and is ideal as AD feedstock. Some paper wastes are also suitable for AD but there is a public preference for recycling such materials. Garden wastes can be digested but are more suitable for aerobic composting, as woody materials contain lignin, which is stable in an anaerobic environment. However, such wastes are commonly found in the feedstock for digesters.

The waste source and the degree of preseparation control the amount of nonbiodegradable matter in the feedstock. At best, this is unaffected by the process and takes up space in the digester. Often, however, it is inhibitory or reduces the quality of the digestate, so it is advantageous to remove it before digestion. After this sorting, the biodegradable fraction is usually reduced in size prior to digestion, commonly by use of a pulverizer, in which the waste is physically broken down and water is added. An alternative method uses a hydropulper, in which water breaks up the waste.

2.3.5. Gas Phase Composition

The methanogenic bacteria are very sensitive to molecular oxygen, requiring a redox potential below -330mV. The start up of anaerobic digesters can be a slow process due to the initial presence of air.

Studies of the digestion of sewage sludge have shown that high partial pressures of carbon dioxide also affect methane production. The mechanism of carbon dioxide inhibition is not clearly understood but it may be due to the reduced pH, to damage to the cell membrane or to the inhibition of key enzymes. The partial pressure of carbon dioxide rises quickly at start up in MSW digestion, to approach 100%, before falling again when methanogenesis begins, so may also have an inhibitory effect. Methane, however, does not affect methanogenesis greatly, even at high partial pressures. The VFA concentration rises but does not exceed safe limits.

The hydrogen produced by acidogenesis and acetogenesis can adversely affect microbial metabolism but both the hydrogentrophic methanogens and the sulfate-reducing bacteria can utilize it. At the low hydrogen concentrations typical of a well-balanced process, the products of acidogenesis are hydrogen, carbon dioxide, and acetic acid. However, at high concentrations the acetic acid is replaced by related compounds, such as butyric and propionic acids, which cannot be utilized in methanogenesis. However, provided the partial pressure of hydrogen is below $9x10^{-5}$ atmospheres, the acetogenic bacteria convert these higher acids to acetic acid. Failing this, they accumulate, inhibiting methanogenesis, so that the VFA concentration also rises. A balance between the generation and consumption of hydrogen is therefore essential and hydrogen concentrations can be a further indicator of the state of the process. Hydrogen is harder to measure than pH or VFA but can give earlier warning of imbalance.

2.3.6. Retention Time

The waste must be held in the digester until biological stabilization is complete. The retention time for single-stage mesophilic digestion is 12–25 days but 6 days can suffice under thermophilic conditions. Even this requires a large digester, a major contributor to the high capital costs of AD.

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Biographical Sketches

Lee G.A. Potts is a graduate of the University of Sheffield with a BEng in Chemical Process Engineering with Biotechnology. He then studied for a PhD with the research focussing upon anaerobic digestion of solid waste at the University of Nottingham. He worked for Greenways Waste Management (now known as Hanson Waste Management) a leading waste management company within the United Kingdom. This position was to investigate alternative solid waste treatment, recycling, and disposal methods to sanitary landfilling. He was also involved in the project management of the installation of a landfill gas utilization plant. He is now with Biwater Treatment designing wastewater treatment plants for water companies within the United Kingdom and overseas.

Duncan J. Martin is a graduate of Birmingham University, with BSc in Chemical Engineering, MSc in Biological Engineering and PhD in Chemical Engineering. He is a Member of the Institution of Chemical Engineers, the Institute of Wastes Management and the International Solid Waste Association. He has worked in the industrial enzyme and Scotch whisky businesses before moving into academia. Now at the Department of Chemical Engineering of NUST in Bulawayo, Zimbabwe, after periods with Teesside Polytechnic and The University of Nottingham. Primary research and teaching interests in Environmental Protection. His main research focus is on solid-state digestion (SSD), the application of anaerobic digestion to a moist bed of solid wastes. He has recently developed a heterogeneous model of the SSD process, radically different from previous hypotheses. This proposes that the major biodegradation reactions are confined to a thin, multilayered reaction front. Within this, an intervening passive layer separates an acid-sensitive methanogenic layer from a layer in which acids are generated. Such a front develops around each particle of seed material above a minimum viable size, then gradually advances through the surrounding waste. Each viable seed particle thus initiates a distinct reaction zone, which forms a discrete, expanding, microreactor. The resulting kinetics bear no resemblance to the conventional, first-order decay kinetics predicted from homogeneous or dispersed reaction models. However, they fit experimental data well. His current work is aimed towards the development of greatly accelerated SSD processes, at little cost and without the use of leachate recycle. Such processes would be applicable to the stabilization of wastes in both anaerobic digesters and engineered landfills. Simple but efficient bioreactor landfills are likely to be of particular interest to less developed countries.