4

Storage and pre-treatment of substrates for biogas production

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Abstract: Biogas substrates are typically moist, which can make them difficult to store because bacteria and mould can grow on them. Ensiling, which involves the production of acid by lactic acid bacteria, is often used to preserve crops cheaply. Biogas substrates are also often fibrous, which can make them difficult to mix and means that some of their energy is locked up within the fibres. Different pre-treatment technologies are being investigated to access the energy in these fibres, to increase the rate of biogas production and to improve the mixing qualities of the substrates. Pre-treatment technologies are based on three principles: physical (including mechanical shear, heat, pressure and electric fields), chemical (acids, bases and solvents) and biological (microbial and enzymatic). Combinations of these principles are also used, including steam explosion, extrusion and thermo-chemical processes. Although many of these processes have been investigated at small scale, few have been analysed at large scale in un-biased studies. Many of these techniques are associated with high energy input (e.g. mechanical and heat pre-treatment), high equipment costs (e.g. mechanical systems where the blades erode) or use large volumes of chemicals (e.g. alkali pre-treatment). Different pre-treatment technologies work better with different substrates, and more research is required in this field to understand which combinations are worthwhile. This chapter describes some of the common pre-treatment technologies along with some advantages and disadvantages.

Key words: biogas, anaerobic digestion, pre-treatment, ensiling, anaerobic digestion analysis.

4.1   Introduction

Anaerobic digestion is a versatile process owing to the wide range of input materials that can be used as well as the various utilisation options for the gas produced and the digestate accumulated. A wide range of industrial residues, agricultural residues and energy crops are used and this versatility is the main strength of anaerobic digestion. However, there are two main difficulties that arise from this diversity – storage and processing.

Storage is an issue because many of the feedstocks accumulate seasonally, such as annual plants or wastes from campaign manufacturing processes, but need to be stored cheaply for the whole year. Because all the substrates contain organic matter and most are wet or moist, there is a high risk of microbial decay. This not only causes substrate loss, but can lead to strong odour emissions, and the toxins and spores formed can pose a risk to workers. To cope with this variety of input materials and the problems associated with them, different storage and stabilisation options have been developed. Ensiling is by far the most common storage strategy for agricultural raw materials, and is described in the next section.

Processing is an issue because substrates can be in many forms, from liquids and pastes to slurries and solids, with fibrous or granular particles. Viscous or fibrous materials are particularly hard to move and mix. In addition, the lignocellulosic complexes present in the fibres of many biogas substrates are recalcitrant to degradation. Different pre-treatment technologies have been developed in recent years to make lignocellulosic materials more available for degradation and to improve the viscosity and flow behaviour of substrates. The motivation behind these developments was to increase gas yield, enhance process stability and speed up the degradation rate. Pre-treatment technologies can be divided into physical, biochemical and chemical principles, but combinations of these are also used. This chapter gives an overview of the ensiling process and pre-treatment technologies for input substrates for biogas plants.

4.2   Storage and ensiling of crops for biogas production

Silage making, or ensiling, is not usually referred to as a pre-treatment step, but can be considered as one because it changes the properties of the substrate and adds a unit operation to the process. Ensiling is the preservation of crops, typically whole-crop cereals, grasses and legumes, by fermentation with lactic acid bacteria (LAB). The product, silage, is primarily used as a feed for ruminant livestock during winter months and also as a year-round feedstock for anaerobic digestion. This is particularly important because energy demands are higher in the winter when there is a lack of fresh crops (Seppälä *et al.*, 2008).

4.2.1 Mechanism

A variety of microorganisms are present on harvested crops, including some that can be harmful such as clostridia, coliforms and mycotoxin-producing fungi. These can grow on inappropriately stored crops and cause loss of substrate as well as disease in livestock and farm workers. LAB are also present on harvested crops and produce acids (mainly lactic acid) from sugars available in the plants. In contrast to hay production, in which the growth of all microorganisms is prevented by removing water, ensiling aims to promote the growth of these LAB and inhibit the growth of harmful microorganisms. This is done by storing the moist crops in a closed airtight system, where the oxygen is quickly used up by the plant's respiratory enzymes. The resulting absence of oxygen inhibits the growth of aerobic microorganisms including aerobic fungi. LAB are very tolerant to low water conditions so, by using a relatively dry crop, such as maize or wilted grass, or by using additives, LAB can grow faster than other, undesirable anaerobic bacteria. The acids produced by LAB cause a drop in pH and most undesirable microbial growth is inhibited (Wilkinson, 2005; McDonald *et al.*, 1991).

4.2.2 Production

A range of equipment can be used for producing silage, from expensive and very effective to cheaper and less reliable. Concrete tower silos are a more expensive option, but the vessel can be well sealed from oxygen (McDonald *et al.*, 1991). Walled bunker silos are less expensive but also a good option for keeping oxygen out. Considerably cheaper options include holes in the ground and silage heaps, which can be sealed with sand, biogas digestate or polyethylene sheets weighed down with, for example, rubber tyres. A large proportion (probably 25%) of silage in Europe is made using big bales, facilitated by the introduction of baler–wrapper machines (Wilkinson, 2005). Baled silage is particularly good for grasses and legume crops due to the method of harvest and the shape and structure of the harvested crop.

The three most important crop parameters in ensiling are: dry matter (DM) content, the amount of fermentable sugar available (water-soluble carbohydrate, WSC) and buffering capacity (Wilkinson, 2005). The right DM content is essential, as water is necessary for the growth of LAB, but too much moisture allows the growth of undesirable bacteria before the LAB have reduced the pH. Maize has a high DM content, which makes it particularly easy to ensile. Although grass has a lower DM content, it is also commonly ensiled. The ensiling of grass can be aided by cutting the grass on a dry day and leaving on the field after cutting, allowing water to evaporate from the plant and thereby increasing the DM content. This is known as

wilting and is typically carried out for one or two days. Wilting for more than 48 hours, however, can lead to WSC losses and mould development. Field wilting is not always possible owing to weather conditions, but ensiling of unwilted wet crops can be carried out by an experienced worker or improved by using additives such as acids to bring about a more rapid pH drop, starter cultures to give the LAB a head start or preservatives such as nitrite to inhibit unwanted microorganisms (Wilkinson, 2005; McDonald *et al*., 1991).

Sugar concentration is also essential, as the production of acids during fermentation is dependent on sugar. The major WSCs of grasses are glucose, fructose, sucrose and fructans, and a WSC concentration below 30 g per kilogramme of fresh crop weight results in poor fermentation (Wilkinson, 2005). For whole-crop maize silage, WSC is not an issue as sugar is released from the corn grains, but in some grass species the WSC concentration can be very low, particularly when cut late in the season. The concentration of WSC is higher when grass is harvested in the afternoon (Nizami *et al*., 2009). Wilting (for less than 48 hours) can be used to increase the sugar concentration as it removes water by evaporation. More carbohydrate is available in the plant material, but as cellulose, hemicelluloses and pectin, which cannot be used by LAB. Sugar may be released from these structural carbohydrates by using hydrolytic enzyme additives. An alternative commonly used additive for crops with low WSC is molasses (Wilkinson, 2005; McDonald *et al*., 1991).

The buffering capacity of plants is also important and is affected by the number of weak acid salts such as citrate present in the plant material, which can recombine with the H^+ formed by the fermentation. This varies between crop types, but is often lower in mature crops. The presence of ammonia in the plant also has a buffering effect, as ammonia mops up the H^+ ions to form ammonium. Ammonia concentration in the plant is related to the use of fertiliser and can be reduced if fertiliser is applied early in the season and there is a long wait before harvest. Acid additives can be used to help ensiling of crops with high buffering capacities (Wilkinson, 2005).

4.2.3 Relevance for biogas production

Many different crops can be ensiled, but the most relevant for biogas production are whole-crop maize and grass, which make up 48% and 4% respectively of the fresh weight of biomass used for anaerobic digesters in Germany, the biggest biogas producer in Europe. In addition, over 90% of biogas plants in Germany use maize silage to some extent and over 35% use grass silage (Gemmeke *et al*., 2009). Grass silage is expected to be of increasing importance for biogas production in Europe owing to the abundance of grasslands and the controversy of using arable land for energy

rather than food crops (Murphy and Power, 2009). What is referred to as grass is typically a mix of grass varieties and clover from grasslands. Other ensiled crops relevant for biogas production include other cereals such as sorghum and barley, as well as sugar beet tops, although a much wider range of materials can be stored in this way and used for biogas production, for example hemp (Pakarinen *et al.*, 2011), pineapple processing waste (Rani and Nand, 2004), mango peel (Madhukara *et al.*, 1993) and green pea shells (Madhukara *et al.*, 1997).

There have been several studies evaluating ensiling as a storage method for biogas substrates, particularly grass. These show that well-preserved silage has a relatively constant methane yield, even after months of storage (e.g. grass (Pakarinen *et al.*, 2008; Seppälä *et al.*, 2008) and cereals (Herrmann *et al.*, 2011)). Ensiling of maize or hemp has been shown to increase the available sugars and the amount of biogas produced (Pakarinen *et al.*, 2011; Amon *et al.*, 2007), and this is particularly true when acid was used as an additive (Pakarinen *et al.*, 2011). This is presumably because acid addition means fewer WSCs are used up by LAB and because the acidic conditions break down hemicelluloses. It also has been shown that some biological additives increase methane yield in maize silage (Vervaeren *et al.*, 2010), but also that some have no significant effect on methane yield from grass silage (Pakarinen *et al.*, 2008).

4.3   Pre-treatment technologies for biogas production

Anaerobic digestion is a well-established process for energy production. The fermentation takes place in four steps associated with different microbial populations: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The time needed for the degradation of biomass to biogas, or macro-molecules to mainly methane and carbon dioxide, varies depending on the nature of the chemical bonding of the carbohydrate in the biomass (Noike *et al.*, 1985). The microorganisms in anaerobic digestion convert simple molecules, including sugars such as glucose, into biogas (see Chapter 5 for a more detailed description). Starch and cellulose are both chains of glucose units, but while starch is used by the plants as an energy store and is therefore easy to break down, cellulose is used to maintain the structure of the plant and is, by necessity, difficult to break down. The breakdown of cellulose is further complicated by the bonds between different cellulose chains, and between cellulose and hemicelluloses and lignin (see Figure 4.1). Converting this lignocellulose complex to sugar is the key to biofuel production, whether that is biogas or bioethanol.

Different pre-treatment technologies have been developed in recent years to increase the availability of carbon, particularly in lignocellulolytic material, for anaerobic digestion. Many of these technologies come from the
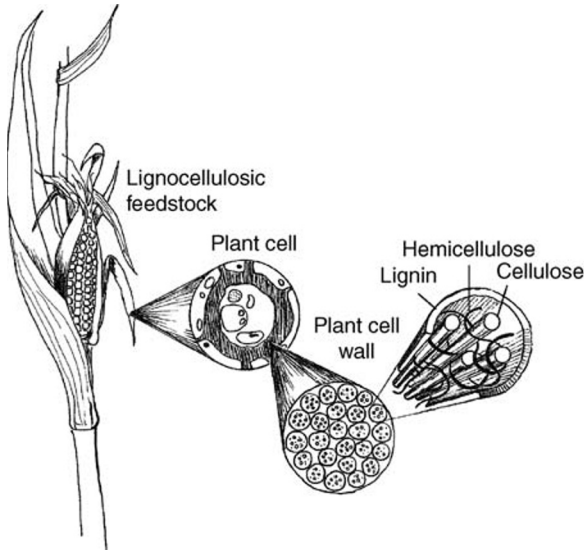
4.1   Lignocellulose complex in plant cell walls (courtesy of Lydia Rachbauer).

wastewater or bioethanol industries. There are a huge number of pre-treatment technologies and it is often difficult to assess which ones are worthwhile. Claims by manufacturers about the abilities of their technologies must be viewed with caution, as they often neglect to mention the disadvantages. Research carried out on behalf of these companies may also be misleading. Even other research is not always neutral, as every researcher has a specialist area and a preferred technology. It is difficult to draw a conclusion from the vast amount of studies published using different pre-treatment methods on different substrates. This is partly because costs are rarely considered in research papers. In addition, technologies that look promising at small scale in batch fermentation may not be effective at large scale in continuous fermentation. Different technologies and the positive and negative aspects of the technologies are now discussed.

4.3.1   Physical pre-treatment

Mechanical pre-treatment

Mechanical pre-treatment is a simple form of pre-treatment aimed at increasing the specific surface area and availability of biomass. In addition to increasing biogas yield, particle size reduction also has an effect on the viscosity in digesters and reduces the formation of floating layers that cause

problems in biogas reactors because they block outlets, are unavailable for digestion and interfere with gas escape (Kamarad *et al.*, 2010).

Different kinds of mills have been tested in the past, mainly hammer mills (crushing) and knife mills (chopping). Mechanical pre-treatment is one of the most expensive steps in biomass conversion because, although increasing specific surface area increases the biogas yield, electrical energy demand is very high. A particle size of 1–2 mm is recommended for effective hydrolysis (Kratky and Jirout, 2011). Another disadvantage is that mills can be damaged by stones and other hard materials, and equipment repairs can be very expensive.

Several researchers have investigated the effect of knife milling on biogas production. Menind and Novak (2010) found an approximately 10% higher gas yield was achieved after milling hay to 0.5 mm compared to 20–30 mm. Another study showed milling sisal fibres from 100 mm to 2 mm achieved an approximately 20 to 25% higher gas yield (Mshandete *et al.*, 2006). Reduction of particle size of wheat straw by knife mills from 12.5 to 1.6 mm requires 2.8–7.55 kWh/t[1] (Kratky and Jirout, 2011). To put this into context, the parasitic electrical demand of a continuously stirred tank reactor (CSTR) digesting slurries is around 10 kWh/t[1] (Murphy and McCarthy, 2005), and is much higher for other substrates. More research is required to say whether or not the electricity input for milling is justified by the electricity saved by improved mixing. Knife and hammer mills are generally used for dry biomass with a moisture content of up to 15% (Kratky and Jirout, 2011; Taherzadeh and Karimi, 2008). Hammer mills are relatively cheap and easy to operate, but have a slightly higher energy input in comparison to knife mills (Kratky and Jirout, 2011).

Thermal pre-treatment

During thermal pre-treatment, also called liquid hot-water (LHW) pre-treatment, the substrate is heated up under pressure to a maximum of 220°C, held for a specific time, cooled down and used in biogas plants. Substrates with low water content need additional water before thermal treatment. The presence of heat and water causes swelling of biomass by disrupting the hydrogen bonds that hold together crystalline cellulose and the structural complexes. Hemicellulose is also broken down during LHW, which aids swelling (Garrote *et al.*, 1999).

One example of thermal pre-treatment technology at large scale is so-called TDH (thermal hydrolysis, from the German 'Thermo-Druck-Hydrolyse'). First, the substrate in the reactor is put under pressure of 20–30 bar. Using a heat exchanger, input material is heated to 140–180°C while the hydrolysed substrate is cooled down. Oil is heated using the exhaust gas stream and heats the substrate to hydrolysis temperature of 170–220°C. The

4.2 Large-scale TDH unit (source: R. Scheuchel GmbH, Ortenburg, Germany).

retention time is 20 minutes. The hydrolysed substrate is cooled down to almost process temperature using the heat exchanger. Finally, the pressure is released (Dinglreiter, 2007). Figure 4.2 shows such a unit.

Various studies have shown that thermal pre-treatment increases biogas yield only up to a certain temperature, and gas production decreases below this temperature. DiStefano and Ambulkar (2006) note the maximum temperature as 175°C for sewage sludge. Using TDH to pre-treat crops, the maximum temperature is 220°C (Dinglreiter, 2007). Thermal pre-treatment of brewers' spent grains shows a lower gas yield with pre-treatment above 160°C as compared with untreated substrate (Bochmann *et al.*, 2010). The maximum temperature depends on the composition of the substrate and also on the retention time of pre-treatment.

Ultrasonic treatment

Ultrasonic treatment is less suitable as a pre-treatment technology than for post-treatment of the liquid effluent from anaerobic digesters. The frequency of ultrasound is over 20 kHz; using these frequencies causes cavities or liquid-free bubbles to form and then implode, producing shockwaves in a process called cavitation. These forces cause the disruption of microbial cell walls in the liquid. In general, this technology is used for the treatment of sewage sludge from wastewater treatment plants, but the effect on biogas production from this ultrasonicated substrate is very low. Ultrasonic treatment only disintegrates microbiological biomass and not the input material (Onyeche *et al.*, 2002).
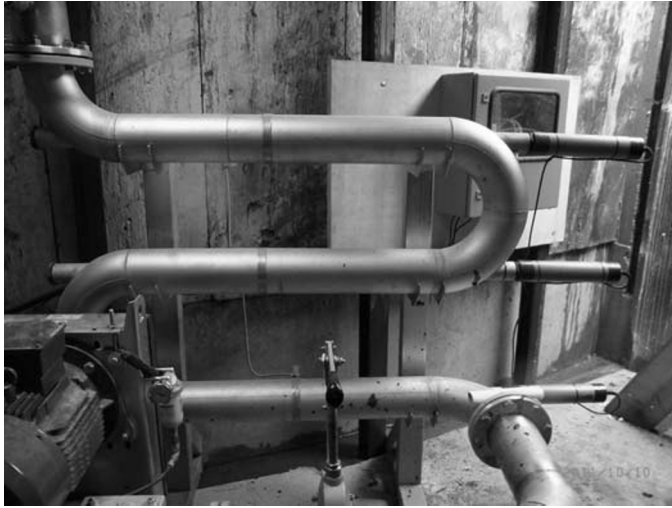
4.3 Electrokinetic disintegration unit (source: ATRES, Munich, Germany).

Electrokinetic disintegration

Electric fields are used for a variety of processes in modern biotechnology. Electrokinetic disintegration is mainly used for sewage sludge treatment. The main inhibiting factor for good anaerobic digestion of sewage sludge is the presence of flocs and aggregates, which are formed by negatively charged molecules on microbial extracellular polymeric substances forming ionic bonds with cations (Tyagi and Lo, 2011; Higgins and Novak, 1997). The application of an electrical field to sewage sludge disrupts these ionic bonds and thus breaks apart the flocs (Tyagi and Lo, 2011). It is also likely electric fields disrupt microbial cells by changing the charge of the cell membranes. It is not clear what effect, if any, this treatment has on lignocellulosic material. Some German companies produce electrokinetic disintegration devices in which the sludge is fed through a section of pipe with an electrode inside applying a voltage of typically around 30 kV (range 10–100 kV) (Hugo Vogelsang Maschinenbau GmbH, 2011; Süd chemie AG, 2011). Figure 4.3 shows such a unit. An increased biogas yield from sewage sludge of around 20% has been claimed (Süd chemie AG, 2011). It has also been claimed that the device can increase biogas production from agricultural residues (Hugo Vogelsang Maschinenbau GmbH, 2011), but a study by the Bavarian State Research Center for Agriculture, LfL, showed no significant increase in biogas production from agricultural residues (Lehner *et al.*, 2009). Like ultrasonication, electrokinetic disintegration may be better suited to post-treatment of the liquid effluent from anaerobic digesters or pre-treatment of substrates similar to sewage sludge.

4.3.2 Chemical pre-treatment

Chemical pre-treatment has been investigated using a range of different chemicals, mainly acids and bases of different strengths under different conditions. The use of temperature and chemicals together (thermochemical pre-treatment) is described in a later section.

Alkali treatment

As mentioned previously in this chapter, lignocellulosic materials are resistant to hydrolysis due to their structure and composition. Alkali pre-treatment removes the acetate groups from hemicellulose, which makes the hemicelluloses more accessible to hydrolytic enzymes. This enhances digestability. Alkali addition also causes swelling of lignocelluloses, although this is a secondary effect (Kong *et al*., 1992). Lignin is also partly solubilised by alkali pre-treatment, and this allows more access to cellulose and hemicellulose. Alkali treatment can be carried out with different concentrations of lime, sodium hydroxide (NaOH) and potassium hydroxide (KOH).

There have been several reports of alkali treatment being effective for solid-state anaerobic digestion. He *et al*. (2008) showed an increase in biogas yield from rice straw of 27.3–64.5% using 6% NaOH for 3 weeks at ambient temperature. Liew *et al*. (2011) carried out simultaneous pre-treatment and methanisation using 3.5% NaOH on fallen leaves and showed that with an optimised substrate to inoculum ratio, the methane yield increased by 21.5%. Interestingly, when a sub-optimal substrate to inoculum ratio with too much substrate was used, the control tests produced extremely low levels of biogas, but the alkaline pre-treated tests increased methane yields 22-fold. These studies demonstrated that alkali pre-treatment can increase gas yield from hemicellulose-rich substrates and dissolve lignin complexes. However, it is important to note that alkali pre-treated substrates have high pH values. The above-mentioned experiments were carried out using small-scale batch tests but, during continuous fermentation, alkali pre-treatment leads to increased pH and salt build-up. The pH increase affects the ammonium–ammonia balance and inhibits methanisation, and high concentrations of cations like Ca^{2+}, K^+ or Na^+ lead to an inhibition of anaerobic digestion due to osmotic pressure (Chen *et al*., 2008). However, the pH increase may be beneficial for substrates with low pH or high lipid content (e.g. as demonstrated by Beccari *et al*. (2001) with olive oil mill effluent and $Ca(OH)_2$). This pre-treatment technology was deemed economically unattractive due to the high costs of bases (Chang *et al*., 1997).

4.3.3 Biological pre-treatment

Microbiological pre-treatment

Microbial pre-treatment, also known as pre-acidification or multi-stage fermentation, is a simple kind of pre-treatment technology in which the first steps of anaerobic digestion (hydrolysis and acidogenesis) are separated from acetogenesis and methanogenesis. A two-stage digestion system is common for carrying out this kind of pre-treatment. The concept of carrying out digestion in separate vessels is similar to the multiple chambers of ruminant digestive systems. The pH value of the first digester (the pre-acidification step) should lie between 4 and 6, thereby inhibiting methane production (Deublein and Steinhauser, 2008; Thauer, 1998). This inhibition causes volatile fatty acids (VFAs) to accumulate. The gas produced during this pre-acidification step has high concentrations of carbon dioxide and hydrogen. The production of H_2 goes hand in hand with the production of fatty acids and is an important indicator to evaluate the pre-acidification step. The extent of H_2 production is most strongly influenced by pH: H_2 production at pH 6 is initially high and then stops and at pH 4 is lower but prolonged and greater overall (Liu *et al.*, 2006). Antonopoulou *et al.* (2008) demonstrated in continuous fermentation tests that H_2 concentration was 35–40% v/v of the total gas amount of the pre-acidification step.

Microbiological pre-treatment has a very positive effect on the degradation rate of substrates in anaerobic digestion. In general, cellulose, hemicellulose and starch-degrading enzymes work best between pH 4 and 6 at temperatures from 30 to 50°C, so this pre-acidification step increases the degradation rate by creating an optimal environment for hydrolytic enzymes, particularly for carbohydrate degradation. Liu *et al.* (2006) achieved an additional biogas yield of 21% at a hydraulic retention time of approximately 30 days. This was caused by higher degradation through increased hydrolytic enzyme activity.

Another positive effect of this pre-treatment method is on the methane concentration in the biogas. In addition to H_2 and VFA production, CO_2 is formed during the pre-acidification step. CO_2 can be present in three forms: at higher pH values in the form of the carbonate ion CO_3^{2-}; at neutral pH as HCO^{3-}; and in acidic environments as CO_2. Due to the low pH, most of the carbonate is in the form of CO_2, which is volatile and is released into the hydrolysis gas produced from the pre-acidification step. This means that for the methanogenesis step, a higher CH_4 concentration is present in the gas phase. Nizami *et al.* (2012) produced a biogas with 71% methane content in a two-phase system digesting grass silage. The same grass silage produced a biogas with 52% methane content in a wet single-stage system.

In large-scale biogas plants, pre-acidification systems are offered by

several plant constructers, varying from continuous to batch pre-acidifica-tion systems. Continuous pre-acidification is offered, for example, by the companies AAT and Enbasys from Austria. Substrates are fed continuously in a two-reactor CSTR system. The daily removal of material to feed the second reactor is balanced by a feed of fresh material to the first reactor. Plug-flow reactors are also in use. This technology guarantees the treatment of the requested retention time, which is not given in the CSTR system. Batch pre-acidification digesters are completely emptied after a retention time of a few days and refilled with new substrates.

Enzyme addition

The purpose of enzyme addition is to break down polymers in the substrate, particularly lignocelluloses. A cocktail of enzymes is typically used, and may include cellulases, xylanases, pectinases and amylases. Enzymes can be applied in three different ways: by direct addition to the vessel of a single-stage anaerobic digestion; by addition to the hydrolysis and acidification vessel (first stage) of a two-stage system (see the previous section on microbiological pre-treatment); or by addition to a dedicated enzymatic pre-treatment vessel. The addition of enzymes to anaerobic digestion has been analysed in different studies. Romano *et al.* (2009) analysed the effect of enzyme addition on anaerobic digestion of a type of pasture grass, wheat grass. The enzyme addition showed a positive impact on solubilisation of the substrate. In this study, no additional gas yield was measured, but a slightly faster degradation rate was found in a single-stage system. In a different study, an additional gas yield was achieved using two-stage digestion of brewers' spent grains with enzyme addition in the acidification stage (Bochmann *et al.*, 2007). Higher VFA production was also achieved through enzyme addition. Ellenrieder *et al.* (2010) analysed the addition of single enzymes like cellulose, amylase or pectinase to maize and grass silage, but no additional benefit on gas yield was determined.

4.3.4   Combined processes

Steam explosion

The principle of steam explosion is related to thermal pre-treatment. The substrate is heated in a closed system to a temperature of 160 to 220°C, causing a rise in pressure. After a process specific retention time (between 5 and 60 minutes), pressure is released abruptly. This sudden drop in pressure causes intracellular water to evaporate. Cell walls are disrupted, causing substrates to lose their structure. Due to the long retention time and high temperatures, the Maillard reaction occurs and Maillard products are

Table 4.1   Biogas yield of steam-exploded substrates compared with untreated substrates

| | Biogas yield (m^3 CH$_4$/t fresh matter) | | | |
	Slaughterhouse residues	Maize silage	Straw	Reeds
Before treatment	450	200	280	210
After treatment	500	250	400	350

Source: Coramexport (2011).

formed. These products can inhibit anaerobic digestion. Many studies in the field of ethanol production have shown high furfural and hydroxymethyl-furfural (HMF) production as a result of long retention times and high temperature. Benjamin *et al*. (1984) and Bochmann *et al*. (2011) demonstrated that these products have a negative impact on anaerobic digestion. Another negative aspect is that the recovery of heat from this pre-treatment is impossible. However, using steam explosion allows substrates such as hay or straw to be used for biogas production. Bauer *et al*. (2009) analysed steam explosion tests of straw and showed calculations of ethanol and biogas potentials. Table 4.1 shows gas yields with and without steam explosion.

Extrusion

Extrusion is a process adapted from other industries such as metal and plastic processing industries. In these industries, material is fed into an extruder and conveyed by screw along a tube, where it is exposed to high pressure, temperature and shear forces. The material is subsequently pushed out of a hole of specific shape to form the final product, which could be a pipe or a sheet. Biogas substrates in extruders are subjected to the same forces, causing tough fibres to break and the plant cells to lyse. In addition, as the substrate leaves the extruder, the sudden drop in pressure causes evaporation of intracellular water, as in steam explosion .

Extrusion tests for biogas substrates typically use twin-screw extruders where the screws rotate counter wise. Extruders are available at ratings from 11 kW to a 55 kW; substrate output is in the range 0.9 to 4.0 t/hour respectively. Depending on the consistency required at the end, the substrate can be placed under a pressure of up to 300 bar at temperatures from 60 to 300°C. For biomass with a total solid content of 30 to 35%, the temperature should not exceed 100°C due to water evaporation and substrate drying.

Extrusion increases the specific surface area of biomass, which allows easier access by hydrolytic enzymes to the chemical bonds. The increasing availability of the biomass results in faster methane production. This facilitates higher organic loading rates in the reactors.

Many biomethane potential (BMP) tests (see Chapter 3) have been carried out with extruded biomass, and additional methane production was found for most of the treated substrates. Hjorth *et al.* (2011) analysed the effect of the extrusion process on anaerobic degradation of straw, unensiled grass, the solid fraction of manure from a screw press, the solid fraction of manure after flocculation and deep litter from cattle. After 28 days of BMP tests, the extruded straw showed up to 70% more methane production than the untreated straw and after 90 days of BMP tests, the methane yield of extruded straw was 11% higher than that of the untreated. This shows that biogas production from straw was faster when extrusion was used to pre-treat it, but the data had a very high standard deviation so the additional benefit may be smaller than presented. For the extrusion process, approximately 10–15 kW per tonne of substrate is needed; this is a similar value to the parasitic electrical demand of a CSTR digesting slurry (Murphy and McCarthy, 2005).

A major problem with extrusion pre-treatment technology is the screws, which have to be changed after a few months due to abrasion. As with other mechanical pre-treatment technologies, stones or metallic materials in the substrates severely reduce the lifetime of the screws. This has a negative impact on the economics of the extrusion process.

Thermo-chemical pre-treatment

During thermo-chemical pre-treatment, the effects of thermal and chemical influence are combined. Different kinds of bases and acids can be used, but ammonia (e.g. the AFEX process) or different kinds of solvents (e.g. the organosolv process) are also used. Temperatures from 60 to 220°C have been studied. Pre-treatment temperatures of more than 160–200°C showed a drop in methane production, depending on the input material (DiStefano and Ambulkar, 2006; Delgénes *et al.*, 2000; Penaud *et al.*, 1999).

The thermal influence during alkali pre-treatment of waste activated sludge leads to a higher chemical oxygen demand (COD) solubilisation (100%) and a higher gas yield (20%) when compared with alkali pre-treatment (Kim *et al.*, 2003). Inhibition effects of alkali addition are similar to alkali pre-treatment without thermal influence.

Zhang *et al.* (2011) analysed the thermal pre-treatment of cassava with acid addition. Sulphuric acid was used in concentrations of 1.32–4.68% (w/w) and the temperature was 150–170°C. The reaction time was 10–36 minutes. A 57% higher gas yield was found for pre-treated cassava compared with untreated. The pre-treatment parameters that obtained the maximum gas yield were 160°C, 3% H_2SO_4 and 20 minutes retention time (Zhang *et al.*, 2011).

The influence of thermal, chemical and thermo-chemical pre-treatment on

dewatered pig manure was analysed by Rafique *et al.* (2010). High concentrations of lime (5%) showed maximum enhancement of gas yield at 70°C. An increase of 78% biogas and 60% methane was observed.

4.4   Conclusion and future trends

A wide range of technologies are available for the pre-treatment of biogas substrates, based on a variety of principles. When substrate composition and pre-treatment technology are appropriately matched, the bioavailability of the substrate increases. This can lead to an improved performance of biogas reactors in terms of gas yield and degradation rate during anaerobic digestion. The energy balance and costs must be considered. The energy demand of pre-treatment depends on the technology used. In most cases, pre-treatment methods with a low energy demand give smaller benefits to the rate of degradation and corresponding biogas yield as compared with pre-treatments with high energy input, but this is not always the case. Higher gas yields result from the degradation of lignocellulose complexes and increase in availability of recalcitrant substances. Many pre-treatment technologies do not increase the biogas yield, but increase the degradation rate. The energy demand of pre-treatment technology is important for a number of reasons, including sustainability criteria as required by the EU Renewable Energy Directive. A negative energy balance can also lead to an uneconomical process. As high investment costs are needed in many cases, a corresponding significant increase in gas yield is necessary to make the process financially feasible.

Many principles of pre-treatment technology were and are developed for other purposes, such as ethanol production from lignocellulosic feedstocks. The influence of pre-treatment technologies on anaerobic digestion has been investigated in recent years and there is still a huge demand for optimisation of these technologies for the biogas industry. Ongoing research is especially important to bring some technologies to a financially feasible level. The investment costs for pre-treatment of recalcitrant substrates are high at the moment due to high expenditure in process engineering. However, if these costs are decreased to an affordable level, new substrates will be made available for biogas production. In closing, it should be mentioned that pre-treating all substrates with one technology is not realistic and pre-treatment may not be financially viable or improve the energy balance for substrates with high degradation rates.

4.5   References

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