1. ABSTRACT

Energy recovery from waste is one of the most important techniques suitable for the necessities of the future and, if the process is made with the aim of biogas production, it generates clean energy, fertilizers as secondary products and a huge variety of compounds usable in industrial scale. This approach follows the circular economy rules with the aim of reducing waste and pollution, therefore its implementation is necessary for the transition to a more sustainable society.

In this work are explained the general details of biogas, especially regarding to its composition and the differents steps of the anaerobic digestion (AD).

In this sense, the goal is to optimize all the different ways of the biochemical process with the purpose to allow the best technological transfer in an industrial plant.

Moreover, a special focus is adopted in order to describe the various purification techniques and the methods that can be used to enhance biogas production, ensuring the maximum yields in terms of methane and the minimum management costs of the entire system.

2. INTRODUCTION

Biogas typically refers to a mixture of different gases produced by the biological decomposition of organic matter in the absence of oxygen. It is basically composed by methane and carbon dioxide, and it may have small amounts of hydrogen sulfide, nitrogen and siloxanes.

Biogas can be obtained from biomass (for definition see DIRECTIVE 2009/28/EC, article 2) eg. products, waste and residues from agriculture, or municipal waste.

Biogas is a renewable energy source since its production does not generate additional carbon dioxide. The amount of carbon dioxide released when the primary bio-resource is converted to energy, is the same as the amount absorbed from the atmosphere in the growth of the bio-resource itself [1],[2].

Furthermore, it can be produced by anaerobic digestion (AD) with anaerobic organisms in a closed system.

Anaerobic digestion (AD) offers significant advantages compared to many other waste treatment processes; it recovers a relevant amount of energy and CO_2 from the biomass, furthermore, it produces residual solid and liquid streams that provide mineral nutrients for agriculture as well as valuable organic material for further biorefinery processing. In addition, AD is performed by a microbial consortium, which has the ability to self acclimate to the inherent variability of the feedstock composition. Obviously, the performance of the AD process can be affected by several factors, such as the technical characteristics of the plant and of its management, the feedstock characteristics and the activity of the microorganisms involved in the different degradation steps.

The conversion of organic matters into biogas involves four different processes: hydrolysis, acid formation, acetogenesis and methane production.

In these different stages which are however carried out in parallel, different groups of bacteria collaborate by forming an anaerobic food chain where the products of one group will be the substrates for another.

Furthermore, the biogas can be cleaned and upgraded to natural gas standards, when it becomes bio-methane.

3. BIOGAS PRODUCTION: A BIOCHEMICAL PROCESS

As mentioned before, the production of biogas through AD offers major advantages over other forms of bioenergy production. In fact, it has been defined as one of the most energy-efficient and environmentally beneficial technology for bioenergy production. Beside that, the degradation of organic waste allows the reduction of odour release and the decrease of pathogens level, while the nutrient rich digested residue can be used as organic fertilizer for land, as an alternative for mineral fertilizers.

Methane fermentation is a complex process, which can be divided into four phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis. In each individual phase, different groups of anaerobic microorganisms are involved. Hydrolyzing and fermenting microorganisms are responsible for the initial attack on polymers and monomers and produce mainly acetate and hydrogen and varying amounts of volatile fatty acids (VFA) such as propionate and butyrate.

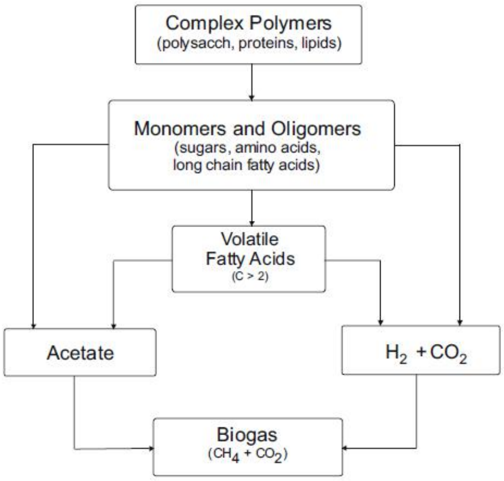


Figure 1
The stages of the methane fermentation process.

Volatile fatty acids are converted into acetate and hydrogen by hydrogen-producing acetogenic bacteria. Although acetogenic bacteria are not well characterized, it has been shown that their metabolism can be inhibited by hydrogen accumulation.

For this reason, it is essential to maintain an extremely low partial pressure of hydrogen but, on the other hand, it has been suggested that hydrogen may be a limiting substrate for methanogens, since it has been observed that the addition of H_2-producing bacteria to the natural biogas producing consortium, increases the biogas production. At the end of the degradation chain, different groups of metanogenic bacteria are involved in the methane production from acetate and from hydrogen and carbon dioxide. In this kind of process, it has to be considered that undissolved compounds like cellulose, proteins, or fats are decomposed slowly into monomers within several days, whereas the hydrolysis of soluble carbohydrates takes place within few hours. This means that the process must be carefully designed and well adapted to the substrates properties in order to achieve a complete degradation. The digestion process takes place at mesophilic (35 - 42 °C) or thermophilic (45 - 60 °C) temperature conditions. It is important to control the temperature during the digestion process, since temperature changes or fluctuations may negatively affects the biogas production. Thermophilic processes are more sensitive to fluctuations and they require longer time to adapt to new temperature. Mesophilic bacteria, instead, tolerate temperature fluctuations of +/−3 °C without significant reductions in methane production. The growth rate of methanogenic bacteria, however, is higher at thermophilic process temperatures, making the digestion process faster and more efficient. On the other hand, at this temperature conditions, the protein degradation occurs, increasing the ammonia amount. Especially the undissociated form of ammonia is considered to be responsible for process inhibition when its concentration is higher then 80 mg/l. When the process is inhibited by ammonia, an increase in the concentration of volatile fatty acids (VFA) will lead to a decrease in pH which will partly counteract the effect of ammonia.

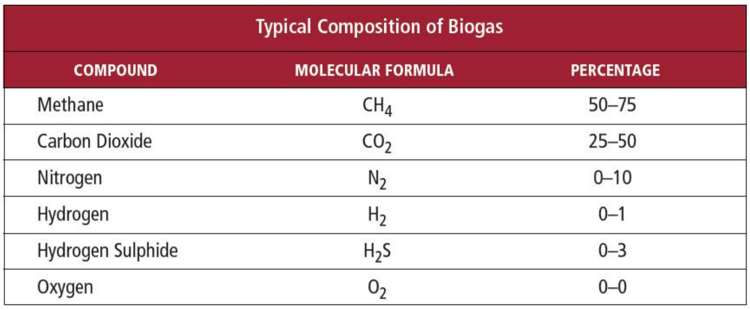
Methane formation takes place within a relatively narrow pH interval, from about 6.5 to 8.5 with an optimum interval between 7.0 and 8.0. The process is severely inhibited if the pH decreases below 6.0 or rises above 8.5.

For the growth and survival of the specific groups of microorganisms, several macronutrients (carbon, phosphor, nitrogen, and sulfur) and micronutrients are necessary. The need of nutrients is very low, so that a ratio of C:N:P:S = 600:15:5:1 is sufficient. As well, trace of elements like nickel, cobalt, selenium, molybdenum, and tungsten are sufficient for the growth rate of microorganisms. The function of selenium, molybdenum and tungsten is not completely clear and their concentrations are very low (ranging between 0.05 and 0.06 mg/l). Iron, on the other hand, has to be added in higher concentration (between 1 and 10 mg/l) [3],[4].

4. BIOGAS COMPOSITION AND PURIFICATION TECHNIQUES

The composition of biogas depends on the substrate composition, as well as the conditions within the anaerobic reactor (temperature, pH, and substrate concentration).

The most relevant compounds present in the biogas are reported in the table below (Figure 2), in their relative most common percentages.

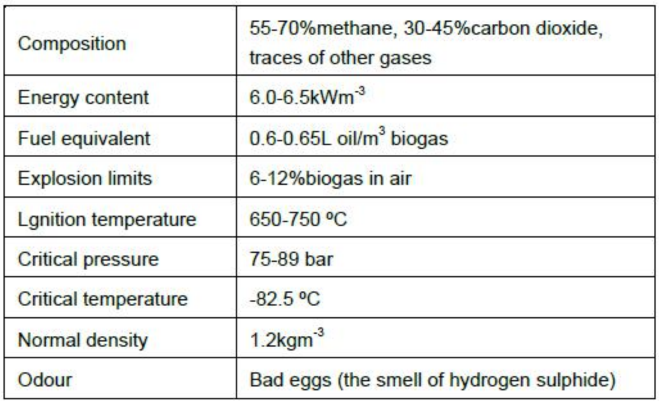


Typical Composition of Biogas

COMPOUND	MOLECULAR FORMULA	PERCENTAGE
Methane	CH_4	50–75
Carbon Dioxide	CO_2	25–50
Nitrogen	N_2	0–10
Hydrogen	H_2	0–1
Hydrogen Sulphide	H_2S	0–3
Oxygen	O_2	0–0

Figure 2
Typical composition of biogas.

Relevant energetic key parameters are also reported in the table below (Figure 3).



Composition	55-70%methane, 30-45%carbon dioxide, traces of other gases
Energy content	6.0-6.5kWm^{-3}
Fuel equivalent	0.6-0.65L oil/m^3 biogas
Explosion limits	6-12%biogas in air
Lgnition temperature	650-750 ºC
Critical pressure	75-89 bar
Critical temperature	-82.5 ºC
Normal density	1.2kgm^{-3}
Odour	Bad eggs (the smell of hydrogen sulphide)

Figure 3
Typical details of biogas.

Different percentages of components in the biogas composition have an impact on its ultimate use. For this reason, it is required an accurate analysis of any components in terms of nature, conditions of production and effects on the biogas properties.

4.1 Hydrogen sulphide [5]

Hydrogen sulphide is a colourless gas, only slightly heavier than air, with the characteristic foul odour of rotten eggs. It is the major contaminant in biogas because is both poisonous and corrosive, causing significant damage to piping, equipment and instrumentation [6].
The concentration of hydrogen sulphide in the gas is a function of the digester feed substrate and of the inorganic sulphate content.
Wastes which are high in proteins containing sulphur-based amino acids (methionine and cysteine) can significantly influence biogas hydrogen sulphide levels.
While boilers can resist at concentrations of this molecule up to 1000 ppm, internal combustion engines operate best when H_2S is maintained below 100 ppm. Hence, the final use of biogas often requires the desulfurization.

4.1.1 Internal biological desulfurization by addition of air

One common method for desulfurizing biogas is the biological oxidation by atmospheric oxygen. To this end, air is injected into the gas space of the fermenter above the surface of the liquid in a quantity of generally 8 to 12% by volume.
As a result of the atmospheric oxygen injection, hydrogen sulfide is oxidized into elemental sulfur by microorganisms that grow on the surfaces in the gas space. This sulfur accumulates on the surfaces and ultimately passes back into the substrate, where it is partly converted into hydrogen sulfide again, while the remainder is removed from the fermenter with the fermentation residue.

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$

The efficiency of this process is limited, however, because the air supply cannot be exactly adapted to the quantity of gas produced. Moreover, one serious limitation of the method is the risk of sulfuric acid formation. Sufluric bacteria, in the presence of atmospheric oxigen, can oxidize the hydrogen sulfide into sulfuric acid, leading to a massive corrosion of all metallic materials [7].

4.1.2 External biological desulfurization

Another possibility for biological desulfurization is the use of desulfurization columns outside the fermenter. This method offers greater operational reliability than internal biological desulfurization, because the air supply can be adjusted more accurately.
For external biological desulfurization to operate optimally, the microorganisms have to be supplied with nutrients and trace elements, and a washing solution temperature of 28 °C to 32 °C has to be maintained. This can lead to problems, especially in winter when the outside temperatures are low. There is moreover a risk of the desulfurization column being congested by the oxidation product sulfur [7].

4.1.3 Iron salts and oxides

In this process, iron salts and oxides (for instance $FeCl_3$, $FeCl_2$, $Fe(OH)_3$, FeO, Fe_2O_3 - except $FeSO_4$, which doesn't lead to any reduction of hydrogen sulphide in the biogas) are added to the fermentation substrate [8],[9]. When it happens, iron salts and oxides directly bind hydrogen sulfide dissolved in the liquind phase of the fermenter, forming slightly soluble iron sulfide (FeS). Eventually it can be removed with the discharged solid fractions.

$Fe^{2+} + S^{2-} \rightarrow FeS\downarrow$
$2\ Fe^{3+} + 3\ S^{2-} \rightarrow 2\ FeS\downarrow + S$

Both divalent and trivalent iron salts are suitable for precipitating sulfides. Addition of ferrous chloride or iron hydroxide have emerged as the two most common processes. Usually, 100 to 220 gIron/tSubstrate are added, althoug it is very much depentent on the substrate nature. This method allows a selective hydrogen sulfide removal with good elimination rates, and it can be integrated in the existing process, without requiring additional desulfurization units. Furthermore, the fermentation substrate can be used as a fertilizer because the iron sulfide contained is rapidy oxidised by atmospheric oxygen, forming soluble sulfate directly available to plant [7].

4.1.4 Fine desulfurization with activated carbon

The upgrading of biogas to biomethane and the protection of catalyst for offgas purification (effluent gas produced by a chemical process), requires that H_2S concentration is very low in the raw gas. This goal can be achieved by fine desulfurization. The most common used method is to use activated carbon filters, where hydrogen sulfide is absorbed on the surface and then catalytically oxidized. The activated carbon is constantly fed with biogas during operation, meaning that its maximum loading capacity is eventually reached, and the activated carbon filter needs to be replaced. Since the loaded activated carbon has to be regenerated in a complex process, in many cases a combination of different kinds of desolfurization techniques is used. It allows to decrease the high operation costs and increase the service life of the carbon filters. Hence, an initial desulfurization with iron salts and oxides is followed by fine desulfurization with activated carbon [7].

4.2 Oxygen

Oxygen is an undesirable part of biogas, since it binds hydrogen and partly even carbon to produce hydroxides, water and oxides. High oxigen concentrations in biogas leads to a decrease of methane production and thus the energy value of biogas. There are several processes used in order to remove oxygen from biogas but the most important are the following.

4.2.1 Catalytic reduction of oxygen with hydrogen

$O_2 + 2H_2 \rightarrow 2H_2O$

The first described option with H_2 as reaction partner obviously suffers from the need of an external hydrogen supply. This process is usually operated in a fixed catalyst bed (with noble metal such as platinum or palladium) which is continuously provided by the gas stream to be treated. Advantages of the process include low equipment costs, low operating temperatures of < 200 °C and simple removal of the water [10],[11].

4.2.2 Catalytic conversion of oxygen with methane as reductant

$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$

The total oxidation of methane as a gas purification step offers some advantages, for instance that methane is available at high concentrations in biogas and the fuel demand of the reaction is comparably low (4 times lower than in the hydrogen case). Moreover, for complete conversion of O_2, reaction temperatures of 250 - 350 °C are required, because of the high stability of methane, with the same catalytic onditions seen before [10],[11],[12].

4.2.3 Absorption on oxygen storage materials

Adsorption methods for the trace oxygen removal from biogas streams are scarcely reported in literature and could be based on copper addition. It is based on the reaction of oxigen with the metal, forming CuO. However, the chemical regeneration of the formed CuO to produce metallic Cu has to be performed by adding hydrogen:

$Cu + \frac{1}{2}O_2 \rightarrow CuO$
$CuO + H_2 \rightarrow Cu + H_2O$

Recently, oygen removal has been obtained using the oxide $YBaCo_4O_7$, which has been extensively investigated thanks to its ability of oxygen absorption and desorption.

$YBaCo_4O_7 + \delta/2O_2 \rightarrow YBaCo_4O_{7+\delta}$

It was found that it reversibly absorbs and desorbs oxygen up to $\delta \approx 1.5$ without changing its basic crystalline structure in a relatively narrow temperature range (between 270 °C and 350 °C). With the catalytic and absorptive processes seen before, it's possible to maintain the amount of oxygen in the gas mixture below 10 ppmv [10],[11].

4.3 <u>Carbon dioxide</u>

Carbon dioxide is a stable component of the carbon cycle in the environment. Carbon dioxide is a colourless, very heavy (ca 1.5 times heavier than air) odourless gas. With its presence in biogas, carbon dioxide decreases the content of other gases, mainly methane, which decreases the heating power of biogas. Existing technologies in order to remove CO_2 from biogas are summarized below with their major strengths and weaknesses.

4.3.1 Water and polyethylene glycol scrubbing

Water scrubbing is used to remove CO_2 and H_2S from biogas since these gases are more soluble in water than methane. The absorption process is purely physical. Usually the biogas is pressurized and fed to the bottom of a column while water is fed on the top. Water scrubbing can also be used for selective removal of H_2S since it's more soluble than carbon dioxide in water. The water which exits in the column with absorbed CO_2 and/or H_2S can be regenerated and re-circulated back to the absorption column. Regeneration is accomplished by de-pressuring in a similar column.
Polyethylene glycol scrubbing relies on the same mechanism as water scrubbing, with a physical absorption process that works because both CO_2 and H_2S are more soluble than methane in the solvent.
The advantages of scrubbing are no special chemicals required (except relatively inexpensive glycol) and removal of both CO_2 and H_2S. The disadvantages of water scrubbing are that it requires a lot of water even with regeneration [13].

4.3.2 Chemical absorption

Chemical solvents generally employ aqueous solutions of amines (i.e. mono-, di- or tri-ethanolamine) or aqueous solution of alkaline salts (i.e. sodium, potassium and calcium hydroxides).
The advantages of chemical absorption are complete H_2S removal, high efficiency and reaction rates compared to water scrubbing, and the ability to operate at low pressure. Because of these advantages, the process is commonly used in industrial applications, including natural gas purification. The disadvantages are the additional chemical inputs needed and the need to treat waste chemicals from the process [13].

4.3.3 Pressure swing adsorption (PSA)

Pressure Swing Adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material, operating at near-ambient temperatures. Special adsorptive materials (zeolites and active carbon) are used as a molecular sieve, preferentially adsorbing the target gas species at high pressure.
The process swing to low pressure to desorb the adsorbent material.
The PSA process relies on the fact that under pressure, gases tend to be attracted to solid surfaces, or "adsorbed". The higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. However, during biogas purification, the adsorption material adsorbs H_2S irreversibly and thus is poisoned by H_2S. For this reason a preliminary H_2S removing step is often included in the PSA process. Activated carbon impregnated with potassium iodide can catalytically react with oxygen and H_2S to form water and sulfur. The reaction is best achieved at 7 to 8 bar and 50 to 70°C.
The advantages of PSA technology are more than 97% CH_4 enrichment, low power demand, and low emission and removal of nitrogen and oxygen. The main disadvantage of PSA technology is an additional H_2S removal step needed before PSA. The process is also relatively more expensive than some others [13].

4.3.4 Membrane

The principle of membrane separation is that some components of the raw gas are transported through a thin membrane while others are retained. The permeability is a direct function of the chemical solubility of the target component in the membrane. Typical operating pressures are in the range of 25-40 bars.
There are two membrane separation techniques: high pressure gas separation and gas-liquid adsorption. The high pressure separation process selectively separates H_2S and CO_2 from CH_4. Usually, this separation is performed in three stages and produces 96% pure CH_4. Gas liquid adsorption is a newly developed process that uses micro-porous hydrophobic membranes as an interface between gas and liquids.
The CO_2 and H_2S dissolve into the liquid while the methane (which remains a gas) is collected for use.
Membrane separation offers different advantages: the process is compact and easy to process, requires low energy and maintenance and membranes are light in weight. On the other hand, membranes are expensive and they allow a low CH_4 yield [13].

4.3.5 Cryogenic separation

Cryogenic separation of biogas is based on the fact that CO_2, H_2S and all other biogas contaminants liquefies at a different temperature-pressure domain. This separation process operates at low temperatures, near -100°C, and at high pressures, almost 40 bars. These operating conditions are maintained by using a linear series of compressors and heat exchangers.
The main advantage of cryogenic separation is the high purity of the upgraded biogas (99% CH_4), as well as the large quantities that can be efficiently processed.
Obviously, the applicability is limited by the considerable equipment required, as compressors, turbines and heat exchangers
Usually, some of the previous purification operations of biogas are integrated in the form of connected reactors, with the aim of creating a continuos cycle.
In the figure below (Figure 4) it is schematized one of the most common industrial plant: two bed reactors are in alternate operation to achieve desulfurization and deoxygenation. They are followed by a CO_2 removal step [13].

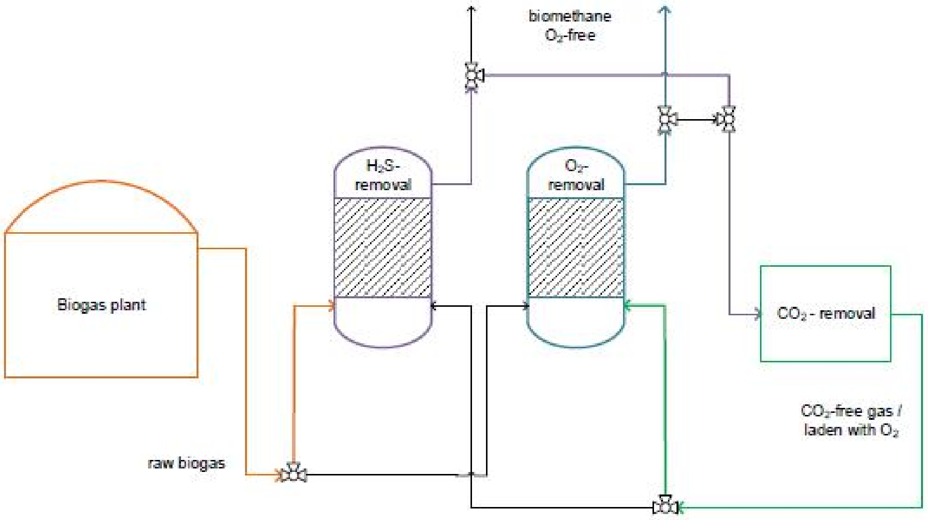


Figure 4 [14] Simultaneous removal of H_2S and O_2 during biogas purification process.

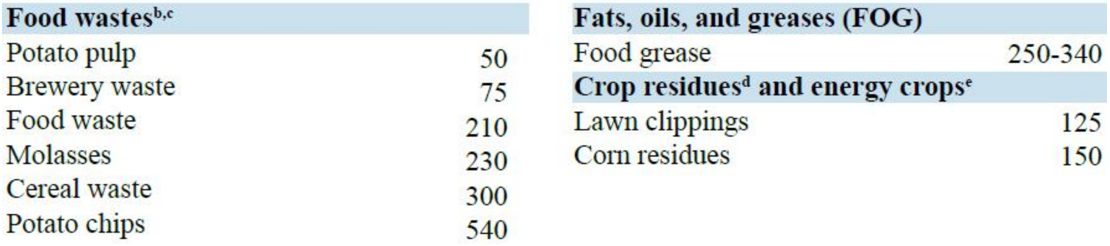
4.4 Methane

The main and most important component of biogas is methane.
The techniques used in order to increase the methane production during the biogas process are presented below.

5. OPTIMIZATION OF METHANE PRODUCTION

5.1 Codigestion

Codigestion refers to the simultaneous anaerobic digestion of multiple organic wastes in one digester and it's used to increase methane production from low-yielding or difficult to digest materials. For the codigestion process, care must be taken to select compatible codigestion feedstocks that enhance methane production (and to avoid materials that may inhibit methane generation). Depending on the source and type of codigestion feedstock, the material size can vary widely but it's important to consider that small particle size lead to an increase of biogas yield because methane-producing bacteria have better contact with the digestible organic matter and any barrier created from the fibrous portions of the feedstock is eliminated.
In the table below (Figure 5) are reported some examples of common raw materials which can be used for biogas process in terms of methane potentials [15].



Food wastes[b,c]	
Potato pulp	50
Brewery waste	75
Food waste	210
Molasses	230
Cereal waste	300
Potato chips	540

Fats, oils, and greases (FOG)	
Food grease	250-340
Crop residues[d] and energy crops[e]	
Lawn clippings	125
Corn residues	150

Figure 5 Methane potentials (m^3 CH$_4$/ton feed) for common feedstocks.

5.2 Ethanol addition

Very recently, it was shown that the addition of acetate or ethanol led to enhanced biogas formation rates during an observation period of 24 h. When in the fermenters were added 50-100 mM ethanol, biomethanation increased by 50-150 %, depending on the composition of the biogas sludge. It was also possible to increase methane formation significantly when 10-20 mM pure ethanol or ethanolic solutions (e.g. beer) are added daily. In summary, the experiments revealed that "normal" methane production continued to take place, but ethanol led to production of an additional amount of it [16].

5.3 Sludge pretreatment

Biogas production can be improved by several pretreatments in order to lyse sludge cells and facilitate hydrolysis. This step is very important with substrates characterized by more complex structures, like lignocellulosic materials, which needs longer period to be degraded, and the degradation is usually not complete.

Lignocellulosic materials mainly consist of three types of polymers: cellulose, hemicellulose and lignin, which are associated each other, creating a physical barrier for hydrolytic enzymes. Furthermore, the cellulose arranges itself in crystalline structures, which are also difficult to degrade. Finally, large particles have a relatively small surface area where the microorganisms can attack the surfaces and break down their structures. Hence, the hydrolysis step is often considered as the rate-limiting step when utilizing these kinds of substrates. Therefore, an initial pretreatment step, which converts raw materials to a form that is more easly accessible to microbial and enzymatic degradation is needed.
In this sense, thermal, chemical, biological and mechanical processes, as well as combinations of these, have been studied as possible pretreatments [17],[18].

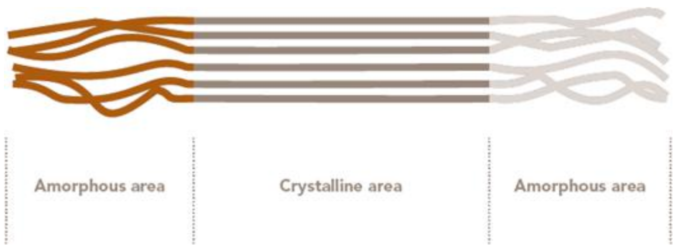


Figure 6
Amorphous and crystalline areas of cellulose.

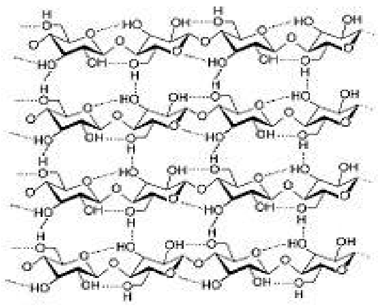


Figure 7
Structure of cellulose. Are shown the inter and intramolecular hydrogen bonds.

5.3.1 Thermal pretreatment

It has been known for many years that a thermal pretreatment can improve the degradability of sludge. While the carbohydrates and the lipids of the sludge are easily degradable, the proteins are protected from the enzymatic hydrolysis by the cell wall. Heat applied during thermal treatment destroys the chemical bonds of the cell wall and membrane, thus makes the proteins accessible for biological degradation.
Thermal pretreatment has been studied using a wide range of temperatures ranging from 60 to 270 ºC. In practice, the optimum temperature is in range of 160-180ºC and treatment times from 30 to 60min. Pressure associated to these temperatures may vary from 600 to 2500 kPa. Temperature and duration of the optimum pretreatment depend on the nature of the sludge: the greater the proportion of difficult hydrolyzing biological sludge substrates, higher the intensity of pretreatments needed.
The limit temperature before digestion was inhibited (presumably because of the formation of inhibitory and/or refractory compounds) is about at 175°C. At this temperature, digestion of the thermally pretreated sludge results in an increase of 60-70% in methane production over not pretreated sludge, while higher temperatures lead to decreased gas production. Clearly, the thermal pretreatment requires the input of a considerably amount of heat, since the sludge feedstock needs to be preheated to the operating temperature (~700kJ/m3). Moreover, the biogas production is not in proportion to the temperature [18].

5.3.2 Chemical pretreatment

Chemical pretreatment is also an efficient method to hydrolyze the cell wall and membrane and thus increase solubility of the organic matter contained within the cells. In this sense, several chemical approaches can be adopted but the most frequent studies involve oxidative methods, such as ozonation and peroxidation.

5.3.2.1 Ozonation

Ozone is a strong cell-lytic agent, which can oxidize the organic substances released from the cells and, within the chemical techniques to disintegrate sludge, it yields the highest degree of disintegration. Moreover, the ozone dose influences the sludge biodegradation and, consequently, the biogas production (Figure 8).
This happens because ozonation treatment has two counteracting effects: degradation of molecules and cell structures that are undegradable for methanogenic bacteria will increase biogas production whereas oxidation of organic molecules that are degradable for methanogenic bacteria will decrease biogas production [18],[19].

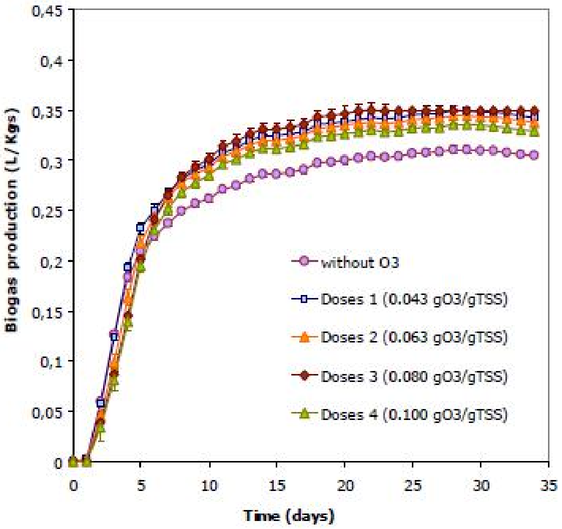


Figure 8
Influence of ozone amount on biogas production.

5.3.2.2 Peroxidation

Several peroxidation techniques, including the well-known Fenton peroxidation and novel reactions involving peroxymonosulphate (POMS) and dimethyldioxirane (DMDO), can enhance the biogas production: a maximum increase of 75% was measured with Fenton, while the POMS treatment increased the biogas production by a factor of nearly 2, against an even higher 2.5 for the DMDO treatment.
Fenton pretreatment disintegrates extracellular polymeric substances and breaks cell walls, thus intracellular water is released. The oxidation process utilizes activation of H_2O_2 by iron salts (Fe^{2+}). A major drawback of this method is the necessity of bringing the sludge to a very low pH. Fenton's reagent is a solution of hydrogen peroxide with ferrous iron as a catalyst. Iron(II) is oxidized by hydrogen peroxide to iron(III), forming a hydroxyl radical and a hydroxide ion in the process. Iron(III) is then reduced back to iron(II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical and a proton. The net effect is a disproportionation of hydrogen peroxide to create two different oxygen-radical species, with water ($H^+ + OH^-$) as a byproduct.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^{-}$
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^{+}$

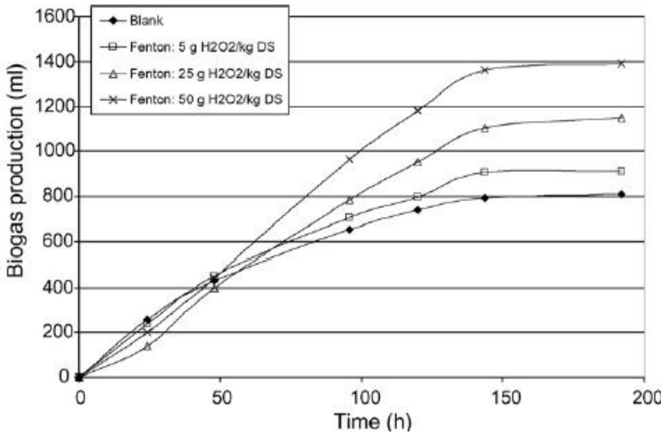
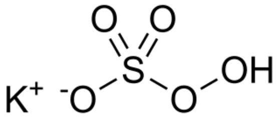
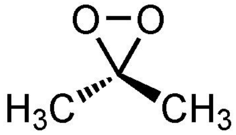


Figure 9
Production of biogas for blank and treated sludge for Fenton peroxidation.

More recent research uses alternative peroxidants such as POMS and DMDO which do not require stringent reaction conditions and significantly increase the biogas production during the anaerobic treatment of raw sludge.

Potassium peroxymonosulfate (PMSO)





Dimethyldioxirane (DMDO)

The POMS ion (SO_5^{2-}) is a derivate of hydrogen peroxide (one H-atom is replaced by a SO_3-group). Its standard oxidation/reduction potential is 1.44V. POMS is used in numerous industrial processes because of its oxidative capacity, and has applications as bleaching agent, disinfectant and oxidant in organic synthesis.
Dimethyldioxirane (DMDO) is a very powerful oxidising agent, which can be used for the transfer of oxygen and for the oxidation of persistent organic molecules. It is part of the group of cyclic peroxides. DMDO is used in several industrial processes such as the sterilisation of medical equipment and as chlorine-free bleaching agent in the paper industry. It is furthermore used for the decontamination of chemical and biochemical weapons used in modern warfare [18],[20].

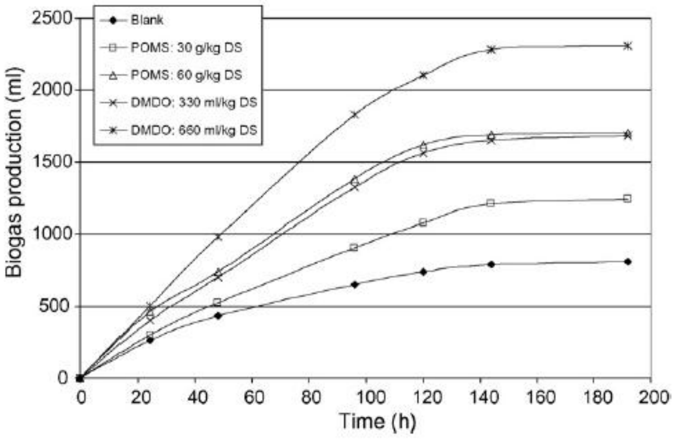


Figure 10
Production of biogas for blank and treated sludge for peroxidation with POMS and DMDO.

5.3.2.3 Other oxidant

Recently peracetic acid (PAA), an oxidant agent, has been proposed to enhance anaerobic digestion biogas production. PAA has a strong effect of oxidation on microorganism, destroying the barrier of spores, dissolving the core and make the material such as DNA protein leaking. Hence this molecule can dissolve and oxidize cells to promote the release of organic matter, thereby reduce the sludge volume and improve the efficiency of anaerobic digestion [18].

5.3.3 Thermochemical pretreatment

Alkali treatment is normally combined with thermal treatment; it‘s so called thermochemical treatment. Considering the biodegrability, it has been shown that the nature of the alkali agent does not infuence the performance of the pretreatment process and no differences were observed with the use of NaOH, KOH, $Mg(OH)_2$, or $Ca(OH)_2$.
However, results tend to underline that extreme pH conditions are not compatible with anaerobic biological treatment. In fact, extreme conditions enhance the formation of complex molecules through intramolecular reactions as Maillard reactions.
It has been observed that the optimal conditions for this kind of pretreatment process were 140°C and pH = 12 for 30 min, which means an addition of about 5g of NaOH/l. Interestingly, it has been noted that thermochemical pretreatment gives the best results in the biogas production compared with thermal, chemical, ultrasonic methods under the same conditions [18],[21].

5.3.4 Mechanical pretreatment

Mechanical pretreatment plays an important role because it favors solubilization of particulate matters in liquid phase. In general, the most often used techniques in mechanical pretreatment are ultrasonication, milling and high pressure homogenization.

5.3.4.1 Ultrasonic pretreatment

Ultrasonication is a mechanical pretreatment method to enhance the biodegradability of the sludge. This technology has several merits like efficient sludge disintegration (>95%), improvement in biodegradability, increase in methane percentage in biogas, no chemical addition and less retention time.
As mentioned above, hydrolysis is the rate-limiting step in anaerobic digestion process, so ultrasonic process accelerates the hydrolysis reactions by disrupting cells enhancing the sludge digestibility. The bacterial cells are disunited by pressure waves and cavitation generated from an ultrasonic generator leading to leaking of intracellular organic substances. The disruption of sludge particles derived from sonication treatment enhances acidogenesis, acetogenesis and methanogenesis reactions, which lead to an improvement in methane generation and reduction of sludge volume. There are two key mechanisms associated with ultrasonic treatment: cavitation, which is favored at low frequencies, and chemical reactions due to the formation of OH- and HO_2 radicals at high frequencies. Specific energy input between 5000 kJ/kg TS and 10.000 kJ/kg TS (TS stands for total solid content) is efficient for enhance methane production, with the process that lasts a maximum of 30 minutes.

Although cell disintegrations of 100% can be obtained at high power levels, power consumption then becomes a serious drawback [18].

5.3.4.2 Milling

A reduction of the particle size represents an interesting pretreatment option for solids to be used in biological processes because it is not necessary to add chemical substances and the system is relatively simple. Smaller particles allow higher reactions rate during the biological processes through the release of dissolved organic matter. Also, smaller particles can stimulate hydrolysis by increasing the surface area and pores volume for the access of the microorganisms and cause a modification of the lignocellulosic structures through alteration of the cellulose crystallinity or lignin distribution. Hence, the aim of milling pretreatment is to increase the surface area and digestibility of the sludge, leading to enhance the volumetric biogas production.
In this case, an important research was done using like raw material a variety of grass called Pennisetum hybrid.
Milling pretreatment was done in two ways:
(i) "wet" milling (by addition of 1/3 volume of deionized water to the milling tank)
(ii) “dry” milling (without the addition of water to the milling tank)
Four milling times - 3, 6, 9, and 12 h - were used for wet and dry milling.
It has observed that dry milling was more efficient than wet milling for a given processing time. Hence, the particle-size reduction significantly increased the digestibility of the raw material but excessive breakage caused acidification and changes in microbiological populations. This investigation showed a 41.04% increase in the specific CH_4 yields after 3h of dry milling pretreatment, and indicated that the milling pretreatment of the Pennisetum hybrid was effective in improving the CH_4 yield. In addition, wet milling pre-treatment can improve the mobility of raw materials. Detailed experiments results are shown in the graphs below [18],[22].

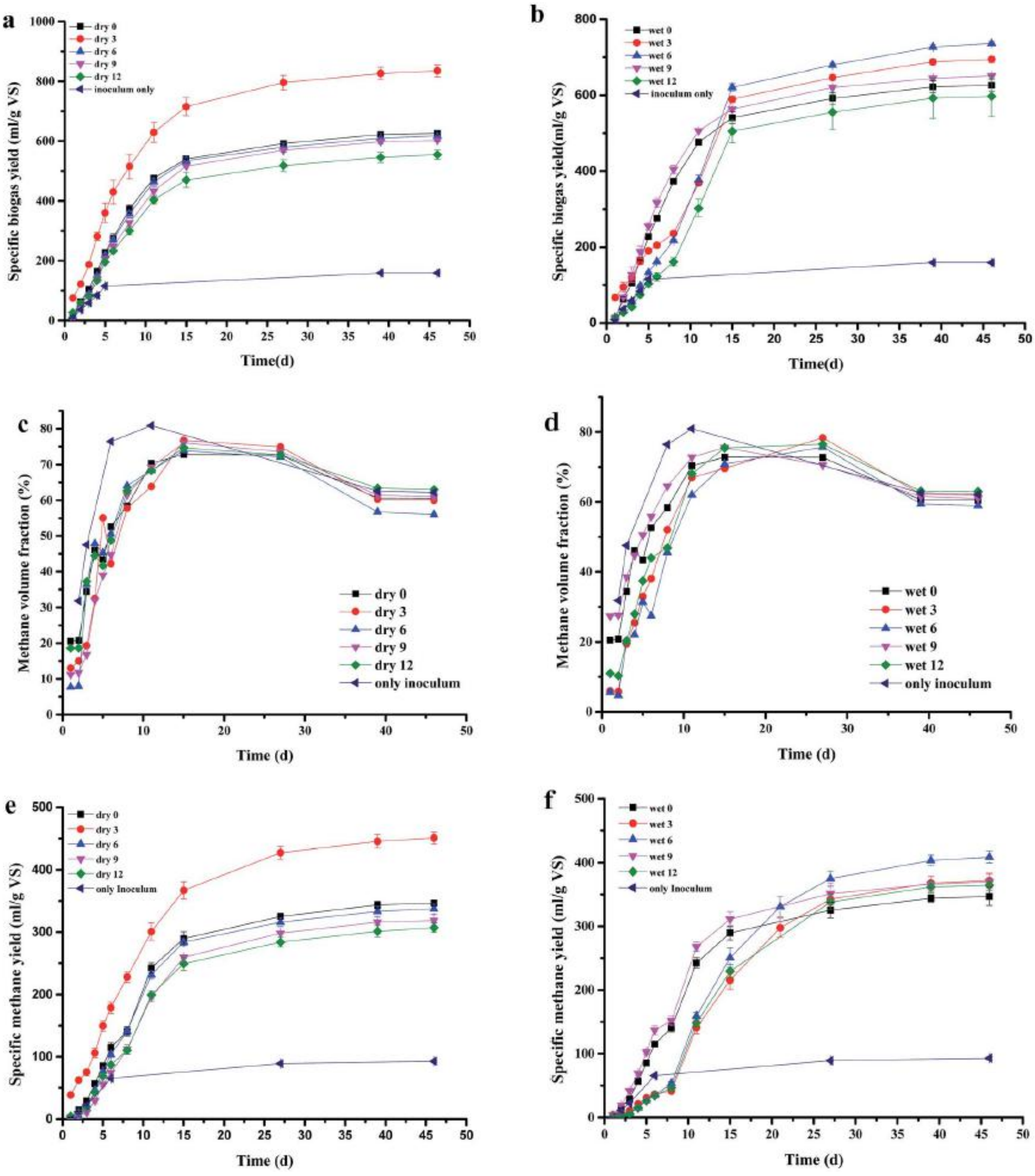


Figure 11
Biogas production by pre-treated grass:
(a) Specific biogas yield of dry milled grass.
(b) Specific biogas yield of wet milled grass.
(c) Methane volume fraction of biogas from dry milled grass.
(d) Methane volume fraction of biogas from wet milled grass.
(e) Specific methane yield of dry milled grass.
(f) Specific methane yield of wet milled grass.

5.3.4.3 High pressure homogenizer (HPH)

One of the most frequently used methods for large-scale operation is high pressure homogenization, which shows several advantages such as asbence of chemical changes, easy operation, low investment and operational costs and high lysis efficiency. The mechanism of the HPH sludge pretreatment is sludge disintegration by pressure gradient, turbulence, cavitation and mechanical stresses acting on solid surfaces. Apparatus for the HPH treatment is a high-pressure homogenizer with a working homogenization pressure ranged between 0 and 100 MPa.

As shown in Figure 12, the homogenizer consists of a pump which forces the sludge sample through the centre of the valve seat. Homogenization pressure is controlled by adjusting the force imparted on the valve. As the sludge sample is pumped through a narrow orifice at high pressure it causes a disruption on the sludge cell membranes. Disruption of the sludge cell is accomplished, thereby releasing its content. The main disruptive factor in this process is the pressure applied on the sample.

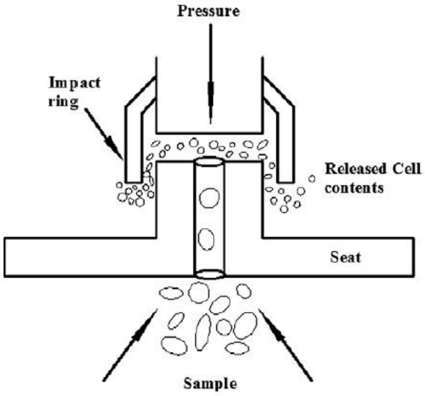


Figure 12
Schematic diagram of sludge homogenization.

Application of the anaerobic sludge digestion is usually limited by a long retention time and a low biogas production.

The biogas production and methane content in the biogas of the anaerobic sludge digestion combined with the HPH pretreatment are shown in Figure 13.

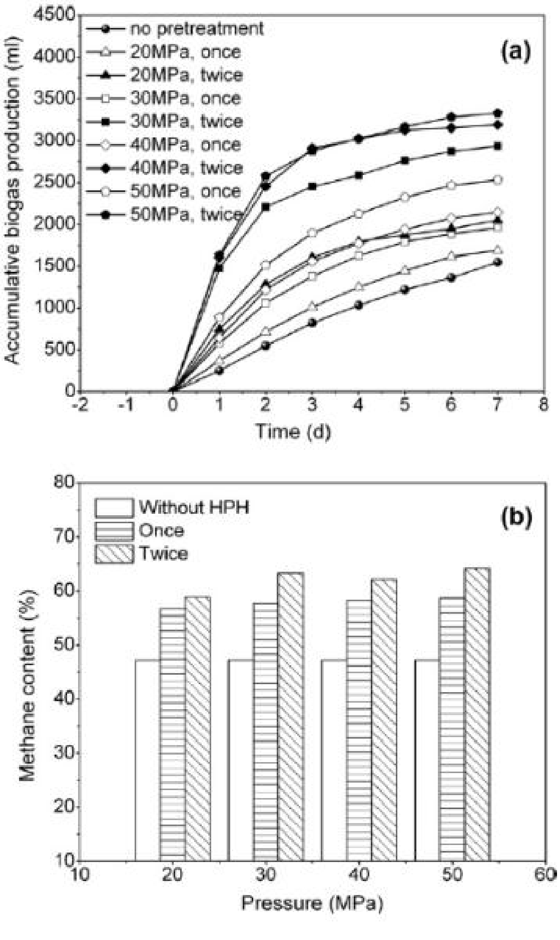


Figure 13
Effect of homogenization conditions on biogas production.

The sludge HPH pretreatment improves the anaerobic digestion efficiency: the accumulative biogas production increases with increasing the homogenization pressure, and two homogenization cycles significantly enhance the accumulative biogas production comparing to one homogenization cycle under the same pressure. With a single homogenization cycle, the accumulative biogas production after 7-day anaerobic digestion increases by about 64% at a homogenization pressure of 50 MPa, compared with the raw sludge digestion without the HPH pretreatment.

The maximum accumulative biogas production is achieved at a homogenization pressure of 50 MPa with two homogenization cycles, which increases by about 115% compared with that for the raw sludge. There is no significant difference between the total biogas production at a homogenization pressure of 40 and 50 MPa when the sewage sludge is pretreated by HPH for twice, indicating that the homogenization pressure should not excess 40 MPa with two homogenization cycles for energy saving. As shown in Figure 13(b), the methane content in the biogas is improved by the HPH pretreatment. For the anaerobic digestion of the raw sludge, the methane content in the biogas is about 47%; and the methane content of about 64% is achieved by the anaerobic sludge digestion combined with the HPH pretreatment at a homogenization pressure of 50 MPa with two homogenization cycles.

Figure 14 shows that the anaerobic sludge digestion is greatly accelerated by the HPH pretreatment. Without the HPH pretreatment, there is no significant change of the biogas production rate in the first 4 days, then follows a slow reduction.

For the HPH pretreated sludge all the maximum biogas production rate for different sludge samples is observed on the first digestion day, then the biogas production rate reduces. The maximum biogas production rate increases with increasing the homogenization pressure and homogenization cycle: the maximum biogas production rate is with a HPH pressure of 50 MPa with two homogenization cycles, 6.5 times as that for the raw sludge without the HPH pretreatment. The maximum biogas production rate with a HPH pressure of 50 MPa with one homogenization cycle is 3.5 times as that for the raw sludge [18],[23].

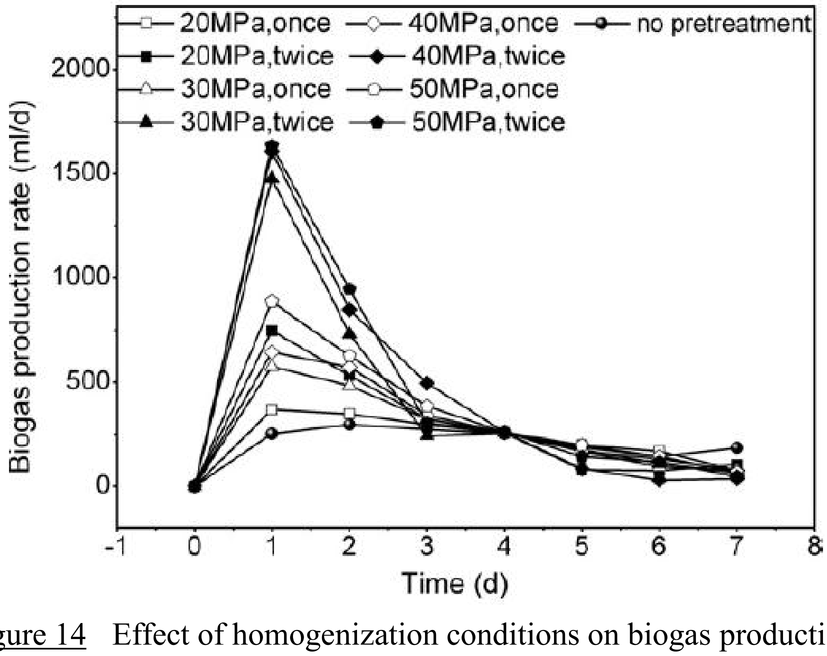


Figure 14 Effect of homogenization conditions on biogas production rate.

6. CONCLUSIONS

Biochemical processes can be successfully used in order to provide energy or valuable chemicals compounds from organic waste ensuring low environmental impact by the pollution's decrease. Hence, in this kind of processes, biogas technology has great importance.

In order to obtain the major effects in this sense, is important to define the best process conditions for the AD, which include pH and temperature first of all, followed by the presence of micro and macronutrients in the right amounts.

With the aim to allow an optimum technological transfer and to develop an efficient and productive system, biogas composition assumes great significance.

In this case, different strategies could be adopted in order to enhance the methane yield and to reduce, totally or partially, undesirable compounds such as hydrogen sulphide, carbon dioxide or molecular oxigen, which could decrease the methane quantity within the biogas or produce damages to the industrial plant.

Clearly, some of the techniques used to increase the methane's amount mentioned above concern about the sludge pretreatment, with special concentration on the thermochemical pretreatment. This method has been proven be the best one in terms of disruprion of the cell's sludge and conseguently of biogas production.

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