Chapter

Employment of Organic Residues for Methane Production: The Use of Wastes of the Pulp and Paper Industry to Produce Biogas - A Case Study

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Abstract

Many organic residues are being wasted since they are not given a comprehensive management; anaerobic digestion is an alternative to reduce the impact of these residues, and to produce biogas. The chapter includes the state of art about biogas and energy production, and later, the analysis of a study case focusing on the use of pulp and paper wastes to produce biogas. The study was carried out through anaerobic digestion at a bench scale using three temperature phases to treat primary and secondary sludge, establishing operational parameters such as temperature, retention time, and organic loadings. Monitoring of volume, methane concentration in the biogas, volatile solids reduction, volatile fatty acids during the process, the performance of the process in function of methane produced per volatile solids removed is calculated. This case study shows that it is feasible to use the sludge from the company's wastewater treatment plant (WWTP) for the generation of biogas, thus reducing waste management problems.

Keywords: anaerobic digestion, biogas, bioenergy, biosolids, paper industry

1. Introduction

The indiscriminate use of raw materials and fossil fuels has led to an infinity of environmental problems, such as water reservoir pollution, acidification of the oceans, loss of ecosystem diversity, and a concentration increase in certain gaseous pollutants in the atmosphere [1]. To reduce dependence on oil and decrease the CO_2 concentration to revert the climate change, it is necessary to use renewable energy sources [1, 2]. Among the possible renewable energy sources biogas, stands out especially, when biogas is obtaining from waste produced from different productive activities [3]. The biogas generation through anaerobic digestion generates several environmental benefits, such as reducing greenhouse gas emissions, depletion in the residuals environmental impact, the clean energy generation, and the possibility of using the generated biosolid as a soil improver or fertilizer, among others [4].

1.1 Anaerobic digestion of waste

Under anaerobic conditions decomposition of matter produces a gaseous mixture known as biogas. Methane is the main fuel gas in the biogas mixture, and to be used as a fuel, its content must be above 45% of the total composition of biogas [5]. Biogas general characteristics are listed in **Table 1**.

Biomasses such as food industry waste, animal excreta, straws, residual planta and municipal waste under anaerobic digestion are able to produce biogas [4, 8, 9]. Through several biochemical steps the macromolecules of organic matter are transforming into CH_4, CO_2 and H_2S under anaerobic digestion [8–11]. However, the organic matter characteristics must allow being used as an energy source for a set of microorganisms that will make the digestion process possible. Therefore, not only a supply of the main nutrients (carbon and nitrogen) is necessary, but also a balance of micro and macro nutrients [12]. Carbon and nitrogen are the principal sources of food for methanogenic microorganisms, and the proportion between these nutrients must be adequate for the correct operation of the process. It is known that the approximate proportion of carbon (C) and nitrogen (N) consumption by bacteria is 30:1 (C/N), this being the optimum point. On the other hand, if there is a ratio of 35:1 the process is inhibited due to a lack of nitrogen, and if it is 8:1 the inhibition occurs due to the formation of ammonia [4, 13].

Anaerobic biodegradation of complex organic materials is a multi-stage process where solid materials are first hydrolyzed, polysaccharides to sugars and alcohols, proteins to polypeptides and amino acids, lipids to long-chain fatty acids (LCFA), and glycerol. From these, the fermentative bacteria produce short-chain fatty acids (SCFA), hydrogen (H_2), and carbon dioxide (CO_2), and ammonia producing by the fermentation of amino acids. Subsequently, acetogenic bacteria from non-acetic FA and neutral materials such as ethanol produce H_2, acetate, and CO_2, which are used by methanogenic bacteria to produce CH_4, CO_2, and H_2O [10, 12, 14]. The process can be divided into four steps according to the proposed models and the complex inter-microbial relationships that carry it out.

Composition	55–70% Methane (CH_4) 30–45% Carbon dioxide (CO_2) 0–10% Nitrogen (N_2) 0–1% Hydrogen (H_2) 0–2% Oxygen (O_2) 0–3% Hydrogen sulfide (H_2S) <0,5 mg/m^3 Siloxanes
Heat content	6.0–6.5 [kWh m^{-3}]
Fuel equivalent	0,60–0,65 [L petroleum m^{-3} biogas]
Explosion limit	6–12% biogas in the air
Ignition temperature	650–750°C (with the mentioned CH_4 content)
Critical pressure	74–88 [atm]
Critical temperature	−82,5 [°C]
Normal density	1,2 [kg m^{-3}]

Table 1.
Common characteristics of biogas [6, 7].

In the specific case of using waste sludge from Wastewater Treatment Plants (WWTP), the nutrients are in the necessary proportions and concentrations. However, the sludge generated in the plants of the forestry or paper industry contains high concentrations of cellulose, and this unbalances the C/N ratio [15]. Besides, lignin can cause toxicity problems and decrease the efficiency of the anaerobic digestion process [10, 15, 16].

In the hydrolysis process, macromolecules such as proteins, lipids, carbohydrates, and nucleic acids are transformed into oligomers (fatty acids, carbohydrates, amino acids, nitrogenous bases, and aromatic compounds) [17, 18]. The bacteria involved in the process are a very complex mix of many genera, most of which are obligate anaerobes; however, some facultative anaerobic bacteria such as streptococci and other enteric microorganisms may be present. This type of microorganisms ferments a great variety of complex organic molecules such as polysaccharides, lipids, and proteins, turning them into a wide range of end products such as acetic acid, a mixture of H_2 and CO_2, mono carbon compounds, organic acids with more than two carbon atoms, and compounds such as propanol, and butanol [10, 19]. The optimum pH for hydrolysis varies according to the substrate. For easily degradable carbohydrates, hydrolysis proceeds in an accelerated manner at pH between 5.5 and 6.5 [17].

In acidogenesis, the pH value decreases, going from 7.0 to values around 5.0; in this stage, the bacteria ferment the soluble products of hydrolysis, mainly hydrogen and volatile fatty acids, and long-chain fatty acids also produce acetate or propionate by ß-oxidation. Thus, together, hydrolytic and acidogenic bacteria convert complex substrates to precursors of methanogenesis: H_2, CO_2, and acetate, in addition to AGV and other reduced compounds, ethanol, lactate [9, 10].

In the acetogenesis stage, organisms that favor an acidic environment participate; during this stage, volatile fatty acids and nitrogenous compounds are slowly transformed. During this stage, the pH value increases from values around 5.0 to values around 6.8. The metabolic products of acetogenic bacteria are converted into substrates for methanogens by the activity of the acetogenic bacteria constituting the third level or trophic group in the population sequence that occurs in anaerobic digestion. The metabolic result of this group is the formation of acetate, H_2, and CO_2. These bacteria are known as hydrogen obligate acetogenic bacteria. This trophic group must have a symbiotic relationship with hydrogenophilic archaea, since they consume the hydrogen produced by the former, thus avoiding its inhibition by-product accumulation [17, 19].

In the last digestion stage, known as methanogenesis, the volatile fatty acid content drops to less than 500 ppm. The pH value increases from 6.8 to 7.4, producing large volumes of gases with 65 to 70% CH_4, around 30% CO_2, and other inert gases such as N_2. Methanogenic archaea are responsible for producing methane from various substrates, with acetate being responsible for approximately 73% of the methane produced. Methanogenic archaea are strict anaerobes, very sensitive to oxygen as they require negative oxidoreductive potentials lower than −50 mV to grow [20]. The main products of this type of treatment are biogas and biosolids, which are used as a source of energy and as a fertilizer respectively. An additional benefit of this type of processing is that a load of pathogenic organisms in the sludge is very low, as is the mass of the sludge. The main uses of sludge from bioreactors are soil conditioning, use as fertilizer, and use for the generation of vegetation cover in sanitary landfills or for the recovery of degraded soils or sites, and also in their bioremediation [17].

1.2 Factors involved in anaerobic digestion

Biomass has a varied composition that includes different organic and inorganic compounds. To optimize the anaerobic digestion process and biogas production, parameters such as chemical composition, operational parameters such as temperature, pH, loading rate, alkalinity, biodegradability, bioaccessibility, bioavailability, and the initial characterization of substrates [11, 21].

1.2.1 Temperature

Temperature is one of the principal survival factors of microorganisms during the anaerobic digestion process [10]. The management of the temperature range is useful to differentiate the type digestion processes. Three operating ranges can be used in an anaerobic digester: psychrophilic (~ 25° C), mesophilic (~ 35° C), and thermophilic (~ 55° C). Microorganisms grow best in temperature ranges between 35 and 55° C. An increase in temperature has a positive effect on the metabolic rate and accelerates the degradation of biomass; however, the use of a thermophilic range is difficult to control and generates energy consumption to maintain the constant temperature of the reactor. In general, the mesophilic process often involves a diversity of microorganisms and is more stable than the thermophilic process. Temperature is one of the principal parameters for microorganisms to grow, degrade organic matter, and consequently, biogas to be produced [11, 21].

1.2.2 pH

The pH value is one of the main operational factors that can affect the anaerobic digestion process. That is because most of the microorganisms prefer a neutral pH range. In the biogas production process, some organisms require a different growth pH. However, the most favorable pH range to obtain maximum biogas production is 6.8 to 7.2. In the anaerobic digestion process, methanogenic microorganisms are too sensitive to pH variations and prefer a pH of around 7.0 [11, 22].

Acidogenic microorganisms are less sensitive to pH and are tolerable in the 4.0–8.5 range. However, the optimal pH for hydrolysis and acidogenesis is between 5.5 and 6.5 [11, 22]. The pH value is an important factor because it influences the ratio of ionized and non-ionized forms. This is because excessive hydrogen, sulfur, fatty acids, and ammonia are toxic in their non-ionized forms. Generally, the pH value indicates a healthy environment for the digester microorganisms [11, 22, 23].

1.2.3 Alkalinity

Alkalinity is the ability of a system to maintain a certain pH. It is a measure of the buffer capacity of the system. The higher the alkalinity, the better the pH despite an increase in H+ generation. In systems where anaerobic digestion is performed, the buffer system is due to the presence of carbonates, in particular the presence of the bicarbonate ion HCO_3^-. Since acidogenic bacteria have a higher activity than methanogenic bacteria, they are capable of causing acidification in the reactor, in case of organic matter overloads. This acidification can be avoided by maintaining an optimal buffer capacity in the digester. Alkalinity is useful for buffering purposes, at typical operating pH values [21, 22].

1.2.4 Volatile fatty acids

The concentration of volatile fatty acids (VFA) product of the fermentation has great importance in the anaerobic digestion process. This because the VFA can acidify the reactor, causing the failure of the process. Under normal operating conditions, the concentration of VFA in the effluent must be very low or negligible, less than 100 mg L^{-1}. On the contrary, if there is a high concentration, it can cause inhibition of methane-forming archaea. The VFA/alkalinity ratio is also an indicator of stability. A ratio greater than 0.4 indicates an immediate failure [21, 24].

1.2.5 Chemical composition of substrates

Substrates chemical composition characterization is useful to identify the appropriate substrates to carry out the anaerobic digestions. Substrates contain the full range of simple and complex chemical compounds, and the proportion of them will depend on their sources (agricultural agriculture and animal manure, municipal, food, and industrial waste). Specific organic compounds may predominate. Although, most of the time the exact composition of the substrates is difficult to determine [22, 24].

1.3 Temperature regimes in anaerobic digestion

As commented in a previous section, the temperature regime is important when looking for the conditions that allow increasing the degradation of organic matter and the production of biomass. For this reason, each of the possible regimes will be briefly analyzed.

1.3.1 Mesophilic anaerobic digestion

It is the type of conventional anaerobic digestion carried out in a temperature regime ranging from 33 to 35° C, which can have a system that allows mixing of the sludge. In this configuration, the retention times are usually long, VS reduction reaches around 40 to 48%. It presents a problem of foam generation, and destruction of the pathogens is not carried out. The quality of the biogas in this type of digestion is good, however, the volumes generated are not so considerable, which in terms of profitability makes it inefficient [25, 26]. It has been founding that for retention times between 5 and 55 days, the methane concentration can be between 62 and 66%, and the reduction in volatile solids can reach 32 to 40% for retention times between 15 and 30 days [27].

1.3.2 Thermophilic anaerobic digestion

The waste sludge treatment process in thermophilic terms is one of the most studied at present. This type of process, carried at a temperature of 50 to 55° C, allows an improvement in the deployment of retention times, and destruction of pathogens. Popat et al. (2010) report that the reduction of most pathogens can occur between 13 and 15 days at constant temperatures between 51 and 55°C. However, the energy cost resulting from the treatment puts it into consideration [28]. The VS reduction percentages are around 50 to 60%, which makes it a point of study for its improvement in energy terms [26, 29]. Besides, Wahidunnabi & Eskicioglu (2014) and Yu et al. (2014) reported that VS removal efficiencies for thermophilic systems range from 40 to 50%. Regarding the production of biogas, with values around 0.30 m^3 CH_4 (kg of VS fed)$^{-1}$ [26, 30].

1.3.3 Three-phase temperature anaerobic digestion

This digestion is a combination of acid/gas phases and temperature phases, from which a good removal of volatile solids is obtaining, it does not produce fetid odors, and the retention times are shorter [29, 30]. Riau, de la Rubia, & Pérez (2010) carried out a configuration for this type of digestion, where the phases are delimiting by time and temperature. The mesophilic from 1 to 3 days, the thermophilic from 5 to 15 days, and a mesophilic with a retention time from 5 to 15 days; The results of his research were 55% SV reductions, coliform and pathogen reduction, as well as a volumetric gas production of ~5.5 L_{CH4} (kgVS fed)$^{-1}$ [31]. Similarly, the experiments carried out by Kim, Novak, & Higgins (2011), affirm the effectiveness of the combination of three temperature phases. In their results, they obtained a VS reduction of about 57% [32].

1.4 Sewage sludge and its use to produce biogas

Most conventional wastewater treatment systems generate large amounts of waste products, which are called sludge. The composition and quantity of the sludge depend on the raw wastewater characteristics and the wastewater treatment process. The main constituents of wastewater disposed of in treatment plants include garbage, sand, foam, and sludge. The sludge extracted and produced in wastewater treatment operations and processes is generally a liquid or a liquid-semi-solid with a high solids content between 0.25–12% [33, 34]. The different treatments to process sludge vary according to the source and type of wastewater from which they are deriving, the process used to treat the wastewater, and the final disposal of the sludge. Sludge is by far the constituent with the highest volume removed in wastewater treatment, so its treatment and disposal are probably the most complex problem [34].

The biological wastewater treatment process produces different types of sludge within each of the individual processes, such as (1) primary sludge produced during the primary wastewater treatment processes; this occurs after sieving and de-sanding. The composition of the sludge depends on the characteristics of the wastewater. It mainly contains large undissolved solids that generally carry on a large amount of organic material, vegetable matter, paper, and other materials. (2) Activated sludge coming from the removal of dissolved organic matter during aerobic or anaerobic treatment of wastewater. This sludge is generally in the form of flocs that contain living and dead biomass. (3) Tertiary sludge, which is produced through subsequent treatment processes, with the addition of flocculating agents [35]. The processes for treating sludge vary according to the type of wastewater from which they are deriving, the process used to treat them, and the last disposal method to which the sludge will be destining. The sludge treatment main objectives are to reduce mass and volume, to handling it easily and to increase its biological stability in order to produce a sufficiently harmless material for its disposal [35, 36].

1.5 Biogas in México

Energy is a vital supply for the development of any society, but when talking about energy, it encompasses aspects such as use and abuse, source of supply, pollution generated in its generation, danger to society in cases of accidents, etc. Global energy consumption has doubled in the last 25 years. Estimation for the next 25 years shows that there will be an increase of 70%. In developing countries, the above will be reflected mainly due to globalization, population growth, and economic growth. Besides, the consumption of fossil fuels is no longer sustainable due to its early depletion, the increase in its price, and the damage it has caused to the environment [37]. México has an enormous potential in renewable resources, and thanks to the reforms implemented in the energy sector, barriers that impede the development of new projects and clean technologies have been eliminated, achieving increases in a clean generation far above fossil energy. According to the clean energy progress report, from 2016 to 2017, fossil generation grew by 2.07% and clean by 6.98% [38].

In México, the production of electrical energy is based mainly on the consumption of different fossil fuels, reaching more than 90% of the total, highlighting the use of oil, natural gas, and coal; on the other hand, the fraction of energy obtained by renewable means is 7.5%, and biogas only contributes 0.02% [39, 40]. However, it is important to note that the percentage covered by renewable energies increases every year, although without yet becoming one of the most important sources [39]. However, the National Energy Strategy aims for approximately 35% of the country's consumed energy to be renewable origin by 2024 and marks that 50% of the consumed energy in 2050 be clean [41]. Experts estimate that the generation of biogas from waste has great potential in México, specifically for the use of livestock waste. It is estimated that from anaerobic digestion of them, little more than 100 million cubic meters of biogas could be generated per year, which would allow covering little more than 8% of the national energy demand [42, 43]. On the other hand, in the case of the wastewater treatment plants, the potential is slightly lower, reaching projections of around 75 million cubic meters per year for 2024; however, studies on wastewater treatment plants of the industrial sector are still needed since their effluents and operating conditions are specific, making it difficult to generalize about possible production values and biogas yields [42].

1.6 Waste from the paper industry to produce biogas

The pulp and paper industry produces large amounts of highly polluting waste; this cause the wastewater and consequently the treatment plant sludge to have particular characteristics [44]. It is estimated that up to 1 m3 of residual sludge can be generated per ton of paper produced, which will contain between 45 and 55% organic matter in addition to the presence of other pollutants and COD between 4,000 and 15,000 ppm depending on whether it is primary or secondary sludge [44, 45]. Due to its high content of organic matter, it can be used for biogas generation from anaerobic digestion, being able to achieve high values of biogas production as well as high conversion efficiencies [45].

The primary sludge is producing when clarifying the wastewater from the process. This sludge has a high content of lignocellulosic material; the fiber content is variable depending on the type of process, and the dewatering of this type of sludge is relatively simple [44, 46]. The solids content can be up to 48%, while the volatile solids and total organic carbon can reach values of 33 and 19%; the presence of heavy metals such as chromium, zinc, nickel, among others stands out [46]. On the other hand, secondary sludge is the sludge generated when carrying out the biological treatment (aerobic, anaerobic, activated sludge) of the wastewater generated in the process. The secondary sludge is recovered in the clarification phase from the treated water and is normally mixed with the primary sludge to incinerate it or to deposit it in a landfill [44, 46]. Traditionally, the sludge generated in the pulp and paper industry is mixed (primary and secondary), later they are dried, and finally, they are used as fuel when incinerated, another alternative is to place them in landfills. However, the large amount of organic matter causes its weathering to generate a great amount of greenhouse gases, so this strategy is not currently allowed in many countries. [46–48]. Since the majority fraction of the industry and paper sludge is organic matter, its use in an anaerobic digestion process has been proposed to recover energy from them. [46]. However, the process is not very efficient because a large part of the organic matter is composed of cellulose and lignin, for which various authors propose the use of pretreatment strategies that allow the breaking of the fibers and increase the efficiency of the process of anaerobic digestion [46, 49, 50]. However, the sludge characteristics depend on the operating conditions, the raw material, among others therefore the anaerobic digestion process must be adjusted and specifically designed.

2. Case of study: the use of wastes of the pulp and paper industry to produce biogas a case of study

This study was carried out to treat residual sludge from a paper-producing industry. A company and leader in the manufacture of paper and cardboard packaging, which treats a flow of 80 to 100 L s^{-1} of wastewater, which results in annual production of primary and secondary sludge of 5,400 to 6,000, and of 4,300 to 5,000 tons $yr.^{-1}$, of primary and secondary sludge, respectively.

This papermaking company uses recycled paper as raw material to manufacture paper with three quality grades: linerboard paper for corrugated packaging, medium paper for corrugated packaging, and white top paper for corrugated packaging. That generates a variation in the wastewater characteristics resulting from the process, making it difficult for the company to treat activated sludge. This wastewater treatment consists of screening and desander pretreatment, primary clarification of primary treatment, and biological treatment. The solids from the primary settler and the flotation process are mixed and concentrated through a sludge press. The effluent from the primary clarification is neutralized and transported to the activated sludge treatment. The mixed liquor flows from the reactor to the secondary settler, where the produced sludge and the clarified effluent are separated. Primary and secondary sludge do not receive any treatment and are disposing on the land of the company. For all the anterior, this study of anaerobic digestions is the first step taken to research giving added value to the generated sludge and avoiding contamination in soils and phreatic levels.

The use of these residual sludge for the generation of biogas was studied through anaerobic digestion, using three bioreactors, one operating at mesophilic temperature (M), another at thermophilic temperature (T), and another at three temperature phases (mesophilic, thermophilic, and mesophilic) (M-T-M).

2.1 Methodologies

Primary and secondary sludge were sampling in the industry. The primary sludge was taking before the sludge press, and the secondary sludge from the sludge return line to the oxidation lagoon. Samples were transporting to the laboratory for their characterization. A mixture of primary and secondary sludge was preparing in a 50:50 ratio, thickening and concentrating the sludge to prepare an organic loading of 1.4 kg m^{-3} d^{-1}.

Total solids (TS) and volatile solids (VS), pH, alkalinity, total nitrogen, volatile acids, chemical oxygen demand (COD) and total and fecal coliforms were measured according to the Standard Methods [39].

Elemental composition (C, H, N, S) and protein were conducted according to the procedure ISO-16948: 2015 [40].

Gas production was measured by displacement of an acidified brine solution (NaCl and H_2SO_4) in graduated cylinders. +.

Volatile fatty acids (VFA) was reassured by titration according to [41].

Biogas composition by a LandTec® gas analyzer.

2.2 Biodigester operation

Three stainless steel bioreactors (14-L each) were used to carry out the experimental anaerobic digestion process. The bioreactors had inlet and outlet valves for feeding and collecting biogas. Also, bioreactors had mechanical stainless-steel propeller-type stirrers, driven by an Arrow brand motor, model 350. The shakers were programmed to shake the content for three minutes every twenty minutes to keep the sample homogeneous by shaking the reactors 20 times per day for 3 minutes the intervals between each shaking were 20 minutes. The digesters were providing with submersible electrical resistance and temperature control. The bioreactors were operating with an organic load mixture of 1.4 kg m-3 d-1 of primary and secondary sludge, in a ratio of 50:50 and a retention time of 30 days. One reactor was operating at a mesophilic temperature (M) of 35°C, another at a termophilic temperature (T) of 55°C, and the other at three temperature phases (M-T-M), mesophilic 35°C, thermophilic 55°C, and mesophilic 35°C. The reactors were operating in semi-batch mode, feeding, and removing substrate every third, day and performing the analysis of Total and volatile solids, pH, alkalinity and acidity, volatile acids, total Kjeldhal nitrogen, total coliforms, fecal coliforms and measuring the volume and biogas composition.

3. Results and discussion

3.1 Initial characterization of residual sludge

Table 2 shows the results obtained from the physicochemical and biological characterization for the primary sludge, secondary sludge, and the 50:50 mixture. The percentage of total solids is within the range of 5 to 9% according to [35]. The analysis were carried out in triplicate for each of the parameters analyzed. The cellulose present in the primary and secondary sludge is the result of the fact that its recovery is not total during the flotation process, and there is a great loss of these residues and has the potential to be reused for obtaining energy due to their high

Parameter	Primary sludge	Secondary sludge	Mixture 50:50
Total solids (mg L^{-1})	81655	78310	92380
Volatile solids (mg L^{-1})	43900	33225	42565
Total solids (%)	5.54	7.01	9.20
Volatile solids (%)	53.76	42.20	46.08
pH	6.07	6.75	6.10
Alkalinity (mg_{CaCO3} L^{-1})	1245	465	777
C (%)	36.35	46.42	48.68
H (%)	33.66	37.41	41.33
N (%)	1.27	3.67	5.98
S (%)	0	0	0
Protein (%)	7.97	23.43	10.98
Kjeldhal total nitrogen (mg L^{-1})	434	590	896
DQO (mg L^{-1})	235	560	550
Total coliforms (NPM gST^{-1})	$5.69E10^{8}$	$2.20E10^{9}$	$1.31E10^{8}$
Fecal coliforms (NPM gST^{-1})	$4.7E10^{7}$	$3.20E10^{8}$	$2.40E10^{7}$
Celulose (%)	92.68	92.65	92.65
Heat energy Kcal Kg^{-1}	81655	2501.16	1044.36

Table 2.
Physicochemical and biological characterization of the primary, secondary, and mixed sludge.

calorific content. The cellulose concentration in the secondary sludge is due to the low biodegradability of its biological wastewater treatment [42]. The results of the alkalinity in the sludge are determined to give sludge buffer capacity, because that the anaerobic digestion process needs to withstand the changes in pH as the process progresses [43]. The content of carbon, hydrogen, nitrogen, total nitrogen, and proteins are necessary substrates for the reproduction of microorganisms and the generation of biogas [22]. The concentration of coliforms present in the sludge exceeds the Official Mexican Standard NOM-004-SEMARNAT-2002, so they require treatment for their disposal [44].

The results obtained for the 50% sludge mixture (primary sludge and secondary sludge) indicate that the combination of both substrates maintains conditions of total solids, volatile pH to carry out anaerobic digestions, having 42.5 g L^{-1} which, corresponds to 46% of SV of organic matter to be degraded, contained in the mixture of substrates.

3.2 Volatile solids

Figure 1 shows the VS results for the 50:50 ratio of substrates with organic load (OL) of 1.4 Kg m^{-3} d^{-1} with a retention time of 30 days. It can be seen that, during the digestions in the three treatments, there was the removal of solids, the final removals of SV (%) for each treatment in its temperature phase were M = 52.49, T = 57.76, and M-T-M = 58.61.

3.3 pH, alkalinity y total volatile acids

Figure 2A and **B** show the behavior of pH and alkalinity parameters, respectively, during anaerobic digestion. **Figure 2A** shows that the T and M-T-M bioreactors managed to increase their pH to 7.3. The opposite case occurred with the mesophilic bioreactor where the increase of pH was only 6.7. **Figure 3B** shows that in bioreactor M there was a variation in alkalinity due to the low pH obtained values. For the T and M-T-M bioreactors, there was a decrease in alkalinity, reaching concentrations of 900 mg L^{-1} after 20 days.

Figure 3 presents the VFA concentration, which decreased during the digestion process. During the digestions, there was no accumulation of VFA therefore, the process was not destabilized. It shows that the concentrations of VFA were decreasing throughout the process in the three bioreactors. Starting with 7100, 7800, and

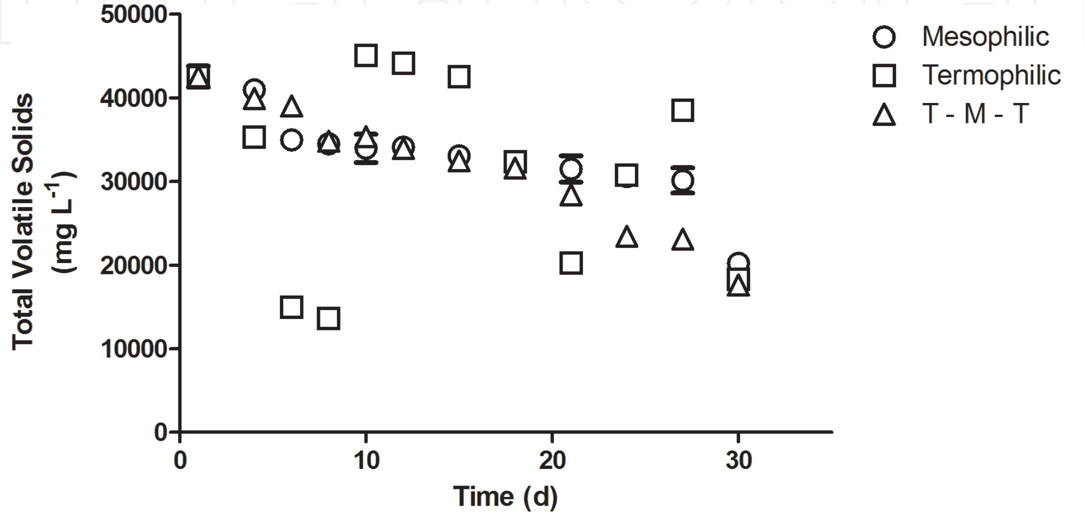

Figure 1.
Volatile solids concentration during anaerobic digestion processes.

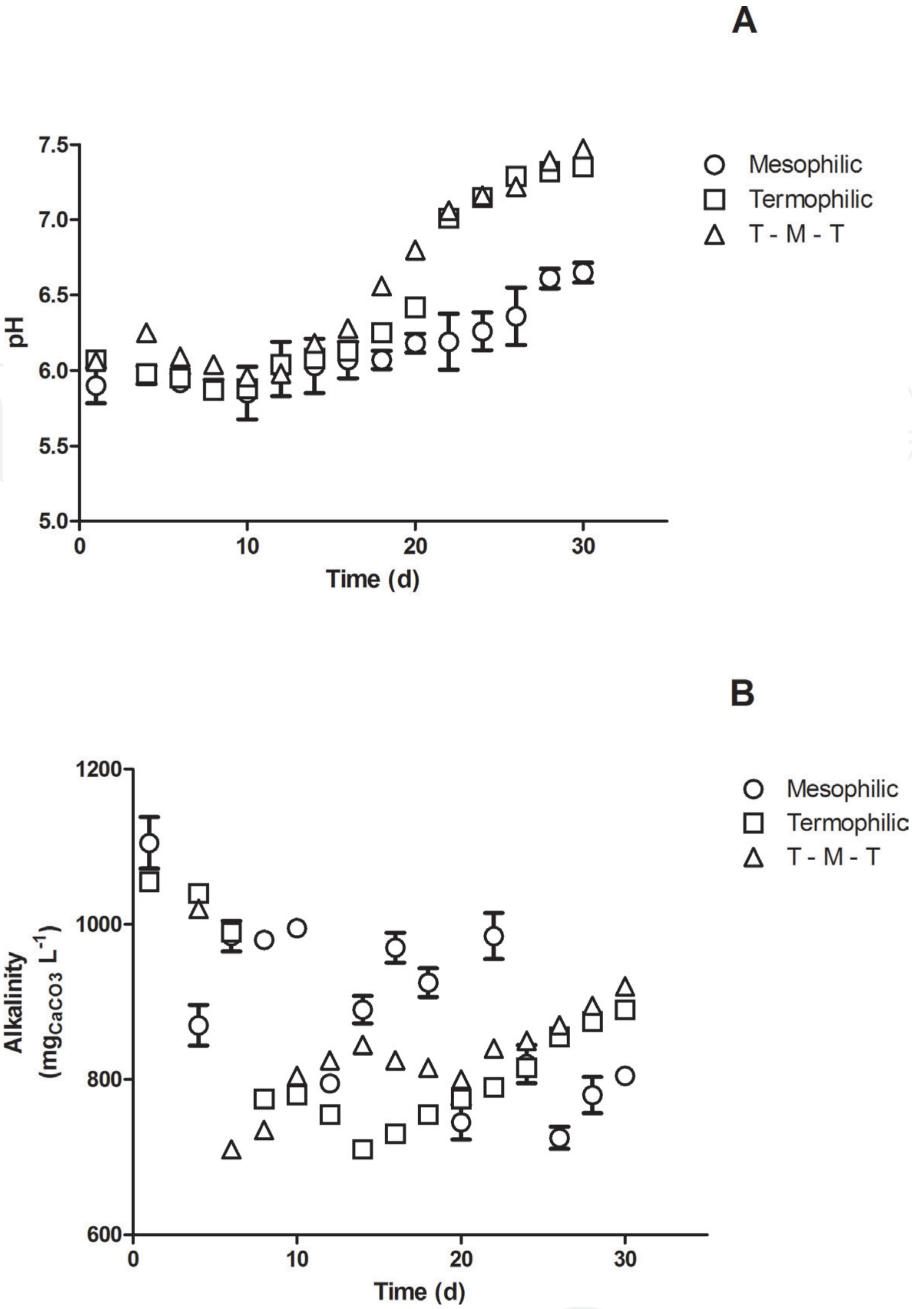

Figure 2.
Behavior of pH (A) and alkalinity (B) during anaerobic digestion processes.

840 mg L^{-1} for the M, T, and M-T-M bioreactors, respectively. At the end of the treatments, the concentrations of 540, 640, 610 mg L^{-1} for the M, T, and M-T-M bioreactors, respectively. The buffer capacity in the digesters, neutralized the possible accumulation of volatile acids and maintained the pH values to stabilize the anaerobic digestion.

3.4 Organic and ammonia nitrogen

Figure 4 shows the results of ammonia nitrogen during the experimentation, and it is observing how the ammonia nitrogen increased through the process for the three different temperatures. The increase in the concentration of ammonia nitrogen was not inhibitory for the development of the digestion process because all the bioreactors at the different temperatures presented biogas production.

Figure 5A and **B** shows the behavior of the biogas volume and methane fraction. It is showing that the T and M-T-M reactors generated a greater volume of biogas

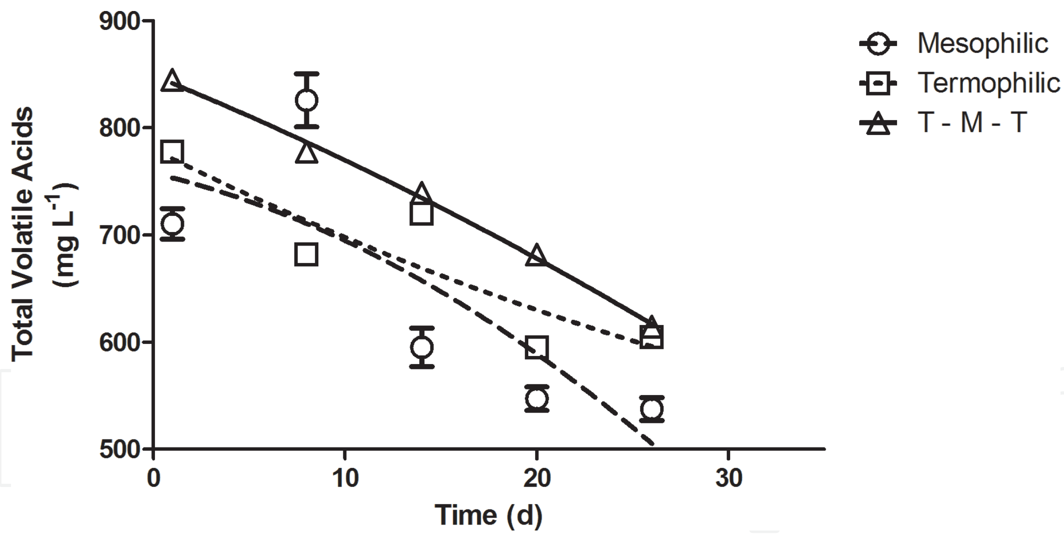

Figure 3.
Concentration of total volatile fatty acids during anaerobic digestion processes.

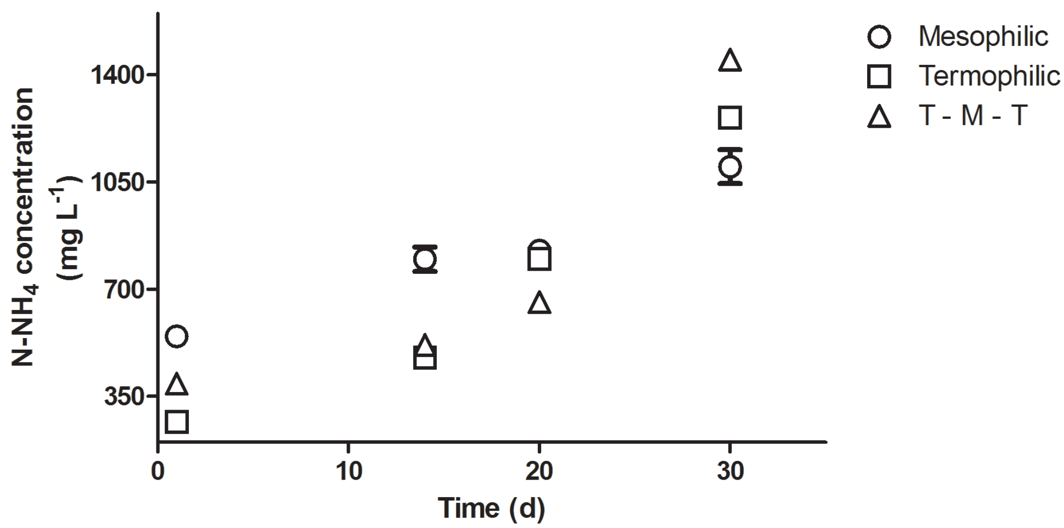

Figure 4.
Concentration of N-NH$_4$ during anaerobic digestion processes.

than the M bioreactor, which presented too low biogas volumes. The methane fraction was higher in the M-T-M bioreactor where a value above 60% was obtained.

Figure 6 presents the methane yields in the anaerobic digestion processes. The M-T-M bioreactor resulted in a higher methane yield until day 24, after this time there was a decrease in methane yield. Methane yield was very low for the M and T bioreactors because of the conditions, but for the M bioreactor the yield was the lowest.

According to the literature review, there are research studies on different biomasses that can be processed in anaerobic digestions, such as agro-industrial, livestock, forestry residues, sludge from sewage treatment plants, industrial residues, where the biogas and methane yields are reporting when digesting these substrates. However, for particular wastes from industry using recycled paper raw materials, there are no studies to date. There are studies of the pulp and paper industry where other types of pollutants are generated from the chemical process, a case that does not apply to this industry. There is research on anaerobic digestions, always seeking to obtain high methane yields for reuse as biofuel or energy production. There is

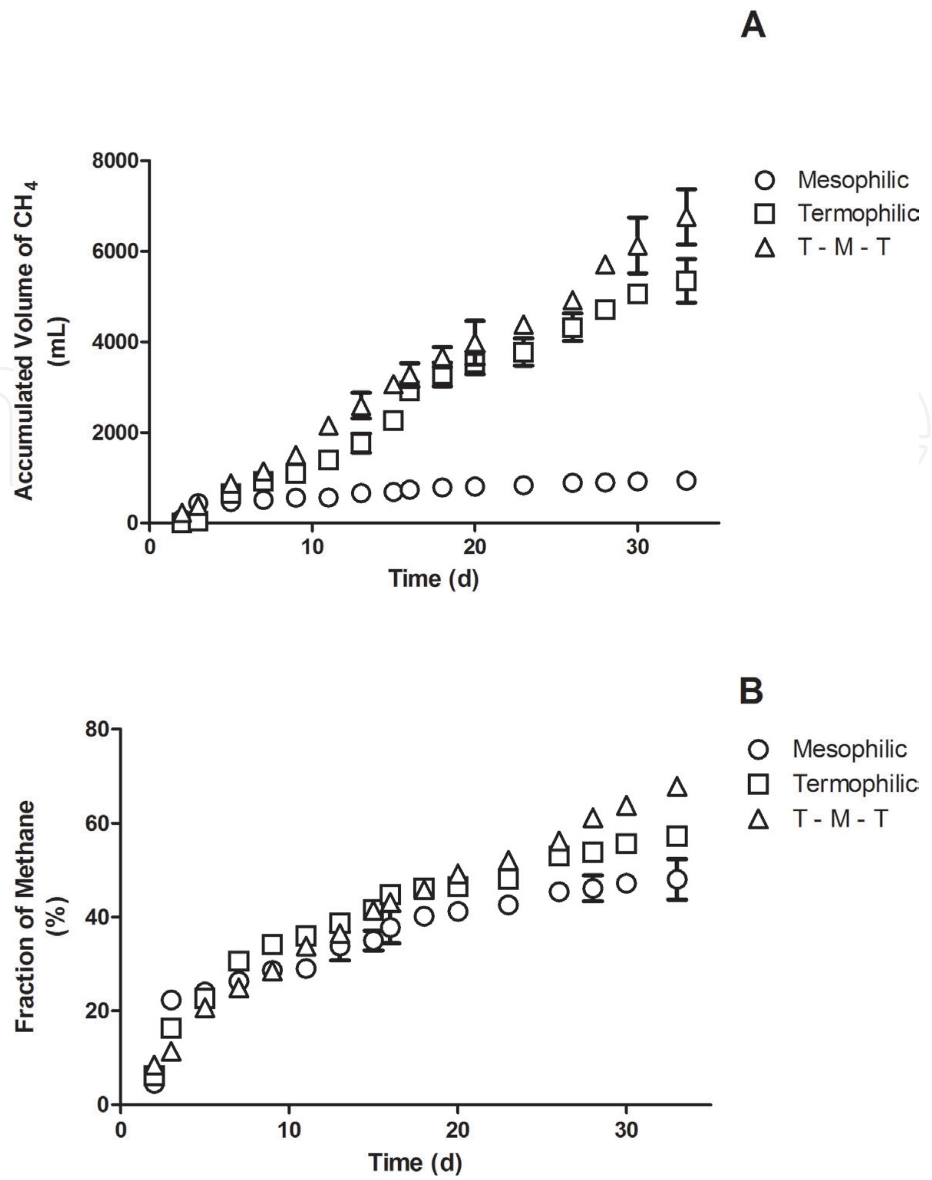

Figure 5.
Behavior of the biogas volume (A) and methane fraction (B) during the anaerobic digestions.

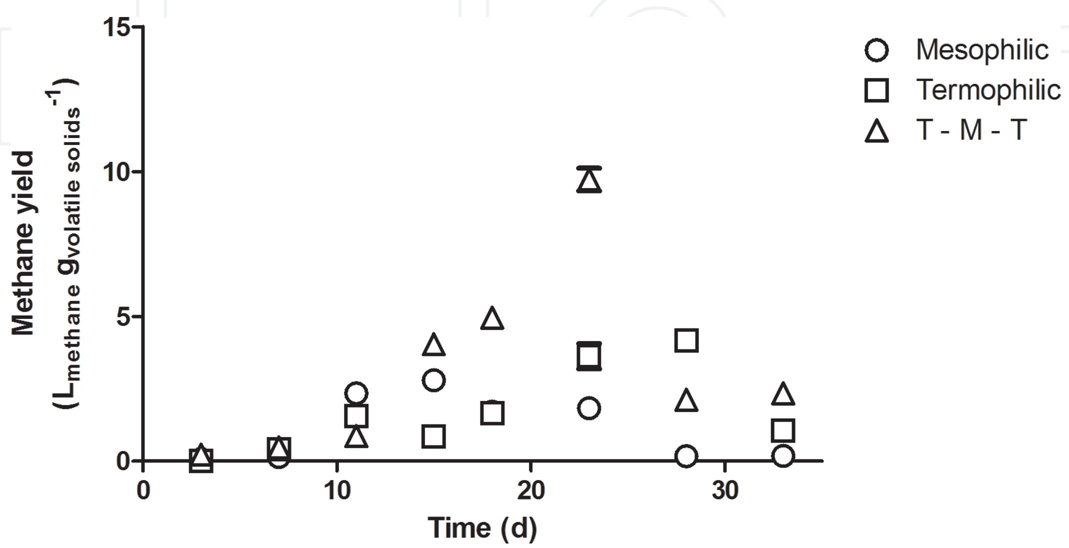

Figure 6.
Methane yields in the anaerobic digestion processes.

also too much difference in the investigations carried out on AD in the production of methane or biogas because it is not only the substrates or cosubstrates but also the influence on the operating conditions of the bioreactors such as temperature, time retention, organic loads, pH, and C / N ratio, among others. The scope in AD is to optimize the process with the best conditions that result in high methane yields. For this reason, this study serves as the basis for future research to work on the combination of lignocellulosic waste from a primary treatment in combination with secondary sludge from an activated sludge process, both resulting from the treatment of wastewater from the industry under study. During the anaerobic digestions, the mixture into the bioreactors was agitated because one of the AD main problems is the mixing of the substrates into the bioreactor. Bad mixing results in low methane production due to the non-homogenization of the substrates [45].

The reduction of volatile solids was observed in the three treatments reaching yields greater than 50%, being greater in the digestion of the three stages M-T-M. The biodegradation of the organic compounds depends on the substrates to digesting.

During the anaerobic digestions, the pH remained between 5.8 and 6.5 in the first 18 days later after day 20 the thermophilic and three-stage MTM digestions the pH increased above 7, which did not happen with the mesophilic digestion that reached a pH of 6.6. The variation of the buffer capacity was influenced so that pH in the mesophilic anaerobic digestion did not increase its pH beyond 6.6. At pH lower than 6.6, the growth rate of methanogens was reduced and the activity of archaea-methanogenic bacteria is reduced both at low and high pH's [46]. Even so, in anaerobic digestion, M was produced in biogas, with 45% methane. For the other T and M-T-M digestions above 50 and 60% methane were obtained, respectively.

The samples in the three anaerobic digestions showed ammonia concentrations lower than 5000 mg L^{-1}, which represented avoiding the inhibition of the VFA during the digestions [47]. It is observing that during the digestions the VFA decreased during the process however, in the M digestion the production of VFA was lower.

The temperature influences VFA production. It has been reporting that at thermophilic temperatures, VFA yields are higher due to faster acclimatization and more active acidogenesis, than at mesophilic temperatures [48].

However, there are other authors [49] that at thermophilic temperatures of 45 to 70°C it does not affect the production of VFA, finding controversies and inconsistencies in research due to the difference between microbial species, raw materials or substrates to be digested. Likewise, the use of different methodologies in AD affects the methane yield in equivalent substrates, making their comparison difficult [50–52]. The thermophilic process presents a better performance at the beginning than the mesophilic digestion due to the accelerated process of hydrolysis [53]. Higher methane yields are produced in the T and M-T-M, the latter having an advantage over the thermophilic since more than 60% of methane was obtained, which is considered biogas rich in methane [54]. Fecal coliform analyzes were performed during anaerobic digestions to determine their stabilization. Thermophilic digestion is a proven technology to produce class "A" biosolids, NOM-004-SEMARNAT-002. Where it turned out that the T and M-T-M digestions manage to obtain a biosolid with fecal coliforms lower than the norm.

4. Conclusions

The sludge generated from the paper process contains a high content of cellulose, which can be used by some microorganisms present in the secondary sludge. These microorganisms could be used as a potential raw material for the production of methane [15, 42].

Anaerobic digestion of the primary and secondary sludge showed promising results for methane production. The research carried out with a mixture of primary and secondary sludge is to increase the yield of biogas and methane, since each one of the substrates provides different physicochemical and biological characteristics. The primary sludge calorific value is high compared to the secondary sludge, and mixing both sludge benefited the anaerobic digestion process.

A higher methane yield was obtained in the digestion of three M-T-M phases with a value of 24.75 L of methane (gr of VS)$^{-1}$, also, a higher volume and percentage of methane, with values of 7000 mL and 67%, respectively.

The three-phase M-T-M process started with a pH value of 6.2 and was increased through digestion, reaching a pH of 7.6. The alkalinity was kept between 800 and 900 mg L^{-1}, making the digestion process tolerate changes during the anaerobic digestion phases. That allowed no accumulation of organic acids, which diminish the production of methane gas [55].

The reduction of volatile solids occurred in the three digestions, with the thermophilic phase presenting a larger removal with 52%, followed by the three phases with 47%, and finally the mesophilic with 30%.

It was found that thermophilic and three-phase digestion have advantages over mesophilic digestion related to the destruction of bacteria and pathogens [56] in this study. The thermophilic and three-phase digestion stabilized the sludge by destroying bacteria since in the thermophilic process and the three-phase M-T-M process, fecal coliforms were eliminated on days 15 and 12, respectively, classifying these sludge as Class A according to the official Mexican standard NOM 004-SEMARNAT.

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Conflict of interest

The authors declare no conflict of interest.

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