Anaerobic Digestion

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Anaerobic digestion is a well-known technology with wide application in the treatment of high-strength organic wastes. The oxidation of the organic material is carried out in the absences of oxygen by microorganisms leading to the release of biogas with methane and carbon dioxide being the main components. The microbial process also produces a slurry known as digestate. This stream contains recalcitrant compounds, complex polymeric substances and biomass residual material .

Keywords: biogas valorization ; lignocellulosic pre-treatment ; techno-economic performance ; process integration ; energy production

1. Introduction

Anaerobic digestion is a well-established technology for treating organic wastes with high water content and that are very prone to biological degradation. This technology has been applied worldwide thanks to its capacity to degrade high loads of organic materials and producing biogas. Wastes should be considered as “renewable resources” that can be used to generate new products [1] instead of outputs without any value. Biogas is the main energetic component derived from digestion, but the process also provides a side-stream product (digestate) that may not be so easily valorized. Proper transformation and stabilization of digestate can make this slurry a valuable organic amendment. Digestate has a high content of humic and fulvic substances and nutrients, making it ideal for agronomic use once its biological stability is improved [2].

The dramatic effect of CO_2 emissions on the global climate, the rapidly changing price of fuels, and social concerns about the depleted fossil fuel reserves, such as crude oil and natural gas, have increased the interest in producing bioenergy derived from biowastes [3]. Anaerobic digestion is a process capable of providing this bioenergy thanks to methane production via biological transformation of substrates. Digestion technology offers major benefits, providing eco-friendly energy and at the same time addressing the waste management crisis [4].

One of the most extended applications of anaerobic digestion technology is the integration of this process into wastewater treatment plants. Wastewater needs to undergo a series of treatments to meet the local allowable discharge limits. Sewage sludge is generated at the same time that the organic loading of wastewater is reduced. This sludge can be stabilized by anaerobic digestion, but it can also be treated in co-digestion reactors to adjust the balance of nutrients and attain economic feasibility of the global process [5]. Basically, digestion is carried out by microorganisms that stabilize the organic materials by transforming them into complex compounds less prone to uncontrollable degradation. This transformation produces a slurry of black or brownish color with a less offensive odor, which is also known as biosolids, if sewage sludge was the original organic material.

Biogas derived from anaerobic digestion can be valorized for producing thermal and electric energy. Biogas mainly consists of methane, carbon dioxide, and low quantities of trace gases. Its composition depends mainly on the type of substrate, process operating conditions, applied organic loading, hydraulic retention time and digester design [6][7]. Biogas can be transformed into biomethane once carbon dioxide is separated and other contaminants are removed. Eliminating these contaminants is of great relevance and this is particularly true for the removal of H_2S. This compound may cause serious corrosion problems and give rise to operability issues associated with its oxidation products. In the case of CO_2, the importance of removing this compound is based on the quality standard of biogas and the type of valorization technology this gas will be destined to [8][9][10].

Enhancing the efficiency of biological processes is of great relevance to increase product yield and process performance. The valorization of organics into energy allows one to reduce the carbon footprint of different waste management options. However, attempts for increasing the efficiency of anaerobic digestion do not always have a successful outcome. There exist several treatments for improving the degradation of organics to facilitate the hydrolysis stage. Thermal hydrolysis is a well-developed technology installed as a pre-treatment unit for enhancing biogas production in several wastewater treatment plants. The first full-scale plant for sludge disintegration through the Cambi process was started in Hamar, Norway, in 1995 [11]. Since then, this company has installed several other plants worldwide [12]. Other commercial technologies include BioThelys™, which is a batch technology just as it is the Cambi™ Process (Cambi, Asker, Norway) [13]. Haarslev is a continuous operating technology [14]. Other thermal hydrolysis processes use heat exchangers to increase temperature such as Exelys™ developed by Veolia Water Technologies (Veoli, Libourne, France) [15]. Turbotec® from DMT Environmental Technology (Tualatin, OR, USA) [16][17], and Lysotherm® from Eliquo Water and Energy BV (Barneveld, The Netherlands) [18] are also other commercial technologies available.

Other pretreatments intended for improving hydrolysis include ultrasonication, available at a commercial scale, whereas other treatment options such as microwave pre-treatment, electrokinetic and high-pressure disruption are mechanical pre-treatments studied mainly under laboratory conditions or using small scale prototypes [19][20][21][22][23]. Other pre-treatment methods include the use of chemicals—acidic, alkali, ozonation—[24][25], and the application of advanced oxidation processes [26][27], and biological options (temperature-phased anaerobic digestion and microbial electrolysis cell) [28][29][30] or combinations on any of the above to increase the effectiveness of solubilization. However, the capacity of recovering the heat of the thermal hydrolysis process makes this technology superior when evaluating the efficiency in energy use. The valorization of biogas by using combined heat and power (CHP) units allows for exhaust gas heat to be recovered in a recovery boiler [31], thus fulfilling the thermal needs of the hydrolysis pre-treatment.

The extended application of anaerobic digestion and the high costs associated with these installations have given rise to extensive research activities to increase the efficiency of the process, enhance biogas production and attain economic feasibility. The evaluation of anaerobic digestion of sewage sludge with different substrates has been widely reported in the literature [32][33][34], and it is still under extensive research. There are plenty of reports evaluating the co-digestion of sewage sludge with solid organic wastes, high strength organic streams and different compounds acting as supplements to favor organic degradation [35][36][37]. Regarding this last subject is the addition of conductive carbon materials—char, graphene, graphite, activated carbon—to the digestion process that has gained recent interest. The addition of these materials favors direct interspecies electron-transfer and increases the degradation of volatile fatty acids and proteins [38][39].

Several factors influence the global performance of a process; therefore, a great variety of key points and interacting relationships need to be evaluated for optimizing efficiency and energy recovery. To approach a decarbonized economy by 2050, efficient bioenergy production is essential—playing a major role will be recycling and reuse—towards a “circular economy”. However, as Valero and Valero [40] stated, absolute circularity in transformation processes does not exist, and this is based on the second thermodynamic law dictating that, in each cycle, some quantity and quality of materials is unavoidably lost. Thus, performing energy balances associated with the conversion of biomass would allow establishing processing routes with minimum energetic constraints. When energy is transferred in the form of heat it has a certain quality; this quality can be lost partly or completely by the heat transfer process. The quality of the transferred energy can best be quantified by the “exergy” concept in which energy is divided into two parts: exergy, also called “available work”, is the maximum theoretical work obtainable from the energy [41]. Thus, exergy analysis reflects the theoretical maximum performance of energy because it is based on the first and the second law of thermodynamics, putting emphasis on energy amount and quality at the same time [42].

Animal manures are usually treated by anaerobic digestion, a residue with high organic content but also with high N concentration, which may inhibit methanogens due to the accumulation of ammonia nitrogen in the reactor. Anaerobic digestion is also widely applied to treating the organic fraction of municipal solid wastes (OFMSW). In this case, the presence of improper materials and relatively high concentrations of heavy metals may add complexity to pre-treatment operations intended to prepare a homogenous feeding slurry. The difficulty associated with the separation of inert materials and the contamination with toxic elements make this digestate not suitable for agronomic use. The application of anaerobic digestion for the conversion of crop wastes and agro-industrial wastes is also a suitable management option. Still, the process needs to confront the seasonal availability of these materials, which is restricted to a short period of the year. The disadvantage of low nitrogen levels, which may cause nutrient deficiencies, and the need to apply long residence time in the reactor should be added.

The addition of a co-substrate allows the adjustment of nutrient balance, improves the stabilization of organic matter, and results cost-effectively because different substrates share the same installations [43][44] with the mixture with higher biogas yields. As a consequence, co-digestion is expected to increase the efficiency of the process between 25 and 400% when it is compared to the degradation of a mono-substrate [45] thanks to the increments in organic loading, enhancement in volatile solid removal and higher biogas productivity.

2. The Effect of Substrate Composition and Digestion Performance

Carbohydrates are present in all types of substrates and particularly plant-derived biomasses and food industry wastes. Substrates from the food processing industry, catering and residential activities are characterized by a readily degradable fraction, which is easily acidified. In recent years, changes in consumer demand have been observed due to preferences for a healthier lifestyle leading to the development of a new market offering fruit and salad products ready to eat. This affects the characteristic of waste produced and represents new valorization opportunities [46]. Another important change in consumer preference has been caused by the global pandemic due to the strict confinement of the population in many countries. These restrictions led to a sudden change in waste composition and an important decrease in the demand of energy [47]. Once the severe spring confinement period has ended, the attempts for reactivating the economy have been intermittent due to the recurrent appearance of infection spreading. This will probably change in one way or the other consumption trends and therefore the quantity and quality of wastes produced.

Fruit and vegetable wastes have high content of saccharides and disaccharides that are easily degradable by anaerobic microorganisms forming volatile fatty acids (VFAs) as intermediaries. When carbohydrates represent a large proportion of the feeding stream, a suppression of methanogenesis may be experienced with the overloading of the digester due to an initial VFA build-up leading to a decrease in reactor liqueur pH [48]. This VFA imbalance may negatively affect the production rate of biogas. This is particularly true for systems working under a feeding recipe where the loading of the reactor is performed in a cyclic manner during short periods of the day [49]. Thus, the biogas production rate is increased right after the feeding procedure, then proceeds at a slower rate until the next feeding procedure starts again. Lower methane composition may be experienced, or variations in production rate are expected based on the accumulation of VFA caused right after the feeding has taken place. Labatut et al. [50] studied the behavior of different types of substrates and their performance when evaluating biochemical methane potential (BMP) tests reporting on different cumulative methane curves with a particular shape directly related to the degradability of substrates. Thus, when operating a digester, special care should be taken on substrate degradation rate, acidification potential, and punctual loadings of the reactor, rather than setting as fixed operating parameters the organic loading rate and hydraulic retention time.

The high acidification potential of carbohydrate-rich substrates, when treated under anaerobic digestion, has aroused interest in transforming the hydrolysis–acidification stage into a fermentative process for hydrogen recovery. The evolution of hydrogen from fermentation is a ubiquitous phenomenon under anoxic or anaerobic conditions, where the oxidation of the organic matter releases electrons that need to be disposed of to maintain electrical neutrality [51]. In these environments, where no oxygen is available, other compounds act as electron acceptors, and therefore, protons are reduced to molecular hydrogen (H_2) [52]. Dark fermentation, also known as the fermentative production of hydrogen, resembles anaerobic digestion due to its flexibility in assimilating different substrates, with wastes being also the preferred option when considering large-scale implementation [53][54]. In this case, hydrogen is produced from strict and facultative anaerobes (*Clostridia*, *Micrococci*, *Methanobacteria*, *Enterobacteria*, etc.) [55].

The sequential production of H_2 and CH_4 has been proposed as a way to increase the economic feasibility and energy recovery of waste treatment plant [56][57][58]. This configuration is a logical approach since both processes have similar capabilities of treating the same type of substrates. However, a second stage is always necessary when producing hydrogen by this fermentation route because acid intermediaries (short-chain fatty acids) and solvents may accumulate in the fermentation broth in the first stage, needing further treatment to stabilize the organic matter completely. The recovery of hydrogen in the first stage and the production of methane in the second one is a more efficient way to extract energy from organics. The mixture of natural gas supplemented with hydrogen is called hythane and its use in combustion engines presents better performance parameters regarding fuel consumption and emissions [59]. This explains the current interest in obtaining a mixture of hydrogen and methane from biological processes, called bio-hythene. Not only is the biological treatment enhanced, but also the final use of biofuels produced is highly benefited.

3. Co-Digestion to Increase Reactor Productivity

The co-digestion process can be seen as a promising way for improving the digestibility of cellulose and hemicellulose, balancing nutrients, and attaining buffering effects when high protein compounds are to be used as co-substrates [60]. Co-digestion may be balanced for optimizing methane production, therefore higher methane yields can be obtained for proper carbohydrates, proteins and cellulose ratios [61]. The fact is that large scale digestion plants have to deal with the near source of resources available in their surroundings all year round. Therefore, flexibility of the processing plant is of great relevance to attaining high biogas yields during the whole operating life given the intrinsic variability of available substrates, and options for balancing and establishing specific feeding recipes may not always be possible.

Tufaner and Avşar [62] reviewed the production of biogas when co-digesting different substrates, indicating that the most important premise for obtaining a significant biogas enhancement and producing high-quality digestate is evidently the use of high-quality feedstock. Some feedstocks may be difficult to digest or unsuitable for mono-digestion because of their unfavorable C/N ratios or high lipid content, thus would benefit from co-digesting with manures that have high protein content. Kitchen wastes are a resource prone to acidification and thus are suitable as a co-substrate when digesting manures. Li et al. [63] reported a 116% increment in methane yield when this co-substrate was added to the digestion of cattle manure. Food wastes and sewage sludge have also been proposed as co-digesting mixtures [64][65]. Another relevant co-substrate widely studied due to its high biogas yield and great capacity for boosting biogas production is crude glycerol derived from the biodiesel production process. Paulista et al. [66] reported a 77% increase when adding glycerol as co-substrate to sewage sludge digestion. However, despite its abundance, the price of crude glycerol in the market is still too high to be considered a feasible option [67].

Table 1 reports different values of biogas yields obtained under batch digestion tests and continuous operation. This table shows a great variability in values, with the lowest ones being explained by inhibitory conditions in the system [68]. Good management and treatment of agricultural and livestock wastes must be of vital importance for any country. Spain has a high potential in this field that should be better exploited considering that this country leads the production and export of fruit and vegetables from the EU-28 [69].

Some works have addressed the possibility of using fruits and vegetables to be co-digested with sewage sludge [70][71] or treating this rich carbohydrate and high-quality waste in a decentralized manner to obtain a digestate of outstanding quality for producing high-value agronomic materials [72][73]. When considering alternatives for the management of fruit and vegetable wastes, it is important to take into account the fact that its production is seasonal and, therefore, a large amount may be generated in short periods, and variations of the type of material are also dependent on consumer preference based on the season of the year. In either case, a flexible approach should consider the design of a waste treatment line capable of absorbing modifications in the incoming substrate. For this reason, it is more interesting to take advantage of synergies that may be established between the treatment of food waste and sewage sludge from wastewater treatment plants (WWTPs) that may exert a buffering effect in the operating dynamic of the reactor.

Table 1. Methane yields reported in literature for different substrates.

Organic Substrate	Specific Production Potential (M^3 CH_4/Kg VS) [1]	Reference
Livestock manure		
Pig manure	0.30–0.50	[74][75][76][77][78][79]
Poultry manure	0.03–0.11	[68][74][78][79]
Cattle manure	0.11–0.54	[80][81]
Organic industrial waste		
Slaughterhouse waste	0.20–0.80	[82][83]
Brewery waste	0.3–0.51	[84][85]
Sewage sludge (SS) and co-substrate		
SS	0.22–0.45	[35][86][87]
SS + grease	0.4–0.8	[86][88]

Organic Substrate	Specific Production Potential (M^3 CH_4/Kg VS) [1]	Reference
SS + glycerol	0.2–0.4	[89][90]
SS + food wastes	0.4–0.6	[64][91]
Energy crops		
Corn stover	0.30–0.40	[75][92]
Sunflower	0.20–0.40	[93][94]
Rapeseed	0.25	[75]
Wheat straw (steam explosion pre-treatment)	0.25–0.35	[95][96]
Rice straw	0.26	[97]
Grass: Napier grass, Canary grass, King grass	0.15–0.60	[98][99][100]
Microalgae and cyanobacteria biomass		
Microalgae *Chlorella* sp.	0.23–026	[77][101]
Microalgae *Nannochloropsis oculata*	0.3–0.35	[102]
Manure + *Arthrospira platensis*	0.48	[103]

[1] VS: volatile solids.

Proteins are abundant in all organic substrates but mostly in animal-derived wastes. Slaughterhouse waste, pig and chicken manure are residues that have a high content in this material. When treating slaughterhouse waste, ammonia accumulation in the reactor may become an issue if a balancing carbon source is not available in enough quantities. Another residue that should also be considered as good co-substrates is animal carcasses. The treatment of this material is under stringent regulations, but the risk associated with the transport of carcasses can be eliminated if livestock farms could arrange a way for safely treating this material before being used as feed in the anaerobic digester [104].

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