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Review

Recent Updates on the Use of Agro-Food Waste for Biogas Production

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Abstract: The production of biogas from anaerobic digestion (AD) of residual agro-food biomasses represents an opportunity for alternative production of energy from renewable sources, according to the European Union legislation on renewable energy. This review provides an overview of the various aspects involved in this process with a focus on the best process conditions to be used for AD-based biogas production from residual agro-food biomasses. After a schematic description of the AD phases, the biogas plants with advanced technologies were described, pointing out the strengths and the weaknesses of the different digester technologies and indicating the main parameters and operating conditions to be monitored. Subsequently, a brief analysis of the factors affecting methane yield from manure AD was conducted and the AD of fruit and vegetables waste was examined. Particular attention was given to studies on co-digestion and pre-treatments as strategies to improve biogas yield. Finally, the selection of specific microorganisms and the genetic manipulation of anaerobic bacteria to speed up the AD process was illustrated. The open challenges concern the achievement of the highest renewable energy yields reusing agro-food waste with the lowest environmental impact and an increment of competitiveness of the agricultural sector in the perspective of a circular economy.

Keywords: renewable energy; anaerobic digestion; agro-food waste; animal manure; plant technologies; co-digestion

1. Introduction

According to the European Union (EU) Renewable Energy Directive [1], the production of energy from renewable sources is becoming an urgent target to reduce the impact of greenhouse gases (GHG), mainly derived from fossil fuel combustion [2]. This directive by establishing an overall policy for the production and promotion of energy from renewable sources in EU, requires the EU to fulfil at least 20% of its total energy needs with renewables by 2020, to be achieved through the attainment of individual national targets. In addition, all EU countries have to warrant that at least 10% of their transport fuels come from renewable sources by 2020. On 30 November 2016, the Commission published a proposal for a revised Renewable Energy Directive to make the EU a global leader in renewable energy production and use by meeting the target of at least 27% renewables in energy consumption in the EU by 2030. The proposal specifies national renewable energy targets for each country, which define how they plan to meet these targets by national renewable energy action plans.

Among non-conventional energy resources (e.g., solar, wind, hydro-wave, geothermal and biomass) offering interesting opportunities as they are unlimited and cheap [3], biomass-produced biogas is able to provide high quantity of energy with significant Greenhouse gases (GHG) savings, as compared with fossil fuels [4]. According to the European Directive 2009/28/EC, the term biomass designates "the biological origin and biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste". Europe and Central Asia generated 392 million tons of waste in 2016, and about 31 percent of waste materials is currently being recovered through recycling and composting [5]. Thus, the development of a circular economy (CE) using innovative technologies to reuse and convert agro-food waste, may represent a multipurpose achievement in terms of renewable energy production and waste reduction. According to [6], biomass conversion may be achieved by thermochemical conversion (used for dry wood residues with C/N> 30 and humidity less than 30%), combustion (occurring in presence of oxygen with carbon oxidation), pyrolysis (used for biomass with less than 15% humidity), biological conversion, including alcoholic fermentation and anaerobic digestion (used for materials with a C/N ratio < 30 and a humidity > 30%). In particular, the anaerobic digestion (AD) of biomass provides a versatile renewable source of energy, the biogas, useful as a substitute for fossil fuels for both power and heat production [7]. The EU sustainability criteria have been extended to cover solid biomass and biogas used in large heat and power plants (above 20 MW fuel capacity) with a reduction in GHG emissions from biomass-based electricity and heat production to a level at least 80% and 85% lower than fossil fuels by 2021 and 2026, respectively.

This review focuses on the production of biogas obtained through AD from residual agro-food biomasses, analyzing the strengths and weaknesses of the different types of substrates and of plant technologies, as well as the most promising tools to improve AD efficiency, with the aim to identify the best process conditions.

2. Microbial Processes of Anaerobic Digestion

In anaerobic conditions, the digestion of different organic substrates operated by symbiotic microorganisms transforms organic materials into biogas, a mix mainly constituted by methane (CH_4) and carbon dioxide (CO_2) along with nutrients, additional cell matter, salts and refractory organic matter. This process is composed of four stages (Figure 1), where specialized bacterial consortia are responsible for the first three phases of anaerobic digestion (hydrolysis, acidogenesis and acetogenesis), whereas the fourth step, methanogenesis, is performed by groups of methanogenic archaea [8].

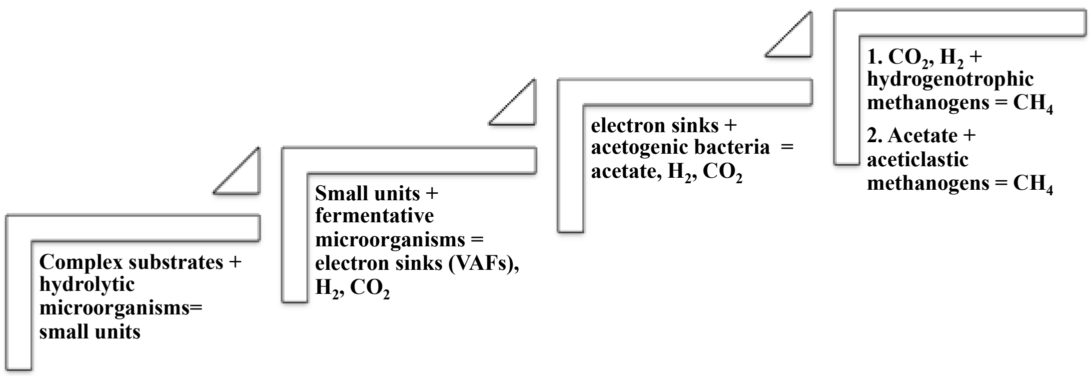

Figure 1. An overview of microbial processes involved in anaerobic digestion.

2.1. Hydrolysis

Hydrolytic microorganisms (Clostridium, Micrococci, Bacteroides, Butyrivibrio, Fusobacterium, Selenomonas, Streptococcus, among others) secrete enzymes, such as cellulase, cellobiase, xylanase, amylase, protease and lipase, that hydrolyze complex insoluble substrate, such as polysaccharides, into smaller units [9]. Cellulose is hydrolyzed to glucose, hemicelluloses are degraded into monosaccharides, such as xylose, glucose, galactose, arabinose and mannose, whereas the anaerobic digestion of solid lignocellulosic material represents the hydrolysis rate limiting step. However, substrate pre-treatments may break the polymer and speed-up the process.

2.2. Acidogenesis

Acidogenesis is usually the fastest reaction of the process where long chain fatty acids and amino acids, resulting from the previous step, are used as substrate for fermentative microorganisms (Streptococcus, Lactobacillus, Bacillus, Escherichia coli, Salmonella) to produce volatile fatty acids (VAFs), such as acetic, propionic, butyric and other short-chain fatty acids, alcohols, H_2 and CO_2. A pH decrease is generally induced by the production of VFAs, which is a beneficial condition for acidogenic and acetogenic bacteria with an optimal pH ranging between 4.5 and 5.5. The concentration and proportion of individual VFAs produced in this stage is relevant to the entire process, as acetic and butyric acids are the best precursors for methane formation.

2.3. Acetogenesis

The accumulation of electron sinks, such as lactate, ethanol, propionate, butyrate and higher VFAs, may promote an increased hydrogen concentration in the medium, which cannot be consumed directly by the methanogens and should be further degraded by the obligate hydrogen producing acetogenic bacteria. This process is referred to as acetogenesis. Syntrophobacter (propionate-utilizing acetogens) and Syntrophomonas (butyrate-utilizing acetogens) represent the major acetogens. These groups of bacteria are strictly anaerobe as they rely on the acetyl coenzyme A pathway, containing highly oxygen sensitive enzymes. The acetogenic bacteria can degrade the electron sinks to acetate, carbon dioxide and hydrogen, and this transition is fundamental for the successful production of biogas. During this degradation process, the anaerobic oxidation of butyrate and propionate has only to occur in syntrophic association with H_2-utilizing methanogens, which consume H_2 and CO_2 for methane (CH4) production, thus preventing the accumulation of H_2.

2.4. Methanogenesis

Methane is produced as a metabolic byproduct in anoxic conditions by the methanogenic microorganisms Archaea. Methane production can occur following two different pathways:

1. hydrogenotrophic methanogenesis, the most common metabolic pathway, where CO2 and H2 are transformed into methane;
2. the aceticlastic methanogenesis, where acetate is directly converted to methane.

Hydrogenotrophic methanogens play a key role in the overall process as Archea maintain a low partial pressure of H_2 (<10 Pa), necessary for the metabolic activity of aceticlastic methanogens and acetogens. Hydrogenotrophic methanogens, such as Methanospirillum hungatei, Methanoculles receptaculi, grow faster (doubling time of 6 h) than the aceticlastic methanogens, such as Methanosarcina thermophile, (doubling time of 2.6 days). As for pH value, the production of methane is affected by the low pH value. In order to support the growth of both acidifying and methanogenic bacteria, the pH value has to be above 6.6 and ideally 7–7.5 [10,11] as methanogens are very sensitive to environmental changes and prefer a slightly alkaline environment (at pH below 6 methanogenic bacteria cannot survive). Inhibitory compounds, such as sulphide, or lack of nutrients can negatively affect the growth and activity of these microorganisms, resulting in the accumulation of VFAs and a subsequent decrease in pH, which further inhibits the entire degradation process.

Biogas contains approximately 55–65% methane, 30–45% carbon dioxide, traces of hydrogen sulfide and a percentage of water vapor. The composition of biogas and the methane yield depend on the feedstock type; fats provide the highest biogas yield but require a long retention time, carbohydrates and proteins show much faster conversion but a lower gas yield. The production of biogas from any substrate, as well as by pH, is highly affected by its carbon to nitrogen (C/N) ratio, and temperature [12]. Nitrogen represents an essential element for the synthesis of amino acids. It is converted to ammonia with buffering effects on the volatile acids produced by fermentative bacteria, thus preserving optimal pH conditions for the process. The C/N ratio should be well balanced for a correct process and to avoid the failure of anaerobic digestion [7,13]. The C/N value should be in the range 15–30, with an optimal value of 25. If the C/N ratio is higher than 25, gas production will be low, whereas, if the C/N ratio is lower than 25, it will result in a pH value higher than 8.5 with toxic effects on methanogenic microbes [14]. A high C/N ratio can promote acid formation by inhibiting methane production, whereas at a low C/N ratio nitrogen is converted to ammonium at a faster rate than it can be assimilated by the methanogens [15], thus becoming toxic.

3. Anaerobic Digestion Plant Technologies

The EU is the world leader in biogas electricity production. The installed electric capacity raised in Europe from 4158 MW in 2010 to more than 10,000 MW in 2017 reaching the total number of 17,662 biogas plants [16]. The growth has been mainly due to the building of plants running on agricultural substrates. Agricultural plants are then followed by biogas plants running on sewage sludge (2838 units), landfill waste (1604 units) and various other types of waste (688 units) [17].

Plant technology depends strongly on the properties of the organic substrates and on the sector in which it is operated (biomasses, waste, sludge). The amount of available substrate affects the feeding system (i.e., continuous, semi-continuous, batch).

A first classification of the process can be based on the dry matter content of the organic matrix and on the temperature of the process. According to the dry matter content, the process may be divided into dry, semi-dry and wet, with solid substances higher than 20%, between 20–10% and lower than 10%, respectively. Dry anaerobic digestion may be the most appropriate process for the degradation of by-products with high total solid content, especially those coming from agriculture and food waste. However, this process is not widely used yet, compared with the wet process. Dry fermentation may potentially achieve a biogas yield similar to that obtained using the wet digestion process, although design and management of the plants can profoundly affect the efficiency of the process. Rheology, substrate heterogeneity, origin and maturity of inoculum, inhibition, co-digestion, pre-treatments and microbial dynamics are the main aspects to be considered when the dry process is applied [18]. Other relevant features include retention time, loading rate, and recirculation of digestate and leachate. Moreover, the operation of the plant requires relevant man labor, mainly related to loading and unloading of the anaerobic cells [19]. As a consequence, anaerobic digestion plants relying on wet anaerobic digestion are more common and preferred over those based on dry processes.

Anaerobic digestion can be carried out under mesophilic (about 35 °C), thermophilic (about 55 °C) or, more rarely, psychrophilic conditions (below 20 °C). The reaction temperature may affect the kinetics, the specific biogas production and the overall efficiency (Table 1). The duration of the process, in terms of hydraulic retention time, is 15–50 days, if the process takes place in mesophilic conditions, 14–16 days, if it takes place in thermophilic conditions, and 60–120 days in psychrophilic conditions. According to several experiences at full-scale level, the mesophilic process is easier to control, for that reason it is still the most common [20].

The AD process can be carried out in one or two stages, depending on the combination or separation of hydrolysis/acidogenesis and acetogenesis/methanogenesis phases, respectively. A two-phase configuration process in the case of food waste digestion significantly improves the methanogenic process as the fermentation plays the role of "pre-treatment", thus promoting the conversion efficiency of the volatile fraction to biogas. According to [21], the payback time for introducing a first digester can be less than 1.5 year. Therefore, the optimal conditions for AD would be thermophilic hydrolysis/acidogenesis and mesophilic methanogenesis, which is consistent with a two-phase anaerobic digestion process [22].

Anaerobic digestion systems were strongly improved in recent decades, through the introduction of accelerants (metabolic stimulants for microorganisms) in order to accelerate and increase gas production [22,23].

Table 1. Mesophilic versus thermophilic process *.

	Advantages	Drawbacks
Mesophilic process	▪ Free ammonia decreasing ▪ Less thermal energy required by digester, even if larger digester size should be considered ▪ Less nitrate concentration in the sludge ▪ Better process stability	▪ Higher retention time (30–50 days) ▪ Bigger digesters size ▪ Less degradation efficiency ▪ Lower pathogen removing from substrate, post-treatment is needed ▪ Higher viscosity of influent, pre-treatment is needed ▪ More clogging risk ▪ Low methane yield
Thermophilic process	▪ Lower retention time (15–16 days) ▪ Small size of digesters ▪ Higher organic load-bearing capacity ▪ Higher efficiency of degradation ▪ Higher biogas production rate ▪ Higher pathogen removing from substrate ▪ Lower viscosity ▪ Less clogging risk	▪ Higher free ammonia concentration ▪ Higher thermal energy required, but higher quantity of energy is produced from biogas ▪ Higher nitrate concentration in the sludge ▪ More sensitive to environmental changes ▪ Decreased stability process ▪ Larger investment

The AD plants can be divided into categories according to the reactor type. The main groups, ordered according to increasing innovation and complexity, are covered lagoons, conventional anaerobic reactors, sludge retention reactors and anaerobic membrane reactors. Advantages and drawbacks of each type of reactor are reported in Table 2a.

The most common AD plants are composed of one or more vertical heated reactors with an internal mixing system based on a wet process operated in mesophilic conditions. This type of digester is referred to a complete stirred tank reactor (CSTR) and represents the first generation of high-rate anaerobic digesters, which is widely used in the case of co-digestion of wastewater, high-dense liquid animal manure and organic industrial waste. The main limitation, if no recirculation is performed, is the failure to retain high microorganism concentrations inside the reactor. In fact, the key factor for a good anaerobic high-rate treatment is the retention of the slow-growing microorganisms. A new generation of reactor, such as the up flow anaerobic sludge blanket (UASB) reactor contains a well-settleable methanogenic sludge. The formation of a dense sludge bed permits the microorganism's retention inside the system. The advantages of UASB reactors over CSTR are compactness, higher loading rates, lower retention times, lower operational costs, lower sludge production and higher methane production rates (Table 2b). Since the anaerobic microorganisms can form granules through self-immobilization of the cells, the performance of the system is highly dependent upon the granulation process, together with the characteristics of the wastewater. However, substrates with a high fraction of particulate organic material cannot be treated using this technology [23].

Membrane bioreactors (MBR) technology is also able to promote the retention of the active biomass within the system (Table 2c). The membrane forms a selective barrier, thus allowing certain components to pass through while retaining the others. In particular, cells are retained, while inhibitory compounds, such as furan aldehydes and carboxylic acids, negatively affecting the biological process, are separated. However, when the particulate and cell concentrations are high, fouling can occur. The combination of anaerobic membrane technology with specific systems (coagulant addition, adsorbent addition, use of granular materials improving aeration) lead the membrane to work with high flow rates and may represent a further improvement of the technology. These integrated systems show several advantages, such as improved methane production and less frequent fouling problems. They can be used to treat high strength industrial and municipal wastewaters in order to achieve solids free effluents and a high efficiency in pathogen removal. However, further investigations are being conducted to increase the efficiency of anaerobic plants. The main issues to be addressed are module configuration, aeration systems, control systems, surface modifications, low-energy membrane cleaning and fouling mitigation methods [24]. Examples of novel strategies for mechanical cleaning are those based on the use of granular medium, membrane vibration and electric field.

Table 2. Comparison among different digester technologies.

(a) unstructured reactor versus conventional anaerobic reactor [22]			
Description		**Advantages**	**Drawbacks**
Unstructured reactor	Lagoons covered by flexible polymeric membranes	▪ Low cost ▪ Low tech ▪ Easy to construct	▪ Lowest gas production ▪ Least controlled system ▪ Longest HRT ▪ Cover maintenance and service life ▪ Large footprint ▪ Solids and nutrients accumulation
Anaerobic sequencing batch reactor—ASBR	Single tank fill-and-draw unit, used for treatment and fermentation OLR is variable	▪ Better process control ▪ Higher process efficiency ▪ Wide range of influent volumes ▪ Efficient quality control of the effluent ▪ Flexibility of use ▪ Low input process and mechanical requirements ▪ Cost-effectiveness ▪ High biogas yield	▪ Insufficient settle-ability causes by poor self-immobilization and biological gas in the sludge ▪ Channelling and clogging ▪ Larger volume ▪ Requires some type of agitation to improve mass transfer
Complete stirred tank reactor—CSTR	Intermittent or continuous complete mixing in one or more high-rate reactors, generally heated. Used for wet process.	▪ Reliability for wastewater, high-dense liquid animal manure and organic industrial waste ▪ Complete mixing ▪ Possibility of two-phase/two-stage system ▪ Simplicity of construction	▪ System sensitivity to substrates ▪ Complicated operation for two-phases system ▪ Not possible to retain high microorganism concentration ▪ Rapid acidification with high VFA production, due to mixing and continuous stirring
Anaerobic plug-flow reactor—APFR	Linear horizontal reactors, with no internal agitation, for dry or semi-dry process.	▪ Low VFA concentration in the effluent ▪ High degree of sludge retention ▪ Process stability ▪ Low retention time	▪ Not suitable for low suspended solids ▪ Low efficiency in case of high influent flow rate with inhibitors

Table 2. *Cont.*

(b) sludge retention reactor [22]			
Description	**Advantages**	**Drawbacks**	**Description**
Anaerobic contact reactor—ACR	Agitated reactor and a solid settling tank for microorganism recycling, generally in mesophilic condition.	▪ Efficient process ▪ Rapidly achieved steady-state times due to mixing ▪ Sufficiently short hydraulic retention time ▪ Limited biomass washout ▪ Low change in biogas concentration and composition ▪ Good for OLR higher than 8 kg COD/m^3/d with COD removal of 78–95%	▪ Dilute nature of the digestate with limited organic loading rate
Up-flow anaerobic sludge bed reactor—UASB	Dense sludge bed in the bottom for the wastewater-biomass contact	▪ Compact and inexpensive ▪ Less reactor volume and space ▪ Higher flow velocity and biogas production ▪ Higher organic load ▪ Lower retention time than AF ▪ No effluent recycling needed	▪ Performance largely dependent on the dense bacterial granules quality used as filter. ▪ Long start-up period ▪ Significant wash-out of sludge during initial phase ▪ Skilled operation ▪ High fraction of particulate organic materials are not suitable
Up-flow anaerobic solid-state reactor—UASS	Quadruple two-phase, two-stage reactor, with AF section, used for solid biomass, with dry process.	▪ Higher processing efficiency in terms of hydrolytic and methanogenic power ▪ Higher volume loading rate ▪ Lower investment cost ▪ Simple operation and management	▪ Feasible in a long-term process without significant disturbance ▪ Restricted use for colloidal substances ▪ Limited by its structure
Anaerobic baffled reactor—ABR	Compartments in one reactor, baffled to force incoming wastewater up through a series of blanked sludge	▪ SRT separated from HRT achieving good COD and solids removal ▪ Low sludge production ▪ Possibility of separating acidogenesis and methanogenesis ▪ High efficiency and flexibility at high loading rates ▪ Higher tolerance to hydraulic and organic shock loads ▪ Lower sludge yields ▪ No risk of clogging and sludge bed expansion	▪ Microbe wash-out from digester ▪ Inadequate mixing and settle-ability of the microbial granules ▪ Incompatibility with certain types of wastewater ▪ Long start-up phase ▪ Effluent requires secondary treatment
Internal circulation reactor—IC	It is similar to two UASB reactors working together, it can separate gas, liquid and biomass simultaneously	▪ Buffer capability to resist various shocking loads Lower cost and higher efficiency in polishing step ▪ Reducing of extra mixing costs ▪ Highest OLR achieved ▪ Good for low-strength wastewater at higher HRT	

Table 2. *Cont.*

(c) membrane reactor [22]			
Description	**Advantages**	**Drawbacks**	**Description**
Anaerobic filter reactor—AF	Biofilm to separate biomass from effluent, at up-flow or down-flow condition	▪ Excellent adaptability for biomass to a new carbon source and to organic load fluctuation ▪ Simpler solution for industrial application	▪ Clogging of filter media ▪ Higher investment costs ▪ Not suitable for wastewater with high suspended solids
Anaerobic fluidized bed reactor—AFBR	Small-inert particles used as the medium for bacterial attachment	▪ Higher OLR ▪ Greater resistance to inhibitors ▪ Good mass transfer efficiency ▪ More effective than AF ▪ Better hydraulic circulation ▪ Greater surface area	▪ Membrane fouling, especially due to proteins at low temperature ▪ Fluidization is still an empirical science ▪ Process improvement at large scale is needed
Expanded granular sludge blanket—EGSB	Modification of UASB reactor, used when volumetric gas production rate is low and mixing is insufficient It can separate gas, liquid and solid biomass simultaneously	▪ Suitable for small-medium size industry ▪ Smaller footprint than UASB ▪ Higher mixing due to higher up-flow velocity ▪ Improved mass transfer and biomass activity ▪ Higher organic and hydraulic loadings ▪ Suitable for wastewater containing lipids and toxic/inhibitory compounds ▪ Devices for precipitation separation, extra degassing and reflux not required	▪ Suspended solids cannot be substantially removed

3.1. Monitoring and Control of Plant Efficiency

An optimal management system for a biogas plant should allow a certain flexibility in terms of the hydraulic and organic load of substrates and a certain diversification of the types of substrates; disposal of waste; maximization of organic conversion efficiency in biogas/biomethane; production of good quality digestate and biomethane; reduction of the size of the plant and operating costs; reduction of the environmental impact.

Several parameters need to be monitored at full-scale level in order to promote the efficiency of the process through an adequate biogas production, being related to the improvement of biomass quality, best environmental conditions for microorganism's growth, and reduction of energy losses: operating parameters of the power supply system; digestion temperature; composition of the produced biogas; quantity of biogas introduced into the engine; pH of the anaerobic digestion process; operating parameters of the gate valves and pumps; operating parameters of the motor-generator group (voltage, current and power output, operating hours, emissions); global self-consumption of plant. The reference parameter commonly used by the biogas plant operator is either the annual production or, alternatively, the operating hours. A list of the main parameters is given in Table 3.

Anaerobic digestion is highly sensitive to process disturbances. The biological process can reach instability due to a variety of perturbations such as: overloading of organic or hydraulic rates; presence of toxic or inhibitory compounds; lack of nutrients for the growth of microorganisms; deviation from the optimal operating temperature. In order to facilitate the management and to favor the stability of the process, full-scale plants usually work with expanded and larger than necessary hydraulic retention times (HRT), and low organic load rates (OLR), both causing a reduced methane yield [25].

In order to optimize the process, even at high organic loads, the on-line monitoring and automatic process control techniques should be used to efficiently operate the AD process. There is no standardized monitoring method, in terms of fundamental parameters and optimal frequency of measurement, as several variables are involved in the process. Generally, a very small number of parameters are controlled, due to the complexity and cost of advanced monitoring.

Spanjers and Van Lier [26] visited approximately 400 full-scale AD plants, mostly used for wastewater treatment. In 95% of them, in-situ and on-line monitoring was limited to pH, temperature, water flow rate and biogas flow rate, level and pressure. Only 10% had continuous monitoring of COD, TOC, VFAs, alkalinity and biogas composition. Madsen et al. [27] verified that many plants operate on the basis of ex-situ analysis and only sensors for pH, redox potential and percentage gas production were used either in situ or on-line. The main issue is the identification of the most critical parameters for early detection of instability. For example, in Li et al. [28], a combination of volatile fatty acids (VFAs), VFAs/total alkalinity (TA) and alkalinity per bicarbonate ion (BA)/TA was proposed as a parameter setting for early warning. Li et al. [29] showed how the formation of hydrogen H_2 and hydrogen sulphide H_2S were also very sensitive to changes in organic load, and useful for evaluating overload problems that would cause a pH decrease. Recurring problems are also related to the type of sensors chosen and the best positioning to ensure correct monitoring and facilitate maintenance. Several electrochemical, chromatographic and spectroscopic devices (UV, VIS, IR/NIRS) can be used for on-line monitoring in order to generate early warning signals and permit specific actions of correction. Among them, the most promising method is NIRS spectroscopy because a large number of parameters can be measured at the same time [30]. However, in the case of small plants (i.e., below 100 kW) this method is still too expensive.

Together with specific sensors, an automatic control system is needed for process monitoring purposes. According to Nguyen et al. [31], a simple monitoring system can be coupled to an advanced control system (for example, adaptive method, fuzzy logic, neural network or hybrid systems), or an advanced monitoring system can be coupled to a more simplified control (ON/OFF, Proportional Integral Derivative control). The basic theory of advanced control is divided into feedback (e.g., cascade control) and feed forward (adaptive control or predictive control). The advantage of feedback control is its simplicity, but in that case the correction happens only after the error has occurred. Feed forward system could be implemented to make correction before the disturbance affects the process. However, these advanced control systems require complex algorithms and mathematical expertise.

In addition to the optimization of the AD plant and process, attention should be paid to the supply chain of the substrate, most suitable pre-treatment techniques and final use and post-treatment of both digestate and biogas. According to Grando et al. [32], a simple monitoring system can be coupled to an advanced control system (for example, adaptive method, fuzzy logic, neural network or hybrid systems), or used in order to check some relevant aspects of the biogas chain including pre-treatment processes of new substrates, new uses of biogas for natural gas distribution networks, fuel cells and fuel for vehicles (instead of just Combined Heat and Power).

3.2. Economic Considerations about Biogas Plant

Total costs for the realization of a biogas plant must be distinguished between initial cost (capital cost) and operating cost. The capital costs are those necessary for the construction (components, sensors, building work), and are strictly related to the characteristics of the plant (batch, continuous or semi-continuous). For AD process, the following voices are taken into account: (a) feedstock handling and storage; (b) building and operating the digester, with heat and power generation; (c) handling and storage of the digestate.

Several studies reported the results of the estimation of total cost related to biogas plant and equipment [33]. Capital cost could be estimated in a range between USD 300 and 800 per m^3, USD 2400–7500 per kWe and USD 5000–7500, referred to the digester volume, to the installed electric power, and to the hourly produced biogas volume, expressed as Nm^3/h, respectively.

Considering the biogas upgrading, the investment cost varies from USD 1950 to 2600 per Nm^3/h, for raw gas capacities larger than 800–1000 Nm^3/h. Generally higher costs are observed for smaller-scale equipment [34].

The operating cost of the plant depends both on the ordinary and extraordinary management costs. The first cost item includes the cost for the production (for energy crops), management and storage of substrates to convert, and the energy cost for operating the plant (e.g., maintaining a constant temperature). The second cost item comprises the costs for periodic maintenance, commonly estimated in the range 3–10% of the investment cost.

Incomes refer to the price recognized by the national Electrical Service Authority for the amount of electricity introduced into the grid, plus any production incentives, now present in different countries, but destined to disappear completely in the future.

As for plant technology, AD operating in wet conditions (≤10% dry matter) requires less capital investment and anaerobic digesters based on wet biomass input typically convert 30% to 60% of the biomass to methane.

In dry conditions (dry matter between 15–20%), facilities require less operating energy, due to the total amount of water to be heated, if compared to wet conditions, and the system provides more gas per unit of feedstock.

Moreover, digesters can operate in continuous flow or in batch flow, and digestion can occur in single- or multiple-step digesters; although multiple digesters allow higher efficiencies for each digestion phase, they require higher investment costs [35].

4. Agro-Food Substrates for Anaerobic Digestion

4.1. Livestock Manure

Manure from farming animals has been traditionally reused as fertilizer, providing a nitrogen and phosphorous source for plants and crops. However, accumulation of carbon and leaching of nitrogen and phosphorous may produce negative environmental impacts. After enteric methane (CH_4), manure represents the second largest source of GHG emissions in intensive dairy cattle [36] and buffalo farms [37]. The total amount of methane released from animal manure is 18 million tons CH_4 per year [38] with a breakdown of 2200 to 12,000 g CO_2-eq for collection, 200 to 2400 g CO_2-eq for transportation, 16,000 to 84,000 g CO_2-eq for storage, and 16,400 to 33,500 g CO_2-eq for land application, depending on the practice and farm size [36]. In addition, volatilized ammonia (NH_3) from manure (up to 70% of excreted nitrogen) can remain as residual in water and terrestrial ecosystems or be converted into N_2O emissions, contributing to both eutrophication and climate change [39].

Anaerobic digestion of animal wastes for biogas production, offers environmental benefits as it can reduce GHG emissions related to manure management by more than 50% [40] and by replacing on-farm fossil fuel-based processes with electricity produced through AD [41]. In addition, AD may represent a supplementary source of income for farmers as renewable energy is produced and the residual digestate has high fertilizing properties. One aspect to be considered is that AD has only minor effects on substrate nitrogen content. Therefore, this process gives no advantages in terms of compliance with the nitrates directive (91/676/EEC) [42].

Animal manure is a mixture of excreta (feces and urine) and materials added during management, such as sand, water from cleaning, straw and other bedding materials and, as other material used as biogas substrate, should satisfy different requirements in terms of suitability, digestibility and absence of inhibitors and impurities [43]. Suitability of a substrate for AD depends on the levels of total solids (TS) and volatile solids (VS), the carbon to nitrogen ratio (C/N) and pH. Livestock manure is usually in a liquid form with a dry matter content (DM) of 1–10%. Dry matter content is a key parameter to design the biogas reactor size and capacity [44]. Too diluted animal manure reduces economic feasibility, whereas too high DM (e.g., higher than 15%) may cause operating problems. An optimal DM content is about 10% and it may be corrected by co-digestion with other solid organic substrate such as energy crops with the aim to enhance biogas yield [45].

Table 3. Main parameters used to check the efficiency of anaerobic digestion plants [40].

Parameter	Unit	Description, Range and Measurement Method
Process stability		
Temperature T	°C	• 25–40 °C (mesophilic systems—optimal 38–40 °C) • 45–65 °C (thermophilic systems—optimal 55 °C) • <25 °C (psychrophilic or cold-rare systems) Variations of only 2–3 °C within the optimal range can affect performance. Measurement during process by i.e., thermocouples
pH	-	Neutral environment, between 6.5–7.5, acceptability 6–8. Measured by pH meter or pH/redox electrode sensor
Volatile Fatty Acids VFAs	mgAc/L	A significant increase highlights a malfunction; it can lead to a drop in pH (acidosis), which also leads to an irreversible block of the process. Typical range 200–2000 mgAc/L. Measured by UV/FTIR-IR spectrometer, gas chromatography or indirect by COD.
Alkalinity TA	mg $CaCO^3$/L	Buffer capacity of the system which contributes to guarantee neutral pH. A stable system has values in the range of 2500–5000 mg CaCO3/L. Direct measure with NIRS or titration, indirect through redox potential sensor and electrical conductivity
VFA/TA	-	Ratio value < 0.3 indicates the stable operation of the digester.
Reactor management		
Operational pressure P	mbar	Measurement during process
Capacity V	m^3/d or t/d	Measurement of mass or volume per day
Reactor volume Vr	m^3	Determined by design/construction
Hydraulic retention time HRT	d	Ratio between the volume of the reactor considered and the flow rate to the reactor. Calculation from process data, indirect by measuring the incoming flow.
Sludge Retention Time SRT	d	Ratio between the total mass of volatile solids in the reactor and the flow of solids extracted from the reactor. Indirect by measuring concentration and flow rate SV.
Organic Load rate OLR	Kg or TS/m^3 d	Quantity of input substrate (influent flow rate), calculated by concentration of organic substance and referred to the volume unit of the reactor. Indirect measurement by flow measure and organic substance concentration (sample weight for ST, SV, or COD and BOD measurement)
Substrate removal efficiency	%	Function of the SV concentration in the influent flow rate (kg/m^3) and SV concentration in the effluent flow rate (kg/m^3)
Biogas flow rate	Nm^3/d or Nm^3/y	Output biogas flow. If connected to the flow and concentration of the incoming substrate, it is called a specific production (m^3/m^3). Measurement during operation by flowmeter.
Methane concentration CH4 and biogas composition	%	% CH4 - %CO2 - %H2S - O2 – other Measurement during operation by electrochemical or IR spectroscopic method

Table 3. *Cont.*

Parameter	Unit	Description, Range and Measurement Method
Plant efficiency		
Gross Energy	kWh	Calculated from biogas flow and methane concentration using Low Heating Value
Electricity production	kWh	Measurement at power unit
Output to grid	kWh	Measurement after power unit
Efficiency of power unit	%	Calculation from operating data
Thermal/electric station supply	kWh	Calculation from operating data
Thermal/electric specific station supply	kWh/m^3	Calculation from operating data
Energy production	kWh	Sum of energy that can be used
Plant efficiency	%	Net energy drawn from gross energy
Plant availability	%	Percentage of hours a year in which it is fully functioning
Use	%	Ratio of the real input to the designed capacity
Total investment	€	All expenses
Funding	€	Pre-determined
Funding percentage	%	Percentage of all subsidies in relation to the total investment
Specific investment	€/m^3	Calculation from operating data ...
Specific treatment cost	€/m^3	Calculation from operating data ...

The concentration of substrate is a significant operating factor affecting the stability and methane yield of the AD process of manure. Nevertheless, an excessive substrate concentration could slow biogas process due to accumulation of inhibiting elements (i.e., total ammonia, free ammonia and volatile fatty acids). A negative relationship between initial substrate concentration and methane content in final biogas volume was observed by Alzate et al. [46]. Another study reported that when substrate concentration was increased from 8 g VS/L to 64 g VS/L, the methane yield and biodegradability were both decreased by 22.4%, 37.3%, 49.1% and 34.6% for pig, dairy, poultry, and rabbit manures, respectively [47]. Although the levels of VS indicate the methane potential in a substrate, they do not provide information on its degradability.

Thus, the ultimate methane yield from manure (Table 4), in addition to the process parameters of the plant, may be affected by several variables, such as animal species, animal diet, and the related nutrient digestibility and intestinal microorganisms, management system, amount and type of the bedding material, along with the storage conditions prior to the AD process [48].

The trend of the AD process is also related to the different origin of livestock manures. In fact, with horse, sheep, and goat manures, after gradual rise in gas production, the peak is reached up to the 3rd week [49], while with pig manure this peak is achieved at the 4th week and in the cow manure at the 5th week; after this time, there is a gradual decline in gas production in the cow manure. The poultry manure provides a high amount of gas in the first week, this is then followed by a sharp decline by the 3rd week, and subsequent weeks show alternate rises and falls in the rate of gas production.

Table 4. Characteristics of manure from different livestock species.

	pH	TS%	VS%	C/N	BIOGAS YIELD
Cattle manure [47,50–56]	5.33 ÷ 8.30	9.4 ÷ 22.75	10.25 ÷ 93.11	10.5 ÷ 26.64	169 ÷ 270 mL/gVS
Pig manure [47,50–55]	6.9 ÷ 7.87	5.4 ÷ 92.10	26.93 ÷ 80.2	6 ÷ 18.91	318 ÷ 409 mL/gVS
Goat manure [55,57]	8.13	81.63 ÷ 97.1	64.01	16 ÷ 20	-
Sheep manure [54,58]	7.8	17.4 ÷ 37.03	16.3 ÷ 76.49	-	0.572 ÷ 1.468 Nm^3/kg VS
Poultry manure [47,51–55]	6.63 ÷ 7.95	42.9 ÷ 90.15	47.5 ÷ 84.46	3.8 ÷ 14.44	192 ÷ 377 mL/gVS
Horse manure [55,59]	8.25	33.49 ÷ 53.38	30.40 ÷ 46.65	22.63 ÷ 40.12	0.164 ÷ 0.212 Nm^3/kg VS
Rabbit manure [47]	-	27.84	87.94	17.9	211 ÷ 323 mL/gVS

4.1.1. Cattle Manure

Although the anaerobic digestion of cow manure may give approximately 63% of biogas yield [60], ruminant manure, in general, and cattle manure, in particular, may be conveniently used to prompt the fermentation phase of AD, because it may provide the required methanogenic bacteria. However, the fermentation of manure as single substrate provides low methane yield, due to a moderate anaerobic biodegradability of about 45–50 % [61]. Moreover, the biogas production from cattle manure is lower than that obtained from other farm animals, since cattle manure often contains an excess of lignin complexes from fodder that are very resistant to AD [62]. Low biodegradability of animal manure is often caused by large amounts of indigestible fractions such as lignocellulose, an element of the plant cell wall, residual from animal digestion, and composed by hemicellulose, cellulose and lignin. Lignin is a natural complex polymer and non-carbohydrate constituent of wood bond to cellulose fibers and it provides mechanical strength and structural support to the plants. Lignocellulose is very difficult to be degraded in anaerobic environments due to its rigid structure produced by lignin. Numerous studies have reported that lignin content and the efficiency of enzymatic hydrolysis have an inverse relationship [50].

Due to the different diets, dairy cow manure generally shows the most abundant amount of lignin (i.e., around 18.0 %), whereas manure from beef breeds contains a lower amount of about 13% [50]. Other authors [47] found a content of lignin in dairy manure of 7.95%, while in pig and poultry manure it was 1.83% and 1.7%, respectively.

Therefore, the extent of biogas production from cattle manure may be affected by management and, in particular, by the diet of the animals as in most cases they are fed on large amounts of substrates containing structural carbohydrates (cell wall components), which result in lower biogas production [63]. On the contrary, feeding cattle diets containing high levels of concentrate increases the biogas production from manure, due to the generation of higher levels of soluble organic-C during anaerobic digestion [63,64]. Accordingly, Costa et al. (2016) [65] observed higher biogas yield in young bulls fed on a high concentrate diet (80% concentrate + 20% forage) corresponding to high levels of net energy.

Comparing organic and conventional management in dairy farms, Matos et al. [66] observed higher biogas yield from cow manure produced by dairy herds under the conventional production system compared to AD with cow manure under the organic production system. These differences in methane yield may be due to the different diet fed to the animals, as in the conventional management diets are based on concentrate that provided more appropriate substrates for the AD process than organic diets, mainly based on roughage.

Animal nutrition also affects the composition of manure-derived bio-fertilizers, altering the levels of the macronutrients N, P, and K [64].

Although high water content and high fraction of fiber make cow manure an unsuitable substrate for the production of biogas as single substrate [67], it may be an excellent “carrier” substrate for the mixed digestion of wastes, allowing AD of concentrated industrial waste, which could be not treated separately [67]. Its suitability to be used as “carrier” substrate is due to high water content (70–90 %), acting as solvent for dry waste materials, high buffering capacity [68] with beneficial effects on the pH in the reactor, and the high level of nutrient for optimal bacteria growth [67].

As to C/N ratio, Table 4 shows that C/N ratios of cattle manure can vary between 10.5 and 26.64. The suitable range for a regular AD process is between 20 and 35 [69]. However, according to Zhu [70], AD could be carried out efficiently even when the C/N ratio is 15 and Kumar et al. [12] observed that any C/N ratio ranging from 13.9 to 19.6 might be adequate for digestion.

4.1.2. Horse Manure

The amount of organic matter (VS) in horse manure is 30–47% (Table 4). As for cow manure, horse dung has a high proportion of slowly degradable lignocellulosic organic material, related to the diet, bedding material used, and the frequency of stall cleaning. The studies on horse manure as a biogas substrate focus on solid state anaerobic digestion (SS-AD) due to the high total solids and fibrous content, which makes this manure unsuitable for continuous slurry-based biogas reactors [71]. SS-AD is suitable for lignocellulosic material but shows drawbacks concerning low VFAs formation, ammonia accumulation and difficult mixing [72]. Straw is the most widely used bedding material for horse stalls, although, other materials such as sawdust, wood pellets and flax straw are also achieving interest [73]. Methane production from horse manure is very variable and is mainly affected by the feeding intensity and by the type of the forages [45]. There are contrasting results about the effect of using different bedding material on methane yield of horse [59,73,74]. The highest specific methane yields for horse manure was achieved with straw pellets as bedding material. The storage of the manure resulted in significantly lower methane yields [59]. However, due to the high total solid content, horse manure may be used for mixed digestion with low solid content substrates [75]. In addition, the high C/N ratio of horse manure makes it a good co-substrate for the AD of nitrogen rich substrates such as pig and poultry manures [59].

4.1.3. Poultry Manure

Poultry manure has a high potential organic substrate (20% or more of DM) for treatment; however, the higher nitrogen content compared to manure from other farm animals (Table 4) makes it problematic for the AD process [76]. Ammonia inhibition is a common problem for the AD process using substrates such as poultry litter [77], and swine manure [78]. The inhibitory effects of free ammonia on the metabolism of methanogens were observed by several authors [79]. Commonly, to avoid ammonia inhibition, poultry manure is diluted with water [80] to decrease the high percentage of total solids (Table 4); however, this technique will decrease the biogas production per unit of fermenter volume, and increase the consumption of water and the processing cost for the slurry discharge. In other studies, the co-digestion of poultry manure with other types of livestock dung, such as cattle manure [81], swine manure [82] or with other substrates, like rotten potatoes [83] has been evaluated. Alternatively, in order to use chicken manure as a single substrate, the technical stripping of ammonia can be applied to evaporate ammonia into the gas phase [84].

In addition, the use of diets integrated with exogenous enzymes and probiotics for broilers reared in cages produced a high biogas yield, with possible benefits for the AD process, which may cause an inducted positive artificial environment for the process [85]. It may be considered as a pre-treatment stage, promoting the hydrolysis of substances present on the excreta and allowing higher performances of the microbial population in the subsequent steps.

4.1.4. Pig Manure

The concentration of lignin in VS of most animal manure is larger than 10% except for pig fattening slurry, whereas the lignin may be higher for sow slurry [50].

This manure is another source of organic matter used as substrate in AD for bacterial growth. It has a high buffering capacity, protecting the digestion process against possible problems due to the presence of volatile fatty acids and any consequent drop in the pH of the system. However, due to its high nitrogen content relative to available organic carbon (Table 4), it may produce a toxic level of ammonia; in addition, it has a large amount of water and very low VS concentration. These characteristics make pig manure unsuitable for AD as single substrate. Thus, co-digestion with additional substrates with high organic carbon should be considered [86]. Co-digestion with energy crop residues such as maize, rapeseed or sunflower residues, for example, resulted in an increase of the amount of biogas produced daily, particularly with maize residues [87].

4.1.5. Inhibitory Substances in Livestock Manure

In the AD process, acetogenic and methanogenic bacteria are different in many traits such as physiology, nutritional needs, growth kinetics, and sensitivity to environmental conditions. A modification in the balance between these two groups of microorganisms may cause reactor instability and this problem is often caused by the presence of a large quantity of inhibitory substances. Among the residues in manure showing inhibitory effects on the AD processes, antibiotics are the more problematic and widespread as they are often used for therapeutic in and sub-therapeutic purposes in confined animals [88], although the European Union (EU) has definitely banned the use of antibiotics for growth promotion in animal feed since 2006 (Regulation EC No 1831/2003) [89], as antibiotic residues in animal manure are of considerable concern for the potential development of antibiotic resistant bacteria in the environment.

Contrasting results were obtained on the effect of antibiotic residues on methane yield. For example, Masse et al. (2000) [90] found that penicillin and tetracycline could decrease methane production, whereas other studies found that oxytetracycline (OTC) had a minor inhibitory effect on methane production during the anaerobic digestion of dairy manure [91]. Low levels of antibiotics, such as tylosin, lincomycin, sulfamethazine, and carbadox did not significantly affect methane production from swine manure, whereas significant effects were observed at high antibiotic concentration [92,93]. Dairy manure and waste milk from cows treated with cefazolin for mastitis problems were conveniently used as substrates for biogas production with significantly higher methane yield as compared with dairy manure alone. Beneragama et al. [94] found that added cefazolin (10 mg$\cdot$L^{-1}) did not affect the total and methane gas yields. Mitchell et al. [95] studied the effect of four common cattle husbandry antibiotics (ampicillin, florfenicol, sulfamethazine, and tylosin) on AD biogas production and antibiotic degradation resulting from the AD process. These authors found that the four antibiotics affected the AD process differently. Although sulfonamides had no inhibitory impact, ampicillin did alter the biogas production rate even if the total biogas production was not affected. However, the antibiotic concentrations tested in that study were higher than those normally detected in mixed feedlot manure.

Heavy metal from mineral supplementation, such as Cu and Zn, may remain in manure and affect methane production potential. In particular, Cu at about 2–6 mg/L had a positive effect on methane yield, whereas concentrations over 8 mg/L reduced gas production [96]. According to Chen et al. [51], the critical concentrations of Cu and Zn are much higher (57.9 mg/L and 53.3 mg/L, respectively) and similar to the values (48–96 mg/L) reported from other authors [97].

4.2. Fruits and Vegetables Waste

Food waste in a supply chain can be classified as pre-consumer waste from agriculture, processing and distribution and post-consumer waste from meal preparation and consumption. A conspicuous part of fruit and vegetables wastes (FVW) consists of residual biomasses from the food-processing industry [98].

Approximately 1728 million tons of fruit and vegetables have been produced worldwide in 2011 and around 15% of fruit and 25% of vegetables are wasted at the bottom of the production chain (FAO, 2014) [99]. High amounts of FVW are produced daily in large cities worldwide, and the effective disposal of such highly biodegradable waste is a challenge [100]. Fruit and vegetable wastes are characterized by high moisture content and high biodegradable organic compounds [101,102] (Table 5) [103–114] with a good potential as substrate for AD [115] leading to the production of biogas and a residual digested material to be used as organic fertilizer [116]. Less than 20% of the amount of FVW is used by AD, the remainder being either discarded, or used as animal feed or burnt with negative effects, such as offensive odors, pollution of air, water and soil [117–119]. The ratio C/N in FVW AD is often around 20 [91]; therefore, an additional nitrogen source should be used to obtain an increased pH value of the substrate, a higher biogas yield with a methane content of 50% and a VS removal of 80% [10].

Table 5. Characteristics of some fruit and vegetable waste (FVW).

	pH	TS%	VS (%TS)	C/N	BIOGAS YIELD
Wheat waste (straw, bran) [103, 104]	-	88.7÷91.0	88	87	-
Barley straw [105,106]	7.87	89.17÷90.5	94.04÷94.3		417 L/kg VS, 229 L methane/kg VS
Corn residue [105–107]	5.05	81.8÷93.02	94.65÷97.50	51÷57	641 L/kg VS, 317 L methane/kg VS
Rice straw [105,107]	6.2÷8.14	88.7÷93.49	76.02÷91.9	50÷70.88	416 L/kg VS, 195 L methane/kg VS
Boiled rice [108]	-	35	99	25.56	0.29 m^3 methane/kg VS
Apple scraps [109]	-	25	90	50.5	-
Fresh cabbage residue [108]	-	5	84	9.73	0.28 m^3 methane/kg VS
Tomato seeds and skin [105]	4.7	32	97.8		424 L/kg VS, 218 L methane/kg VS
Sugar cane bagasse [106]	-	93.51	83.91÷89.72	20.37	363 m^3/ton VS
Tea residue [106]	-	90.96	86.64	-	385 m^3/ton VS
Grape marc [105,109]	3.58÷4.40	20.44÷60.90	88.66÷98	18.57÷29.23	225–360 L/kg VS, 98–116 L methane/kg VS
Brewery spent grain [13,110,111]	5.08	21.1÷30	84÷96.5	11.25÷25	392–491 L/kg VS, 187–273 L methane/kg VS
Spent coffee grounds [112,113]	-	32.37÷95.88	92.76÷93.84	35.3	-
Coffee cut-stems [113]	-	88.56÷95.88	92.76	-	-
Palm oil mill effluent [114]	7.74	6.73	-	-	-
FVW (from supermarket) [100]	4.66	19.54	96.21	-	-

As for cow and horse manure, particular attention should be paid to vegetable matrices such as cereal waste showing high fiber contents. Fiber content and composition (i.e., neutral detergent fiber, acid detergent fiber and acid detergent lignin, hemicelluloses and celluloses) should be determined in order to estimate the biogas potential of fiber rich biomasses [105]. However, in these cases, pre-treatments should be used to enhance their digestion process.

Post-consumer waste and residual biomasses from the agro-food processing industry (e.g., low quality fruits and vegetables, damaged production left in the field) can also be considered as promising for AD. The world generates 2.01 billion tons of municipal solid waste annually.

When looking forward, global waste is expected to grow to 3.40 billion tonnes by 2050 [5] with many environmental problems but with a great potential as biogas substrate. Food waste, deriving from catering services, as well as the organic fraction of municipal solid waste, have been investigated as potential matrices for anaerobic digestion. However, the process can have some limitations linked to the long time required for the stabilization of organic matter and the low efficiency in VS removal [120]. As already stated for other matrices, co-digestion may represent a good strategy for improving the AD process [121].

5. Substrate Composition and Microbial Communities

Numerous authors reported that the diversity of microbial communities involved in AD is correlated with the type of biomass. For example, Ziganshin et al. [122] evaluated the influence of different agricultural waste materials, such as chicken manure combined with cattle manure, cattle manure alone or in combination with maize straw or distiller grains, and Jatropha (an energy plant widely used for commercial production of biodiesel) press cake on the composition of the microbial communities involved in AD at laboratory scale. As control substrate, cattle manure combined with maize silage, was used. Bacterial communities involved in the AD of the control substrate were rather stable and similar to each other. Conversely, in bioreactor fed with special biomass, such as chicken manure or Jatropha press cake, different communities indicating partial ammonia inhibition or other inhibiting factors were found. AD of chicken manure is based on syntrophic acetate oxidation as the aceticlastic methanogenesis is inhibited by dominant acetate-consuming process. However, the use of Jatropha as substrate led to the enrichment of fiber degrading microorganisms belonging to the genera Actinomyces and Fibrobacter. The most abundant bacterial phyla were the Firmicutes (mainly Clostridia) and the Bacteroidetes, whereas the archaeal communities were dominated by methanogenic Euryarchaeota belonging to the orders Methanomicrobiales and Methanosarcinales.

In all digesters, different clostridial phylotypes were found with variable proportions. However, the highest prevalence of these species was observed in biogas plants fed with vegetable biomass. In particular, Clostridium thermocellum and C. stercorarium were found to be the major microorganisms involved in the hydrolysis of plant biomass [123]. C. thermocellum was studied in detail for cellulosomes architecture and cellulose metabolism. In fact, cellulosomes are involved in the AD of recalcitrant cellulose, with the release of compounds necessary for the growth of acetogens and methanogens. Another clostridial family frequently found in all the bioreactors, in particular in the reactors fed with maize straw or Jatropha press cake, was Ruminococcaceae. The functional role of this group seems to be mainly the cellulolytic digestion of plant fibers based on the production of a cellulosome enzyme complexes and cellulose adhesion proteins [124].

Wirth et al. [125] used a metagenomic analysis to study the complex interaction among microbial communities involved in biogas production with the aim to understand the role played by microbes that are unknown or undetermined in the available databases. These authors noted that in an anaerobic fermenter fed with plant biomass and pig manure slurry, members of the Firmicutes and Bacteroides phyla were mainly responsible for hydrolysis and secondary fermentation. In particular, many Clostridium species, possessing cellulolytic and H_2-producing activities (both essential properties for the efficient biomass degradation), were identified. In the Archaea domain, the most abundant order was Methanomicrobiales that, during methanogenesis, used CO_2 as a carbon source and H_2 as an electron donor, suggesting that hydrogenotrophic pathway, leading to CH_4 formation, may be more significant than previously recognized [126]. Methanoculleus marisnigri was the principal species among the Archaeal habitants, confirming the results obtained in anaerobic digesters operating under different conditions [127]. These findings showed that an optimized balance between H_2 producers and consumers was a critical parameter for the efficiency of the biogas microbial community [125]. A study on the microorganisms involved in AD of fruit and vegetable waste obtained from the central food distribution market in Mexico City [10], showed that the bacterial sequences were distributed among three major phyla: Firmicutes (89.5%), Actinobacteria (6.9%), and Bacteroidetes (2.3%). Within the phylum Firmicutes, the most prevalent were Bacilli (mainly Lactobacillus species), followed by Clostridia, that were responsible for acidogenesis or syntrophic acid degradation. The hydrogenotrophic methanogenic genus Methanobacteriales represented more than 93% of the archaeal microorganisms in the digester. Hydrogentrophic methanogens dominated the methanogenic community despite the fact that the digester was inoculated with cow manure, which usually contains acetoclastic methanogens.

6. Strategies to Improve the Efficiency of the AD Process

6.1. Co-Digestion

The combination of substrates affects both microbial activity and biogas composition of AD. Co-digestion of different substrates allows the overcoming of many problems related to AD of the single organic materials. As for manure, although it represents one of the most promising biomass wastes for biogas production by AD, it provides low biogas yield, due to the low carbon content. Integration of manure with other biomass substrates for co-digestion is a valid solution to increase the economic benefits of this process. According to many studies, anaerobic co-digestion of cattle manure produces synergic effects such as buffering capacities on inhibition due to low pH, also supplying trace elements and supporting necessary methanogenic bacteria [128]. Another advantage of co-digestion of cattle manure with other organic materials is the improvement of the stability of the anaerobic process because of a better C/N balance [129], while when cattle manure is used as mono-substrate, AD is unstable due to the low C/N ratio (5–8) [130].

In addition, for FVW, co-digestion of these matrices together with livestock manure seems to be the best strategy to improve the AD process and biogas yield. Ferrer et al. [131] yielded significant methane increases of 41%, 44%, 28% and 12% by co-digestion of horse manure with tomato, pepper, peach and persimmon, respectively.

Tomato residues are a valid matrix for the production of biogas [132], although imbalanced nutrients, such as carbon and nitrogen, limit the use of this biomass as mono-substrate in AD [133]. Li et al. [133] mixed tomato residues with dairy manure and corn stover and gained the highest methane yields with a mixture of 33% corn stover, 54% dairy manure and 13% tomato residue.

Macroalgae (MA) represent valuable substrates for co-digestion with many wastes, such as market place wastes, in terms of biogas yield, due to the high carbohydrates content, high growth rates and ability to absorb carbon dioxide [134,135].

Comparing the production of biogas and methane by co-digestion with that yielded by mono-digestion of a set of five biomass materials (vegetable food waste, cow dung, pig manure, grass clippings, and chicken manure), Poulsen and Adelard [136] found higher yields with co-digestion than with mono-digestion of the same substrates. In another study [137], cow manure was processed with food collected from restaurants (including rice, salad, fish, meat, vegetable soup and beans flour) and fruit (orange, banana, plantain and pineapple peel) waste. The highest biogas yield was obtained in combination with food waste followed by the co-digestion with fruit and food waste and by the co-digestion with fruit waste only (16482.5, 9096.5, and 8390 mL of biogas, respectively).

Anaerobic co-digestion of food waste (FW) and cattle manure (CM) enhanced the methane yield by 41.1%, with a methane yield of 388 mL/g-VS, as a consequence of a C/N ratio of 15.8, corresponding to a FW/CM ratio of 2 [138].

Garcia-Pena et al. [10] by processing a mixture containing 50% food and vegetable waste and 50% residual meat, achieved a yield of methane twice that gained from processing food and vegetable waste alone. In addition, Cabbai et al. [139] by mixing garbage from cafeterias, restaurant, houses, fruit and vegetable markets and bread stores with civil sludge for anaerobic digestion, yielded 18–47% more methane than that obtained digesting any single waste type. When FVW was co-digested with artichokes, an increased biogas yield (65–70%) was obtained as compared with FVW alone [11].

Moreover, the co-digestion allows the decrease of the costs of processing several wastes at the same time [140] and the treatment of two or more matrices at the same time has a lower impact than their separate treatment [141].

Many studies focused on the assessment of the suitable proportion of the different substrates co-digested in order to obtain the highest biogas yield. Deressa et al. [142], exploring the production of biogas from FVW with cow manure (CM), in a ratio of 75/25, found that the co-digestion of FVW+CM provided biogas (31–37 mL/g) without the need for nutrient or chemical addition to the system.

Nagarajan et al. (2014) [143] found that co-digestion of vegetable wastes (i.e., beat root, carrot and potato) with cow manure, in a ratio of 2/1, enhanced methane yield.

Similar results were found by Hubenov et al. [144] processing swine manure (SM) and a mixture of FVW (40% of waste potatoes, 20% waste tomatoes, 20% waste cucumbers, and 20% waste apple). These authors noted an increase of methane yield as a consequence of the increase of FVW in the organic mixture with an optimal ratio of 70/30 (SM/FVW). In addition, Kafle et al. [115] investigating the potential of anaerobic co-digestion of Chinese cabbage waste silage (CCWS) with SM, found positive results of co-digestion by mixing SM and CCWS at a ratio of 75/25, while biogas yield significantly decreased when CCWS content in the mixture increased to 67% and 100%.

Al Mamun and Torii [8] studied the co-digestion of cafeteria wastes (CW), vegetable wastes (VW) and fruit wastes (FW) and found that the optimal mixing ratio to be used in AD (at mesophilic temperature for 35 d) was 1:1:1.

6.2. Chemical Pre-Treatments

A high VS/TS ratio and hemicelluloses content have a positive impact on the biogas yield while lignine has a negative effect [145]. Pandit et al. [146] found that the addition of rice straw to the vegetable and food wastes may promote the growth of microorganisms responsible for ligno-hemicellulose degradation with positive effects on the biogas production trough AD. However, substrate pretreatments are often necessary to degrade lignin polymers to further increase biogas productivity. For example, although straw has a positive effect on the methane yield by increasing the C/N ratio, it belongs to the class of difficult-to-degrade lignocellulosic materials; thus, a pretreatment stage is needed to improve the rate and degree of enzymatic hydrolysis during the degradation process. Zhang et al. [147] assessed the co-digestion of urea-ammoniated rice straw and FW with an inoculum of an anaerobic digester effluent. Urea pretreatment enhanced the hydrolysis of raw rice straw and increased biogas production. Moreover, the addition of cobalt and nickel to the raw material showed a positive effect on the reaction rate of co-digestion. In particular, the presence of nickel significantly enhanced the stability of co-digestion and increased the methane content. Alkali pretreatment of cattle manure with $Ca(OH)_2$ was an effective method for improving the biogas production from dry manure and the best condition was the treatment at 60 °C and pH 12 for 12 h [148]. This treatment probably increased the accessibility of microorganisms to the energy producing components (i.e., hemicellulose and cellulose). When different pre-treatments were compared for AD of Chlorella protothecoides algal biomass, methane yield was higher with sonication than with thermal and alkaline treatments [149].

Most chemical pretreatments have negative environmental effects, whereas N-Methylmorpholine-N-oxide (NMMO), a non-derivatizing solvent breaking the intermolecular interactions in cellulose, does not generate toxic pollutants and it is recyclable. A study investigating the effects of NMMO pretreatment on biogas production from horse and cattle manures, both with a high content of straw, showed that this step improved the methane potential of pretreated materials [150].

In spite of their efficiency, these pre-treatments are too expensive and they are not always necessary, since some organic substrates, although particulate, once immersed in water, tend to solubilize immediately. Panico et al. (2014) [151] proved that in an AD process fed with organic solid particles with a porous texture and a chemical composition mainly made of simple carbohydrates, the hydrolysis can be faster than expected. This kind of organic solid can be easily disintegrated in water, resulting in immediate availability to microorganisms for their metabolism.

6.3. Microbiological Tools to Improve Biogas Production

The use of selected microorganisms can improve biogas production in different ways. One of these applications is biological pre-treatment which is the most accepted pretreatment of lignocellulosic materials as it requires low energy consumption, it is high specific, cost-effective and environmentally-friendly. The microorganisms mostly used for pre-treatments of lignocellulosic materials are white-rot fungi (Coriolus versicolor, Aspergillus sp, Trichoderma sp, Phanerochaete chrysosporium and Penicillium camemberti), which are preferred to fermentative bacteria (Pseudomonas sp, Cellulomonas sp, Streptomyces sp, Bacillus sp and Actinobacteria) [152]. These microorganisms are the most efficient and extensive lignine degraders as they are able to decompose lignin with little consumption of cellulose component.

Other microbiological approaches to increase the hydrolysis of the biopolymer complexes are focused on "bioaugmentation" of the AD microbial community through enrichment with specific functional components, taking advantage of the abilities of the inoculated community to encode either specific cellulolytic enzymes (e.g., cellulase, b-glucosidase, xylanase) or multienzyme complexes (e.g., cellulosome) [153,154]. Other useful techniques are based on the use of microorganisms coming from the rumen ecosystem. This substrate is first colonized by anaerobic ruminal fungi, characterized by highly hydrolytic capabilities. Ferraro et al. [155] tested the use of bioaugmentation with anaerobic ruminal fungi and a pool of hydrogen-producing fermenting bacteria on wheat straw and mushroom spent straw with the aim of improving anaerobic digestion performance. Different process configurations were applied and the final results revealed that the two-stage configuration allowed an enhancement in CH_4 production. Furthermore, results on microbial community confirmed the efficiency of the bioaugmentation treatment, mainly related to the Methanosarcinales increase, mostly composed by Methanosaeta. Other studies [156] used brewery spent grain as model lignocellulosic substrate and some rumen bacteria (Pseudobutyrivibrio xylanivorans Mz5T, Fibrobacter succinogenes S85, Clostridium cellulovorans and Ruminococcus flavefaciens 007C) in addition to microbial biomass from biogas digester treating brewery wastewater. This study revealed that treatment of brewery spent grain with P. xylanivorans Mz5T, C. cellulovorans and F. succinogenes S85 promoted biogas production and significantly increased methane production, confirming that bioaugmentation is a promising method for increasing methane production from this substrate.

Another microbiological method to enhance the biogas production is the use of animal manures, such as cow dung, pig dung, poultry droppings, etc. as source of various kinds of microorganisms. In particular, cow dung contains microorganisms capable of enhancing the degradation during AD [157]. Different sources, such as sewage water, rumen fluid, sago industry effluent and termite gut, can be used as carriers of aerobic and anaerobic bacteria [158,159]. Cellulosic materials can also be used as source of specific microorganisms for AD [160]. The size of the inoculum is an important factor influencing the degradation of total organic materials, with an increment of methane yield when increasing substrate to inoculums ratio size. For example, Budiyono et al. [161] demonstrated that a concentration of 50% rumen fluid increased substrate degradation, including lignocellulosic materials as compared with lower concentrations. Recently, the use of selected microorganisms for substrate degradation is increased as a consequence of the higher efficiency of the microbes used in the process. Furthermore, the preparation of microbial consortium composed by selected microorganisms increased not only the degradation level, but also the competence of microorganisms for degradation. The use of special microbial consortia during a pilot scale study increased the efficiency of the process by reducing the duration of fermentation, as a consequence of the action of more specific enzymes secreted by these microbial consortia [162].

An alternative to the use of selected microorganisms to speed up the AD process is the genetic manipulation of anaerobic bacteria. Although different approaches were tested, the most widely accepted methods for genetic manipulation in bacteria were mutagenesis and conjugation.

The mutagenesis of wild strains may produce muted microorganisms with the desired degradation capacity also reducing the time needed for biogas production. Different methanogenic strains, mutated for the property of inhibitor-resistance, showed enhanced biogas production. In particular, the degradation activity of mutant strains of methanogens, such as Methanococcus voltae PS, Methanococcus maripaludis, Methanosarcina, and transformed strains of Clostridium sp., Klebsiella, E. coli, Lactobacillus, was increased in comparison to wild strains [163,164].

7. Conclusions

The production of biogas from residual agro-food biomasses obtained through AD represents a promising tool for alternative production of energy from renewable sources. The use of livestock manure, and particularly that from ruminant species, may provide significant environmental benefits by reducing GHG emissions related to manure management. Manure AD may also provide a supplementary source of income for farmers as renewable energy is produced and the residual digestate has high fertilizing properties. Similar advantages can be also attributed to AD of fruit and vegetables waste in the perspective of a true circular economy. Currently, the most promising aspects to consider in order to improve AD process for biogas production include advanced AD plant technologies, such as the combination of anaerobic membrane technology with specific systems (e.g., coagulant addition, adsorbent addition, use of granular materials improving aeration) leading the membrane to work with high flow rates and reduced fouling problems. In addition, on-line monitoring of the process (e.g., through NIRS spectroscopy) should be performed to control the main process parameters and allow efficient biogas production. As for manure from ruminant, improvement of biogas yield may be achieved by feeding ruminants with diets containing high levels of concentrate, due to the generation of higher levels of soluble organic-C during anaerobic digestion. However, co-digestion of fruit and vegetable matrices with livestock manure seems to be the best strategy to improve the AD of these high lignocellulose containing substrates. Alternatively, these substrates can be subjected to pretreatment with non-derivatizing solvents (e.g., N-Methylmorpholine-N-oxide) breaking the intermolecular interactions in cellulose without toxic pollutant residues. Another advantageous technique to increase biogas yield in high lignocellulose containing substrates seems to be the bioaugmentation with anaerobic ruminal fungi and a pool of hydrogen-producing fermenting bacteria with an enhancement in CH_4 production, using a two stage configuration. The improvement of AD efficacy by inoculating specific microorganisms for biomass degradation, can be achieved either with naturally occurring microorganisms or with genetically modified microorganisms. Both the approaches have the advantages of enhancing the efficiency of the AD process, as these microorganisms are able to reduce the duration of fermentation. However, further research focusing on the development of engineered microorganisms with increasing degradation activity is needed.

Future perspectives to improve biogas production from AD of agro-food waste should take into account the following aspects. Due to the origin and composition diversity of agro-food waste, which gives specific properties to them, an improved and specific characterization is needed to combine them in the correct proportion to enhance biogas production and process stability. To this aim the cooperation between biogas plants and laboratories specialized in waste characterization may promote AD efficiency. The seasonality of agro-food waste availability existing in areas characterized by small farms may cause input variability, which can be solved by the cooperation among farms dealing with different products. Communal plants could also contribute to the reduction of the economic and environmental transport costs.

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