

Review

Reviewing the Anaerobic Digestion of Food Waste: From Waste Generation and Anaerobic Process to Its Perspectives

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Abstract: Discharge of waste in general, and food waste, in particular, is considered one of the major environmental problems today, as waste generation increases continuously, reaching values of 32% of all food produced worldwide. There are many different options that can be applied to the management and evaluation of waste treatment, and Anaerobic Digestion seems to be one of the most suitable solutions because of its benefits, including renewable energy generation in form of biogas. Moreover, if FW (food waste) is digested in anaerobic digesters from Waste Water Treatment Plants, a common solution is provided for both residues. Furthermore, co-digestion of food waste and sewage sludge provides benefits in terms of anaerobic process stability enhancing the buffer capacity of ammonia (for example) and biogas formation, which can be increased up to 80% when compared with monodigestion. The present paper reviews food waste anaerobic digestion from its generation, characteristics and different options for its management, and it does focus specifically on the anaerobic digestion and co-digestion process, stages, limiting rates and parameters, utilizing numerous experiences, strictly related to food waste. Pre-treatments are also considered as they are important and innovative for enhancing biogas production and its methane yield. The paper shows an extensive collection of pre-treatments, its basics, improving factors, and numerical data of biogas formation improvements that are related both to substrate modification and to the synergistic effect of co-digestion, which could lead to an increase of methane production from 11% to 180%.

Keywords: food waste characterization; bioenergy; biogas; methane yield; hydrolysis; pre-treatments; perspectives

1. Introduction

Materials, intended or not, for human consumption that are discharged, lost, degraded, contaminated, or eliminated from the food supply chain (FSC), as well as the previous or forward stages and operations are known as food loss (FL) and food waste (FW) [1]. According to the Food and Agriculture Organisation of the United Nations (FAO) [2], FL is defined as any kind of change in the availability, or the quality of edible material that prevents it from being consumed by people. Due to this, food waste can be a consequence of FL.

Traditionally, FW was considered as the FL accrued at the retail and final consumption stages, so its generation is relegated to retailer and consumer behaviour [3]. Nowadays, the definition of FW also includes the losses incurred in the FSC stages or any other step of the agri-food industry, therefore it is defined as “any food and inedible parts of food, removed from (lost to or diverted form) the food supply chain to be recovered or disposed (including composted, crops ploughed in/not harvested, anaerobic digestion, bio-energy production, co-generation, incineration, disposal to sewer, landfill or discarded to sea”.

The FSC begins, in any case, with the agricultural sector (farming) that produces by-product (i.e., manure, waffle, cornstalk) and FW and FL in the form of low quality products, damaged production, or products with no commercial value. Adequate products are used by the processing and manufacturing industry, where FL and FW are mainly generated within the entire process chain due to problems in storage, damages during transport, contamination along the process, or in separation stages that create by-products not intended for human consumption (i.e., feathers, skins, fruit peels . . .) [4]. In the case of food markets and retail systems, FL and FW is generated in association with problems in storage, conservation, or unsold perishable products [3]. At the final stage of the product live cycle (end consumer), the FW is generated by a purchasing excess, over preparation processes, bad storage conditions, and other consumption behaviour patterns.

It is estimated that around a 33% of all food produced worldwide is wasted globally in form of FW and FL [5,6]. Particularly the European Union (EU), 90 million tons of FW are generated annually [7]. That means that each European Citizen produces 76 kg of FW per year [8] only at household level, but if all the FSC is considered, then this number does increase up to 179 kg of FW and FL per capita [9]. This kind of waste production represents 12% of all the food entering a home [10], and a 25% of all the food of the FSC. This implies that within the complete FSC, 40% of FW, and FL occurs during postharvest and processing stages and another 40% during the retail and consumer levels.

The generation of FW effectuates an impact in social, economic, and environmental spheres [1]. The most remarkable effects are environmental: for example, soil depletion due to landfill saturation, or the ground needs for agricultural raw materials and the consequent soil contamination. FW and FL also contribute to emissions of Green House Effect gases in transportation, storage and distribution operations, in landfill disposal due to methane emissions, or other disposal operations, such as incineration [11]. Social effects are related with ethical behaviours in terms of excessive resource consumption, and economic impacts may be ascribed to the costs that are related to food waste. Meaning that waste treatment methods for FW are currently evaluated, not only according to their treatment efficiency, but also in their environmental and social impacts [12]. Life cycle assessment seems to be a perfectly fitted tool for evaluating this determinants, especially environmental ones [13,14], such as carbon print, or its influence in climate change [15].

In this context, many legislative instruments arise to minimize the impact of FW. The Environmental Protection Agency (EPA) [16] defines a hierarchy in FW management: (a) Source reduction, (b) feed hungry people, (c) feed animals, (d) industrial uses, (e) composting, and (f) incineration or landfilling.

In the context of the EU, already in 1995 the Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste [17] was launched, with the objective for 2016: *“not later than 15 years after the date laid down in Article 18(1), biodegradable municipal waste going to landfills must be reduced to 35% of the total amount (by weight) of biodegradable municipal waste produced in 1995 or the later year before 1995 for which standardised Eurostat data is available”*.

As a follow-up on the Council Directive 1999/33/CE [17], the DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, of 19 November 2008, on waste and repealing certain Directives [18] has the scope of establishing *“measures to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use”*. According to this, a waste hierarchy has been established in waste management: (a) prevention; (b) preparing for re-use; (c) recycling; (d) other recovery, e.g., energy recovery; and (e) disposal, as shown in Figure 1. This hierarchy must be followed, both by consumers (a, b) and by waste managers (c, d and e) [18,19].

Some remarkable objectives for 2020, set in this directive, are:

“by 2020, the preparing for re-use and the recycling of waste materials [. . .], shall be increased to a minimum of overall 50% by weight”.

“by 2020, the preparing for re-use, recycling and other material recovery, [. . .] shall be increased to a minimum of 70% by weight”.

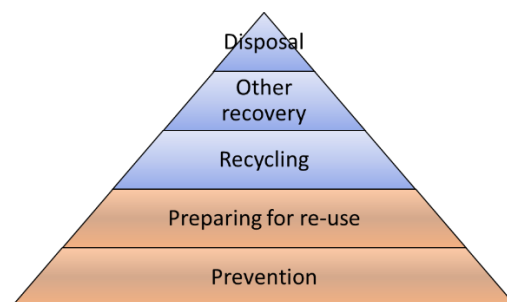


Figure 1. Waste management hierarchy according to Council Directive 1999/33/CE [17].

Due to the above, the main scope around those legal instruments is to progressively change the traditional point of view from residues as “waste to eliminate”, to perceive them as a new resource for other uses, including industrial ones. FW can be utilized for production of highly valued materials such as biodegradable plastics, enzymes, and organic acids [20]. It can be also used for developing value-added bioproducts [21], such as methane [22–24], biopolymers and organic acids [25–27], ethanol [22,28,29], and hydrogen [30,31]. Energy and fuel applications are the ones creating more added value, along with animal feed and electricity generation [32], to be composed of ethanol, hydrogen, methane, and biodiesel.

Anaerobic Digestion (AD) is a process enabling the creation of biogas (methane-rich gas) via microbiological digestion of the organic fraction of residues in anaerobic conditions (FW in this case). The result of the anaerobic digestion, known as digestate, can be treated as a residue (with a smaller volume), or as a by-product to be used as an agricultural fertilizer. AD process represents a way of recycling, recovery (in form of energy and industrial use as fertilizer), and a reduction system of landfill disposal; partial if digestate is eliminated, or complete if digestate is re-used [4,33]. In addition to prevention and the preparation for reuse, obligations for generators and citizens, AD is a process that accomplishes all of the steps of the European Waste Hierarchy, previously shown in Figure 1.

In light of this, AD is one of the most remarkable and adequate solutions for recovering residues. This paper is intended to review in general terms the recovery of FW and in particular, the AD process as a biofuel or energetic recovery in form of biogas, the anaerobic process, its characteristics, and factors implicated in biogas production. Furthermore, experiences with anaerobic digestion and co-digestion are reviewed, along with pre-treatments to enhance biogas production.

FW Characterisation

Characteristics and composition of FW strongly depends on where in the process the non-edible and non-usable materials are generated. FW generated in the first part (agriculture and livestock) are mainly composed of non-edible materials, separated from feedstocks. They are completely different in composition from FW generated in the final step of food supply chain (markets), where other material fractions are included, such as glass, metals, paper, plastics, and so forth, which stem from packaging. In the case of FW generated by the consumers, its composition depends strongly on different eating and cooking habits [34].

For those reasons, many researchers had characterised FW, each one with its own compositions and characteristics, depending on its origin, geographical location, social behaviours, habits, and local products . . . [35].

From the point of view of AD and waste reuse, it is important to thresh the composition regarding organic components like lipids, proteins, and carbohydrates (LPCH) and volatile fatty acids (VFA), content of total solids (TS) and volatile solids (VS), nitrogen content (N), carbon content (C), and its ratio (N/C). A review of FW characteristics and composition is provided in Table 1.

Table 1. Food waste composition reported by various authors.

Food Waste Composition											
FW Type and Origin	TS [%]	VS [%]	Proteins [%]	Lipids [%]	Carbohydrates [%]	VFA [%]	C [%]	N [%]	C/N Ratio	Reference	
Household individual sorted materials										[36]	
Meat and bone			70–75	23–30	1					[37]	
Fish and fishbone			75.6	20.2						[38]	
Egg and shell			35	32	2					[39]	
Dairy products			25–35	20–45	53					[39]	
Fruit			4	2	83					[40]	
Vegetable			27	1.4	27					[41]	
Individual fractions from OFMSC											
Animal kitchen waste		33.3	54.4	35.7	9.9					[42]	
Vegetable kitchen waste		13.4	21.6	19.4	57.6						
Raw animal waste		38.6	59.8	27.2	13						
Raw vegetable waste		10.8	19.4	11.1	69.4						
OFMSC in Sweden		90.8	18.2	20	29.4	0.35	50	2.8	17.85	[43]	
Fractions of OFMSC in Denmark											
Animal food waste	41	84	12	25	52 ^a					[44]	
Vegetable food waste	24	93	5	14	53 ^a						
Food waste		29.3	26.6	35	32.5		48.4	3.8	12.7	[45]	
Food waste	18.1	17.1		23.3	61.9					[46]	
Food waste	23.1	21.0					56.1	2.3	24.5	[47]	
Food waste for AD	30.9	26.35					46.8	3.54	13.2	[48]	
Kitchen waste	24	23.2	15	23.9	55.2		54	2.4	22.5	[49]	
Food waste	23.2	21.7	2.9	6.5	13.7					[50]	
OFMSC from municipal biowaste	20	18	30	4.4	10.7				17	[51]	
Food waste	16.7	15.3	2.4	1.4					11.5	[52]	
Notes ^a : Only easily-degradable carbohydrates											
Metal Elements in FW [g/kg-TS]											
	S	Ca	Mg	K	Na	Fe	Zn	Cu	Mn	Mo	Reference
Food waste	3.4	1.7	0.7	9.6	10.1	0.041	0.032	0.005	0.008	0.00003	[45]

Whilst the composition in terms of carbohydrates, lipids and proteins gives an overall idea of the composition, together with the solids content, a more extensive characterisation in terms of carbon content or nitrogen is necessary to finally differentiate them.

From the elemental composition, some conclusions arise, such as the suitability of FW for degradation processes, like AD, due to its high carbon content and moisture level, indicating that water accounts for 70–80% [34].

2. Industrial uses of FW, Different from Anaerobic Digestion

Giving added value to residues creates a circular economy beneficial to all the sectors that are involved in raw materials, products, waste management, and potential users of the new bioproducts. In the case of FW, the entire economic sector achieves benefits from circular economy: Primary sector (farming, agriculture . . .), secondary sector (If residues are intended for producing biomaterials), and tertiary sector (markets and retail facilities).

2.1. Biomaterials Production

From organic waste, and especially from FW, biopolymers can be produced [53] by obtaining the necessary monomers through the fermentation of carbohydrate feedstocks by microbes [54]. These biopolymers are a suitable option for substituting petrochemical products, as they have similar properties and they ensure biodegradability [55].

Examples of these biopolymers are polylactate, a plastic constituent obtained from lactate and lactic acid, polyhydroxyalkanoates, such as polyhydroxybutyrate, with characteristics that are similar to polypropylene and polyethylene, and succinate, which can be used for plastic and detergent production [56,57].

Recent research shows that biopolymers production from FW could be implemented with bioenergy production when combining anaerobic and aerobic processes. In this case, part of the volatile fatty acids from the anaerobic process can be transformed into polyhydroxyalkanoates, combining both biogas and biopolymers production [58].

2.2. Energy Production

Biodiesel, which is fuel suitable for diesel engines, is defined as fatty acid alkyl esters of long-chain fatty acids and short-chain alcohols, derived from natural oils (either animal or vegetable origin) or any fatty acid [59], and obtained by transesterification. Biodiesel is growing interest as any kind of fatty acid source is suitable for transesterification. On the one hand, edible oils are a good option for biodiesel products, but, on the other hand, they have been questioned due to the competition against food materials (food vs. fuel) [60–62]. Therefore, the most efficient element for biodiesel production are non-edible or waste oils [63], such as recycled frying oils, as representation of food waste [64,65]. Those oils can be treated solely or co-treated, as occurs with substrates for anaerobic digestion [66]. In this case, fats from slaughterhouses or other industrial oils [67,68] are a clever solution.

Bioethanol can be defined as a bioalcohol, which is obtained from the fermentation of carbohydrates from sugar-rich elements. Bioethanol can be used as fuel in gasoline engines (Otto cycle engines). Feedstocks for first generation ethanol are food crops (starch, sugar wheat, or corns crops), which have to compete with food generation against food vs. fuel dilemma. This can be overcome with second generation bioethanol, more readily accepted due to the use of non-edible materials such as feedstocks, including food waste and agricultural waste, which are considered a renewable and abundant source. Fruit waste is the most representative feedstock for second generation bioethanol on account of its high carbohydrate content. Pre-treatments are commonly used to improve the saccharification and the final fermentation process of the substrates [69].

If FW or other substrate is treated in a fermentation process using *Clostridium acetobutylicum* bacteria, biobutanol is obtained as an alternative to bioethanol. It has several advantages as compared

with it, represented by a lower vapour pressure and improved combustion efficiency. It can also be dissolved with any other oil to reduce its viscosity [70].

Incineration is, surely, one of the most mature technologies, consisting in the complete combustion of residues, to reduce its volume into organic ashes and utilize the released heat for energy production. Despite this, FW is not so suitable for this technology and its utilization is limited due to its high moisture and water content [44], together with air emissions from combustion, facing the environmental indicators [71].

As other thermal processes, alternatives to combustion, pyrolysis, and gasification can be mentioned. On one side, pyrolysis converts FW from solid state into liquid (pyrolysis oil) or gas (syngas) [1,71], products that can be used as fuel or raw materials for chemical processes, through the effect of temperature (400–800 °C). The carbon residues resulting from pyrolysis can be refined to obtain activated carbon or other carbonated products. On the other side, gasification oxidises FW by means of high temperatures (800–900 °C), to produce synthesis gas, a gas mixture that can be used directly as fuel in combustion processes, or as input in chemical production processes, to obtain methanol, for example, among other products.

The applicability of these thermal processes depends strongly on waste characteristics and composition, so FW has to be pre-treated before its conversion into pyrolysis oil, syngas, or gasification [71,72]. Specifically, water content seems to be the most limiting characteristic for thermal processes. Some processes independent from water content are Hydrothermal Carbonization (HTC) and Hydrothermal Gasification (HTG). On one hand, HTC is used to convert FW, or other materials, into a valuable energy resource known as hydrochar [73], with high carbon content and energy potential. On the other hand, HTG can generate hydrogen gas from biowaste, such as FW, especially the carbohydrate rich ones [74].

AD is a well-established technology that enables the transformation of any biodegradable residue, especially FW, into biogas (a rich methane gas mixture) [75]. This technology is perfectly suited for any part of the FW chain and can be applied to all kinds of biodegradable waste, such as organic fraction of municipal solid waste (OFMSW), agricultural waste, industrial waste, food waste, and so on. It is considered to be a flexible process that can be used as the final conversion process in most industries, giving added value to those non-convertible residual flows. This is why interest in AD has been continuously growing and has been promoted by many national energetic programmes [75,76].

AD can be used for biogas production, but it is also considered to be a good option for hydrogen production, as it is released in one of the stages of the anaerobic fermentation process [36].

3. Anaerobic Digestion of Food Waste

AD study and applications have been growing in the last decades [48,71,77–81], for many reasons, especially its suitability to treat any kind of biodegradable residue like FW or municipal waste, and the needs for renewable energy generation and other waste destinations that are different from landfilling [33].

FW is perfectly suitable for AD [82] because of its composition and moisture content. In general, terms, carbohydrates and proteins are traduced in a common biogas yield with faster transformation. On the contrary, lipids present a slower biodegradability development, but they provide a higher level and quality of biogas [83,84]. Therefore, it is important to understand the mechanism of AD process and all of the reactions involved.

3.1. AD Process

During the anaerobic degradation process, the OM content of FW (or any substrate) is transformed into biogas in a chain process that includes mainly four consecutive steps [85]. These four reactions are (a) hydrolysis, (b) acidogenesis, (c) acetogenesis, and (d) methanogenesis [86]. Figure 2 shows two different and complete schemes of AD reactions and development.

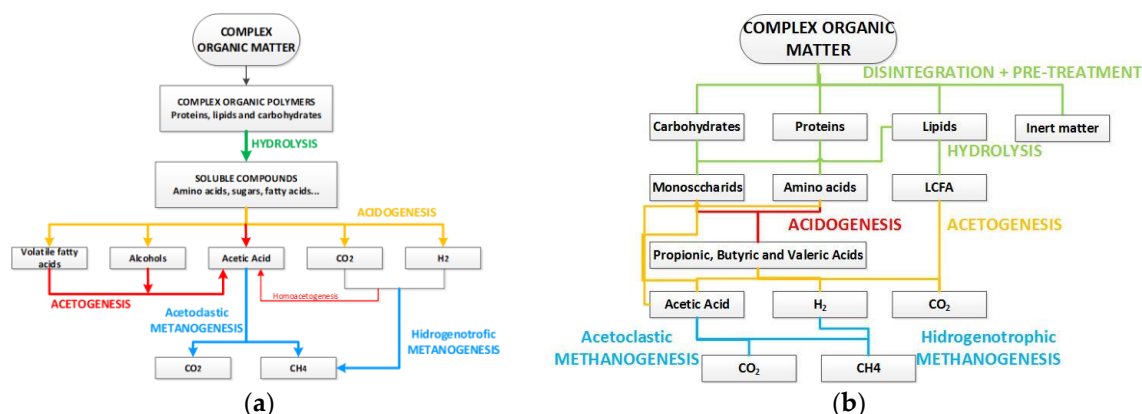


Figure 2. Anaerobic digestion process and reactions. (a) Simplified way and (b) adapted from [75] for ADM1 Simulation.

The process is carried out by numerous microbiological species and different bacteria working through syntrophy (the growth of one partner is improved, or depends on the nutrients, growth factors, or substrate provided by the other partner). This means the positive development of the process is related to a correct balance of bacterial populations. Some bacteria that are associated to hydrolysis are capable of degrading the OM either in aerobic or anaerobic conditions. That is why they are named facultative bacteria. Otherwise, bacteria that are responsible for the other reactions are strictly anaerobic [87].

To completely degrade OM from substrates, present as lipids, carbohydrates, and proteins (organic polymers), it has to firstly be hydrolysed in order to reduce those macromolecules and transform them into other soluble compounds such as aminoacids, sugars and long chain fatty acids. This process is known as hydrolysis, an extracellular reaction carried out by enzymes that should be primarily adsorbed on the surface of solid substrates [88,89]. This is the reason why hydrolysis is considered the stage-limiting step for AD development.

Secondly, the small molecular materials created during hydrolysis are converted during the acidogenesis phase into volatile fatty acids (acetic, propionic, and butyric acids), and other by-products, like NH_3 , CO_2 , and H_2 gases, and small parts of alcohols, aldehydes, and ketones. Acetogenesis is an intracellular reaction (as all the following reactions are) that is carried out by fermenting bacteria.

Thirdly, products obtained in the previous reactions are transformed into acetate, H_2 , and CO_2 during the acetogenesis phase through acetogenic bacteria. These ones are suitable applicants to be transformed into methane and carbon dioxide, among other gases that constitute biogas.

Finally, in the methanogenesis phase, methanogens transform short-chain fatty acids, alcohols, and gases (CO , CO_2 , and H_2) into methane (CH_4). This can occur via acetoclastic methanogenesis or hydrogenotrophic methanogenesis. In the first case, acetoclastic methanogens mainly use acetate to form methane, whilst hydrogenotrophic methanogens use H_2 and CO_2 . In addition, carbinol and CO can be also transformed into methane [34]. All of these reactions are shown in Figure 2.

During methanogenesis, a large number of intermediate products are formed by a unique bacteria population. It is an extremely complex process: on one hand, it uses a reduced substrate group, and, on the other hand, methanogens are the most strictly anaerobic microorganisms (methanogens growth only occurs under a red-ox potential below -330 mV).

In general terms, reference [90] states that carbohydrates are degraded into saccharides and sugars to produce VFA, alcohols, and organic acids. Lipids are degraded into glycerol, glycerine, and long-chain fatty acids, to further be transformed into VFA. Proteins, which are mainly considered as the encapsulation of nitrogen, are transformed from peptides to amino acids, and finally into VFA.

AD is an extremely complex process that should simultaneously digest all substrates in order to produce the substrate for the next phase reaction. This requires a stable environment for the different

microbial growth. It is therefore important to maintain the key parameters of AD process within the correct range, to ensure the appropriate operation of AD.

3.1.1. Hydrolysis as Stage-Limiting and Rate-Limiting Reaction in AD

When a process develops as a result of various chain reactions, as in the case of AD, generally one step has a slower development and, consequently, is considered as the limiting stage of the process [91,92]. In the AD process, hydrolysis is considered to be the stage-limiting process, being closely linked to substrate nature, its particle size, temperature, pH, and organic load [93], as it is the first stage of the process. A good contact or interaction between substrate and inoculum is required for a correct hydrolysis development [45] to enable enzymes in developing the extracellular reaction through adsorption on the surface of particle substrate [94]. Moreover, a correct evolution of hydrolysis, if surface area that is available for bacteria is sufficient, results in a better and significant development of further reactions (acidogenesis, acetogenesis, and methanogenesis) and subsequently in more biogas production [95–97]. This results in hydrolysis as stage-limiting and rate-limiting, as it is responsible for developing the subsequent reactions and enhancing biogas production [98–100].

Most organic matter is present in the form of particulate organic matter (POM), especially FW. During hydrolysis, particulate compounds are transformed into monomeric or dimeric soluble substrates, which can be incorporated into the cells for its methanation. Thus, in the case of organic matter, hydrolysis not only comprises classic hydrolysis of Organic Matter (OM) polymeric material, in the shape of lipids, proteins and carbohydrates (LPCH). Other transformation processes should also be reported (enzymatic or not) to transform the particulate matter into accessible polymeric compounds and expose the maximum contact surface for enzymes to act upon. Therefore, hydrolysis can be disaggregated into two different processes, (a.1) “disintegration” of POM into lipids, proteins, and carbohydrates, and (a.2) the proper enzymatic hydrolysis of LPCH [101]. As these two stages take place simultaneously and they are impossible to decouple, they are commonly included within a unique kinetics reaction. Meaning that, on a practical level, hydrolysis of POM and its rate is defined as the rate at which the POM is converted into assimilable substrate for anaerobic archaea. Parameters influencing hydrolysis and hydrolysis rate are mainly (a) temperature, (b) pH, (c) substrate structure, and (d) particle size.

Temperature and pH

Temperature’s global effect on hydrolysis is originated by the combination of enzymatic kinetics, bacterial growth, and substrate solubility effect on improved activity [94]. There has been a lot of effort to determine the kinetic constants of anaerobic treatment [102–104], which are typically considered a first order kinetics that increases with temperature [89].

First order kinetics variations are commonly estimated by Arrhenius equation:

$$k = A \cdot e^{\frac{-\Delta G^*}{R \cdot T}} \quad (1)$$

where “k” represents kinetic constants (hydrolysis constant in this case), “A” Arrhenius constant, “G*” and “R” standard activation energy and perfect gases constant, expressed in $\frac{J}{mol}$ and $\frac{J}{mol \cdot K}$, respectively, and finally, “T” represents the process temperature measured in absolute temperature [K].

For its part, pH has a complex feature, similar to the global AD process, as many different enzymes intervene in hydrolysis, each one with a different optimum pH for its growth. Net pH effect in hydrolysis is determined by the optimum pH for the different enrolled enzymes [99].

Substrate Structure

Substrate structure and its accessibility for hydrolytic enzymes is a key parameter, as a dissolved substrate is easier to hydrolyse, as compared with a particle substrate [87]. Substrate accessibility can be modified by forming complexes with other compounds. As an example, proteins can be affected

by humic acids [105]. Likewise, cellulose is readily biodegradable, and, when mixed with lignine, its degradability can be reduced by up to 25% [106]. Another example could be particulate matter with a porous texture and with a chemical composition dominated by simple carbohydrate, such as fruit waste, which can be easily disintegrated in water, thus resulting in immediate availability to microorganisms [107].

Particle Size

Particle size is directly linked with substrate contact surface [95,108]. While particle size increases, the contact surface is reduced and the available space for enzymes is minimized, meaning that in an hydrolytic enzyme excess, particle size can be a limiting factor [109]. A good contact between substrate and inoculum in AD is necessary, as enzymatic processes are extracellular reactions and they are benefited by adsorption to a particulate surface [45,92]. Smaller particles with higher surface area will present higher reaction efficiency during AD, and consequently biogas yield is increased [110]. Nevertheless, reducing particle size can improve hydrolysis development, and an excessive reduction can result in the over-stimulation of hydrolysis and consequently of acidogenesis with high production of VFA and ammonia, both process inhibitors [107,111].

3.2. Key Parameters

3.2.1. Temperature

Temperature is one of the most significant parameters, as it influences the activity of enzymes and co-enzymes responsible for hydrolysis development, methane yield, and digestate quality [88,89,112]. Anaerobic microbes and bacteria can grow in psychrophilic (10–30 °C), mesophilic (30–40 °C), and thermophilic (50–70 °C) conditions. As a general rule, the performance of AD increases with temperature, as well as the bacteria growth rate, metabolic rate, and biogas production rate [113,114]. Reference [115] pointed out that thermophilic conditions produce double biogas than psychrophilic conditions. As reported by [116], thermophilic reaction suffers less from ammonia inhibition.

However, higher temperatures also represent some disadvantages. While endogenic reactions (acetogenesis) are enhanced with temperature, exergonic reactions, such as methanogenesis, reduce their performance. That is the statement for the events reported by [117], where in mesophilic conditions, 70% of the biogas is formed via acetoclastic methanogenesis, and the rest through hydrogenotrophic methanogenesis. In psychrophilic conditions all methane is produced by acetoclastic methanogens, hydrogen is oxidized and transformed, together with CO₂ into acetate, and then into methane. However, in thermophilic conditions, homoacetogenic bacteria are capable of transforming acetate into hydrogen and carbon dioxide (In the opposite direction), and the methane inengenerated, almost entirely by hydrogenotrophic methanogenesis means.

3.2.2. VFA and pH

VFA mainly comprise acetic, propionic, butyric, and valeric acid. They are by-products, formed in the acidogenic stages of the AD process, which can be ultimately transformed into CH₄ and CO₂. VFA play an important role in biogas production [118], as they are a key to constituting the final methanogenic stage, but an excess of it can cause a pH variation [119].

pH is another key parameter for the correct development of the anaerobic process. Anaerobic bacteria need different pH ranges for their growth: Fermentative bacteria around 4–8.5, and 6.5–7 for methanogens [120], so achieving a correct pH environment is essential for the process stability. VFA and pH are closely related. An excess of VFA can cause a drastic pH reduction. In addition, VFA can be significantly affected by pH. When the pH is low, the main VFA present in the mixture are acetic and butyric acids. If the pH is high, around 8, acetic and propionic acids are the dominant ones [121]. That is why controlling pH ratio can be a reliable method to achieve the stability in the process [122,123].

3.2.3. Carbon, Nitrogen and C/N Ratio

An optimal balance between nutrients is needed by anaerobic bacteria to enable their proper growth. A balance between C and N should be achieved, being commonly expressed by the C/N ratio. Many researchers considered a C/N ratio between 20 and 30 the optimal condition [124]. For example, [125] achieved the maximum methane potential at a 27 C/N ratio, and [126] did it also at 27 C/N. Other researchers, like [24], obtained it at a 15.8 C/N ratio when co-digesting FW with cattle manure. However, the optimal C/N ratio depends both on the substrate and the inoculum.

3.2.4. Ammonia Content and Formation

Ammonia is formed during the biodegradation of proteins or other nitrogen-rich substrates [127,128]. Ammonia and the C/N ratio are directly related as high nitrogen contents produce ammonia formation, whilst C content has a positive effect on avoiding ammonia inhibition [125,129,130]. Ammonia can act in two different ways, on one side enhancing the buffer capacity of AD neutralizing VFA [131,132], and, consequently, enhancing biogas production. On the other side, ammonia can act as an inhibitor for bacteria growth, especially acetoclastic methanogens [133–135], being responsible for methane production via acetate transformation. For example, an ammonia concentration between 400 and 5700 mg/L produces a 56% loss of methanogens activity, while acidogens were not affected [133,136]. Ammonia content increases with temperature and pH, so it is related with other basic parameters [137]. Ammonia as an inhibitor has been widely studied in order to set or establish the threshold between its positive effect (exploiting its buffer capacity) and its negative effect (as inhibitor). As an example, in semicontinuous AD of FW, the inhibition effects were observed when the ammonium concentration in the AD reactor exceeded 2 g/L [138]. Below this threshold, ammonium acted as a buffer neutralizing the acidification effect from VFA accumulation. Over the limit, ammonia strongly inhibited methanogenesis shifting methane formation from acetate by acetoclastic methanogens to a syntrophic acetate oxidation, leaving hydrogenotrophic methanogenesis as the only methane formation way. However, it did not affect the hydrolysis and acidification stages, causing an acetate and propionate accumulation with its consequent pH decrease.

High concentrations of ammonia can lead to lower biogas production, and also to ammonia emission from the effluent, making the digestate less suitable as fertilizer [139–142]. Many techniques for ammonia removal had been studied and approached, combining physical, chemical, and biological techniques [141,143–147].

3.2.5. Long-Chain Fatty Acids

Long-chain fatty acids (LCFA) are the main by-products of the lipid degradation process [148,149]. LCFA are, subsequently, converted into hydrogen and acetate during acidogenesis stage through a β -oxidation reaction, and finally, into methane. This is the reason why acetogenesis could be considered a rate-limiting stage of the AD process [34,150], along with hydrolysis. Inhibition from LCFA can be caused, according to various research studies, by high concentrations of LCFA that result in a pH decrease and the subsequent growth reduction of the methanogenic archaea [151–153], or because of the LCFA adsorption onto the microbial cell wall and membrane. This affects the metabolic process of transportation [151,154,155]. Moreover, inhibition that is caused by LCFA has a synergic effect, meaning that the inhibition degree due to a mixture of LCFA's is higher than the effect that is caused by each individual acid [156].

When considering that theoretical methane potential of lipids is higher than carbohydrates, as it will be discussed later, serious problems in biogas plants are caused by the inhibition of LCFA. Strategies for recovering this inhibition have been studied by many researchers, for example, by increasing the biomass/LCFA ratio [155] or using discontinuous feeding [157].

3.2.6. Metal and Heavy Metals Traces

Together with nutrients (C, H, O, N), light metals (Na, K, Mg, Ca), and heavy metals (Cr, Co, Zn, Cu) are necessary for anaerobic bacteria to develop enzyme synthesis and activity maintenance [158,159], although an excess of metal concentration can lead to AD inhibition.

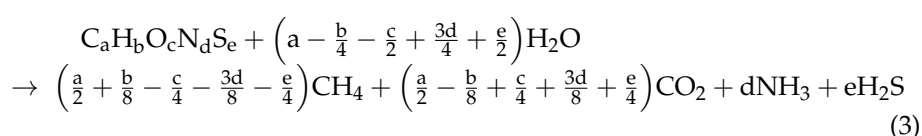
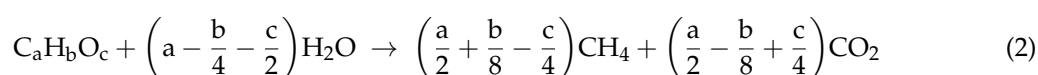
In FW, concentration of heavy metals is almost insufficient [46,160] while light metals such as Na, K, and Ca are, generally, found at high concentration levels [47,84,161], as can be observed in Table 1, which summarizes metal concentrations in FW reported by several researchers.

Heavy metals are supposed to cause inhibition due to a disruption of the enzyme function and structure of microorganisms [133]. Regarding light metals, Na, for example, creates an optimal environment for methanogens in 350–400 mg/L [133] and concentration, respectively. K was capable of enhancing methanogenesis in mesophilic and thermophilic conditions. Ca, on its own, has a controversial effect: Some researchers discovered that no inhibition was found when the Ca concentration was really high, specifically up to 7000 mg/L [162], others found out that the optimum Ca concentration range is 150–300 mg/L [163], or with a toxicity threshold even lower, up to 200 mg/L [164].

3.3. Anaerobic Mono-Digestion of FW

AD is a synergistic process between microbes' population. AD mono-digestion means that the substrate, FW in this case, is treated solely with the consortium of anaerobic microbes, under anaerobic (non-air and non-oxygen) conditions. AD is more suitable for food waste treatment than other conventional treatments, because of its composition, as it recovers energy, and, in addition, digestate can be applied for agricultural uses.

Biogas production and methane production from FW AD can be estimated through its composition, previously reviewed. Biogas yield is affected mainly by LPCH content and its balance. Some theoretical results in terms of biogas yield and biogas composition from degradation of proteins, lipids, and carbohydrates, can be determined through methane production equations, especially the Buswell-Muller formula [165] and the Boyle formula [166] when elemental and chemical composition of compounds are known:



According to this procedure, to obtain the theoretical biogas yield and composition, it is interesting to know the chemical composition of LPCH, as shown in Table 2. This provides the maximum biogas yield that can be obtained, assuming that the entire substrate is transformed into biogas, although part of the substrate is converted into biomass (3–10%) [167] and it is thus not available for biogas formation.

Table 2. Chemical composition of lipids, proteins, carbohydrates, theoretical biogas yield and biogas composition from lipids, proteins, and carbohydrates (LPCH) calculated using Buswell-Mueller [165] and Boyle [166] formulas.

C [%weight]	H [%weight]	N [%weight]	O [%weight]	S [%weight]	Ref.	Theoretical Biogas Yield [Nl/kg-TS]	Theoretical Biogas Composition [%CH ₄ vol.] [%CO ₂ vol.]	Ref.
76	12	-	12	-		1390	72 28	
46	5	18.5	30	0.5	[37]	800	60 40	[149]
40	7	-	53	-		750	50 50	

Carbohydrates ((CH₂O)_n) exhibit the fastest conversion rate but the lowest biogas yield [133,168,169], around 750 NI per kilogram of total solids, with a biogas composition of 50% CH₄ and 50% CO₂. Carbohydrate-rich substrates, in FW terms, such as fruit and vegetable waste or sugar industry wastes, are enriched with simple sugars and disaccharides [75]. Anaerobic degradation of simple sugar may result in VFA formation and accumulation, leading to a pH decrease and methanogenesis inhibition [75]. Mixing them with low organic content substrates [124,170] might balance operational conditions and biogas production [171].

On their behalf, proteins (C_aH_bO_cN_dS_e) represent a fast conversion to biogas and a biogas yield [169,172] slightly above carbohydrates (800 NI per kilogram of total solids) with a higher methane composition, 60% CH₄ against 40% CO₂. As protein structures are different from each other, biogas content may vary significantly. CH₄ content that is given in Table 2 is typical for amino acids. Since many proteins can be present in a less oxidised form, methane content can increase up to 70%. Not only is methane released, but also ammonia and hydrogen sulphide can be obtained, as they are the only compounds that present N and S in their composition (a common point between amino acids is that those have an amine group (-NH₂) [75]). If an excess of ammonia is released it can deliver in a process inhibition [173]. FW protein rich materials, such as meat residue, slaughterhouse waste, or manure require a suitable adjustment of C/N ratio and an optimum key parameter control to avoid process inhibition and system failure due to problems described.

Finally, lipids (CH₃(CH₂)_nCOOH) show the highest biogas yield, as they have a higher carbon composition (C:16–C18 typically), providing 1390 NI of biogas per kilogram of total solids of which around 72% is CH₄. However fats require longer retention times due to their slow biodegradability [83], and, in addition, a lipid excess can lead in a process inhibition due to an excessive VFA and LCFA release and accumulation [34] due to toxic products formation [157]. Lipid-rich products, regarded in FW terms as slaughterhouse residues and wastewaters, dairy products, edible oil products, and mill loses [75], present a huge biogas yield, but leading in blocking AD process, adsorption to biomass causing mass transfer problems and foam formation [172], and inhibiting hydrolysis and microbial process due to VFA and LCFA releasing [169,174–176]. Mixing lipid-rich elements with carbohydrate-rich substrates produces a nutrient balance for microorganisms' enrichment, reducing the accumulation of inhibitors.

To manage full AD implementation, as well as to predict methane production, experimental results are necessary, and BMP (Biochemical Methane Potential) is required [177]. BMP is an experimental measure of the substrate biodegradation potential and methane gas generation [178] that provides the maximum methane output that is achieved in laboratory incubation tests under optimum anaerobic conditions [179]. The theoretical BMP (TBMP) can be estimated as the weighted average of individual TBMP for organic components [44,180,181], as explained previously with Buswell-Muller and Boyle's formulas.

Food waste biodegradability has been thoroughly researched, as can be observed in Table 3. Most of the studies reported that mono-digestion of FW was not sufficient and limited due to lack of nutrients (nitrogen and phosphorus) and metal traces, and the inhibition that is created by the accumulation of ammonia and VFA, resulting in the high biodegradability and protein and lipid content [182–184].

This problem can be solved with digester modifications, such as nutrient recirculation, pre-treatments, temperature increases [48,185], or with an even better solution: Co-digestion.

Table 3. Food waste (FW) biodegradability through anaerobic mono-digestion and co-digestion experiences.

Mono-Digestion Experiences								
Substrate		Operational Conditions		CH ₄ Yield [ml _{CH₄} /g _V S _{deg}]	Reference			
Food Waste				234	[36,186]			
Food Waste				234	[183]			
Food Waste		Two stage		546	[187]			
Food Waste		Full scale		399	[188]			
Food Waste		Batch		410	[24]			
Animal FW		Batch		500	[42]			
Vegetable FW				400				
Animal FW		Batch		500	[44]			
Vegetable FW				400				

Co-Digestion Experiences								
Sub 1	Sub 2	Ratio	Operational Conditions	CH ₄ Yield [ml _{CH₄} /g _V S _{deg}]	Improvements			Reference
					(a)	(b) [%]	(c) [%]	
SS	FW	50:50	Lab Scale	215	Increased OLR	+24.27	+85.3	[189]
SS	FW	20:80		157	Increased buffering capacity from ammonia	+54.60	+35.3	
SS	FW	75:25	-	439		+47.81		[186]
SS	FW	80:20	Continuous pilot scale	326	Increased buffering capacity from ammonia	+10.80	+21	[183]
CM	FW	67:33	Continuous lab scale	388	High buffering capacity and trace element supplement		+41.1	[24]
CM	FW	50:50	Batch	298	High buffering capacity of ammonia		+44	[190]

Table 3. Cont.

Co-Digestion Experiences								
Sub 1	Sub 2	Ratio	Operational Conditions	CH ₄ Yield [ml _{CH₄} /g _{VSDeg}]	Improvements			Reference
					(a)	(b) [%]	(c) [%]	
FW	ShW	83:17	Lab scale	300	Trace element supplement. Ammonia accumulation		−61.9	[191]
WAS	FW	90:10	-	186	Nutrient balance. Increased buffering capacity from ammonia	CH ₄ yield increases while addition of FW increases.		[192]
WAS	FW	50:50	-	321				
WAS	FW	10:90	-	346				
frW	CM	20:80	Batch	380	Nutrient and C/N ratio balance. High buffer capacity	CH ₄ yield increases while addition of FW increases.		[193]
frW	CM	30:70		340				
frW	CM	40:60		380				
frW	CM	50:50		450				
FW	PWw	93:7	Continuous Lab scale	358	Trace elements supplements.			[46]
FW	PWw	83:17		388				

Notes:

(b) Improvement is defined as the increase in CH₄ yield compared to (CH₄ yield of main substrate + CH₄ yield of co-substrate) → Synergistic effect

(c) Improvement is defined as the increase in CH₄ yield compared to CH₄ yield of the main substrate itself → Global effect.

Abbreviations:

SS (Sewage Sludge) CM (Cattle Manure) ShW (Slaughterhouse Waste) WAS (Waste Activated Sludge) frW (Fruit Waste) PWw (Piggery Waste Water)

4. Anaerobic Co-Digestion of Food Waste

Anaerobic co-digestion can be defined as the simultaneous treatment of various substrates, at the same time, in the same anaerobic digester with the same inoculum.

Digesting FW solely is a suitable solution for FW generation and management. However, not all biogas yield is released, and, in addition, inhibition may occur. The main reason might be a nutrient imbalance between organic compounds (LPCH) in the anaerobic digester, a lack of trace elements (Fe, Zn . . .) combined with a macronutrient excess (Na, K, Ca . . .), and a non-optimum C/N ratio [24,46,47,194]. Problems and inhibitions caused by each organic element were formerly reviewed in previous sections.

Anaerobic co-digestion (CoAD) means mixing substrates, for example, FW and sewage sludge [36], FW and manure [24], or even straw [82] and slurry [195], to balance nutrients in the digester providing a more stable environment for anaerobic bacteria [190,196,197].

The main advantage of CoAD, is the synergy that is created between substrates in terms of biogas yield, biogas composition and methane enrichment. This means that biogas created whilst digesting two substrates simultaneously, is higher than the sum of each mono-digestion ($AB > A + B$). Actually, CoAD can enhance biogas production from 35% to 400% over the mono-digestion of each substrate [198,199]. Other important advantages are achieved with CoAD [199–206], such as, (a) improvement of process stabilization, (b) dilution of inhibitory substances, (c) higher buffer capacity due to higher ammonia from organic wastes, (d) nutrient balance, (e) optimum C/N ratio achievement, (f) trace element supplement, (g) increasing the total amount of OM loaded, (h) synergy between substrates in biogas yield, (i) improving moisture content, (j) methane enrichment and its subsequent greenhouse emissions reduction, and (k) economic feasibility.

FW can be used in CoAD as co-substrate or main substrate, according to its compositions, the other substrate should benefit the balance. When FW is used as a co-substrate, the main substrate is, typically, sewage sludge (SS) and animal manure (AM). These two (FW and AM) are characterized by a low C/N ratio resulting in a high accumulation of ammonia in the digester. Adding FW increases the C/N ratio and it improves digestion as a consequence of ammonia reduction [183,204,207]. FW also dilutes inhibitors and toxicity caused by heavy metals and pathogens, clearly existing in SS and AM. However not only is the main substrate benefited by co-digestion of FW, but also SS and AM act with a high buffer capacity, which are able to withdraw pH-low problems caused in FW mono-digestion by VFA and LCFA accumulation during the degradation of OM, especially the lipidic content [208,209].

The use of FW as a main substrate requires employing a co-substrate capable of reducing inhibition problems of AD of FW and enhancing biogas yield. As stated in previous sections, methanogenic activity while digesting FW is often inhibited due to the accumulation of VFA and LCFA from lipids and carbohydrates biodegradation, to the lack of nutrients, such as N or P, and trace metals. FW has been traditionally digested along with straw and other lignocellulosic substrates, solid waste leachate, wastewater (industrial and agroindustrial, such as piggery wastewater), slaughterhouse waste, manure, and sewage sludge [4]. These co-substrates create a synergy in biogas yield due to several reasons: Lignocellulosic substrates (i.e., straw) increase the C/N ratio and biogas production; moreover, it decreases hydrolysis rate because of its low degradability, and consequently reduces VFA accumulation and inhibition, providing stability [210,211]. Wastewater and OFMSW leachate dilute FW lipidic content and feed it with nutrients and metal elements that are not present, or in small amounts, in FW. Nevertheless, the main achievement of this co-digestion is the improvement of enzymatic reactions, and, consequently, hydrolysis improvement [66,191,212]. However, organic loading in co-digestion has to be regarded carefully, especially when co-digesting FW with manure or leachate due to its high biodegradability, which can lead to a process saturation and failure [110,213]. Organic loading rate and mixture ratio must be carefully regarded when digesting FW with high biodegradable wastes, for example, slaughterhouse waste, which also presents high lipid content. This can deliver, not only LCFA and VFA accumulation and inhibition, but also foaming and fat accumulation in the reactor, because of its high lipid and carbohydrate content.

Co-digestion of FW with sewage sludge (SS) from wastewater treatment plants is an excellent and suitable solution, not only for its benefits in terms of synergy in biogas production, methane yield, and process stability, but also because of its advantages in economic and environmental aspects, which will be discussed further on and is the reason why co-digestion of FW and SS is reviewed in a separated section. Table 3 summarizes co-digestion experiences, providing data of biogas enhancement and the improved mechanism of co-digestion.

Anaerobic Co-Digestion of Food Waste and Sewage Sludge

Improved biogas and methane yield in CoAD of SS and FW has been widely studied and comes from various aspects: (a) mixture and C/N ratio, (b) nutrient balance and dilution of inhibitors and toxic elements, and (c) changes in hydrolysis rate.

Sewage sludge is characterised by a low C/N ratio ranging between 6 and 9 [189,195]. On its own, FW has a higher C/N ratio that can improve the C/N ratio of substrates blend if a correct mixture ratio is utilized, providing more carbon, essential for improving digestion process and kinetics [214–216]. Optimum C/N ratio has traditionally been settled between 20 and 30 [186,192,217–219]. A higher C/N ratio is usually a cause of process disability due to a nutrient (N) deficiency, whilst low C/N ratios represent low carbon availability in combination with high ammonia formation and its subsequent toxicity for the AD process in high concentrations [220].

Nutrient balance provided by FW and SS sludge co-digestion has its fundamentals in achieving the optimum C/N ratio, and creating an equilibrium between LPCH content. Each one has its own benefit in biogas yield terms, but a balance must exist to achieve the optimum environment and intermediate product creation for the process. Adding FW can also dilute toxic compounds such as heavy or light metal and organic compounds, mainly present in SS [133,221]. This may affect the digestion progress [222,223], but if proper dilution is achieved, then digestion performance can improve [224,225] as well as methane yield [226].

Hydrolysis, considered to be the rate and stage limiting step of AD process [216], is also improved when adding FW to SS digestion. In general terms, SS has a rich content in proteins [227,228], connected with the lowest hydrolytic and biogas yield of LPCH. Adding FW, in the form of simple biodegradable matter accelerates hydrolysis because of the faster growth of anaerobic archaea [205,229,230]. This acceleration in microbial growth not only increases hydrolysis yield and kinetics, it does the proper within the acidification and methanogenesis steps, resulting in a higher potential [94,186,228,231].

However, some constraints have to be regarded in order to improve the feasibility of FW CoAD with SS. This process is mainly limited due to the high variability of FW depending on its procedure, nature, and characteristics. Anaerobic microorganisms are acclimatized in a specific environment, and sudden changes in substrate and reactions might break the equilibrium [105]. Addition of FW, especially carbohydrate-rich ones, results primary in an increase of VFA concentration [218] that should be transformed into methane. However, a VFA excess or accumulation causes acidity in the digester and slows down the process. A high-lipid income in the digester may result in LCFA accumulation with the same acidity consequences. On its own, protein-rich substrates are the causes of ammonia accumulation. Overloading digesters with FW has to be avoided in order to reduce changes in microorganism activity and its subsequent reduction of biogas and methane yields.

5. Pre-Treatments for Anaerobic Digestion of Food Waste

Pre-treatments are usually employed to increase substrate solubility and accelerate biodegradation rate when digesting particulate organic matter [110,232]. Hydrolysis, including the “disintegration stage”, is considered the stage and rate-limiting step of AD, as its target is to prepare OM for a feasible digestion. If the accessibility to substrate is increased, the conversion yield will be significantly increased as well, and the process develops with no interruptions [233]. Pre-treatments are, therefore, any previous action to substrate in order to weaken its cell wall and structure, facilitating hydrolysis by terms of allowing for enzymes and methanogens to consume organic compounds inside the cell [95,234].

Pre-treatments can be classified into various categories, such as (a) mechanical and physical, (b) chemical, (c) thermal, and (d) biological pre-treatments. All of them aim for the same target, improving hydrolysis and facilitate solubilization, through different mechanisms. The basis of these pre-treatments is described below, provided together with experiences and results in Table 4.

Table 4. Pre-treatments for anaerobic digestion and co-digestion of food waste: Basis and influence.

Pre-Treatment	Substrate	Factors Affected	Results and Improvements	Reference
Mechanical and Physical Pre-Treatments				
Screw press and screening	OFMSW	- Separation of unwanted objects and size classification.	- Biogas yield increases by 15%	[4]
Grinding	FW	- Size reduction (2.5–8 mm).	- CH ₄ yield increased by 9–34%	[45]
Milling	FW	- Excessive size reduction.	- VFAs accumulation due to hydrolysis overloading	[95]
Comminution	FW + SS	- Size reduction	- Biogas yield increases by 10–25%	[92]
Pressure (10 bar) + Depressure (1 bar)	FW	- Break of cell walls. - Increased solubilization	- Biogas production increased by 35%	[235]
Sonication	FW	- Increased surface area and pore size.	- CH ₄ production increased by 94%	[236]
			- Biogas production increased 94%	[237]
Ultrasonication (US)	SS	- Enhanced solubilization due to cell lysis	- Increased biogas yield. - Increased VS reduction	[238]
Chemical Pre-Treatments				
Alkaline pre-treatment	OFMSW	- Cell wall disruption - Inducted particle swelling and increased surface area.	- CH ₄ production increased by 180%	[239]
Acid pre-treatment (HCl until pH = 2)	FW	- Biomass destruction - Cell wall disruption.	- CH ₄ production decreased by 60% due to inhibitors formation (low pH)	[235]
H ₂ SO ₄ pre-treatment	Lignocellulosic waste	- Hydrolyze cellulose. - Cell wall disruption.	- CH ₄ production increased by 57%	[46]
Thermal Pre-Treatments				
Heat (90–120 °C)	FW	- Disintegrate cell walls.	- CH ₄ production increased by 30–40%	[240]
Heat (80 °C)		- Dewatering, pasteurization and disinfection of organic wastes	- CH ₄ production increased by 50%	[241]
Heating (120 °C–30 min)		- Increased solubilization	- Biogas production increased by 11%	[235]
Microwave (145 °C)	FW	- Disrupted cell wall and increased solubilization	- Biogas production increased	[242]
Freezing + thawing (−80–55 °C)	FW	- Cell disruption because of temperature shock	- Biogas yield increased by 30%	[113]
			- Biogas production increased by 23%	[235]

Table 4. *Cont.*

Pre-Treatment	Substrate		Factors Affected		Results and Improvements	Reference
Biological Pre-Treatments						
Biological solubilization	FW + Waste Water	-	Increasing solubilization	-	Reduction of organic concentration in the digestate	[243]
Composting	OFMSW	-	Increased hydrolysis potential by pre-degradation	-	CH ₄ production increased by 73.3%	[244]
Microaeration	FW	-	Inducted particle swelling and increased surface area.	-	Biogas yield increased by 23%	[245]
Two stages	OFMSW	-	Low and high pH stages respectively separated.	-	CH ₄ production increased by 21%	[246]
Combination of Pre-Treatments						
Bacterial hydrolysis and alkaline addition	FW + SS	-	Increased hydrolysis potential. Cell wall disruption and inducted particle swelling	-	Biogas yield increased by 140%	[247]
Thermo-acid (HCl + 120 °C)	FW	-	Increased solubilization	-	Biogas production increased by 18%	[235]
Thermo-acid (HCl at 100 °C)	OFMSW	-	Increased solubilization	-	Biogas production increased by 120%	[248]
Bio-Physico-Chemical (Bacillusat + US + Acid)	Oil + Waste Water	-	Enhanced oil degradation	-	Biogas production increased by 280%	[249]

5.1. Mechanical and Physical Pre-Treatment

Mechanical and physical pre-treatments are based on separation of large and unwanted materials from the OM, and reducing its particle size, as increased contact surface allows for a better contact and interaction between substrate and microorganisms [34,45]. If particle size is sufficiently reduced, methane yield can be improved up to 40%. The most common procedures to reduce particle size are milling, screw press, disc screen, or shredder with magnet methods. As an example, researchers found an improvement a biogas yield improvement of 9–34% when grinding FW previously to its anaerobic treatment [45], an increase in biogas yield of 20% if substrate was comminute [92] or a 94% increment in both, biogas and methane yield, if FW is previously grinded and sonicated [236,237]. However, an excessive reduction of particle size can lead to a hydrolysis overloading and the subsequent VFA accumulation. This has been reported when treating milled FW [95], causing a collapse in the methanogenic reaction.

Another mechanical pre-treatment gaining ground is sonication, consisting in disrupting cell structure and floc matrix of particulate matter by means of ultrasonic waves [250]. In this case, biogas enhancement is due to an improved solubilization [237] that can increase the methane yield up to 90% [236]. However, this pre-treatment is not yet feasible to use in-situ in big-scale plants.

Other physical type of pre-treatment aims to increase surface area and pore size by disrupting biomass structure and increasing solubilization [235,251]. This is the case of pressure-depressure pre-treatments that can increase biogas yield up to 35% [235] when substrate is first under pressure (10 bar), and finally depressurised, achieving the breakup of cell walls. Irradiation can also be considered a successful pre-treatment disrupting biomass cell structure and decreasing crystallinity of cellulosic components [252,253].

5.2. Chemical Pre-Treatments

With these pre-treatments, cell disruption and biomass accessibility is searched for by addition of strong acids and alkalis in order to previously destroy biomass [254]. The main objective is to hydrolyse cellulosic materials, especially food waste containing vegetable and lignocellulosic substrates [4,110]. Experiences by using alkali pre-treatment show that biogas yield can be increased up to 170% [239], because particle swelling was inducted, thus increasing surface area. Also, lignin surface is disrupted and the structural linkages between lignin and carbohydrates (CH) are broken, so CH are more accessible and subsequently converted into biogas [251]. On its own, acid pre-treatments are useful for treating lignocellulosic substrates [255], as it is useful for disrupting the strong cells. However, for FW it is not so suitable, leading to a biogas yield decrease of 66% [235] due to the formation of inhibitor at low pH such as carboxylic acids and phenolic compounds [256].

5.3. Thermal Pre-Treatments

Exposing substrate to temperature changes over a period of time, is known as thermal pre-treatment [257]. These pre-treatments could be included in a physical category, however, due to its feasibility and suitability, are usually considered in a separated category. The thermal pre-treatment purpose is to disintegrate cell walls and membranes to increase solubilization of OM [258]. Subjecting FW and substrates to temperatures between a range of 50–160 °C results in an increase of biogas production around 30–35% [191,240,259] or even 50% [241]. For temperatures that are out of the range, AD performance and biogas yield are decreased compared with the biogas yield obtained with non-treated substrate, as inhibitory and refractory compounds appear in the digester. That is exactly what happens when thermal pre-treating slaughterhouse waste [260], lipids were turned into VFA acid, and the AD process resulted in foaming inside the reactor, leading to an overload of the system.

Feasibility of thermal pre-treatments came also from other benefits of applying them, for example, pathogen removal [261] or dewatering performance [241], which reduced the viscosity of digestate, making it more feasible for later transportation.

Freezing and thawing is also considered as a thermal pre-treatment, but, in this case, submitting substrate to sub-zero temperatures (freezing) and afterwards recovering its temperature (thawing). In this case, biogas yield increased around 30% [113], due to cell disruption that is caused by the temperature change. This pre-treatment has not been widely used, mainly because of its high operational cost, but it is extremely adequate and feasible for FW as freezers are always present in agri-food industry facilities.

5.4. Biological Pre-Treatments

Biological pre-treatments often consist of aerobic or anaerobic treatment before the main AD process, in order to increase the enzymatic population or increase the process development [4].

Aerobic pre-treatment, for example, [244] subsequently increases hydrolysis potential, resulting in higher biogas creation up to 70%. However, an excessive aeration can lead to a biogas production decrease due to VFA formation and accumulation [245].

Anaerobic pre-treatments, on their own, consist of separating various phases in two different reactors (hydrolysis-acidogenesis from acetogenesis-methanogenesis) [246], so optimal conditions are achieved in both processes and key parameters, especially pH, can be controlled and optimized to lead to higher biogas formation. In one reactor, pH is lowered to acidity conditions (from 4 to 6), and hydrolysis-acetogenesis is carried out, even breaking down inhibiting chemicals for the second stage microorganisms [260]. In the other reactor, the pH value is maintained from 6.5 to 8 for a proper growth of methanogenic population [262]. Also, less VFA are found in this reactor as they are easily converted into methane, avoiding VFA accumulation. This stage separation achieves biogas increases up to 20% [262], as many researchers found when comparing single stage and two-stage anaerobic digestion, revealing bioaugmentation and its effects [263] However, two-stage digestion is not so commonly used in full-scale plants, as single stage reactors are simpler to operate [199].

6. Environmental Impacts of Anaerobic Digestion of FW with Sewage Sludge

As waste management plays an important role in environmental engineering, studying its environmental impact appears as an essential part of its feasibility and applicability [264]. Through the years, many tools have been used. However, the most suitable and powerful tool for determining environmental, and even economic and social impact of waste management is Life Cycle Assessment (LCA) [265]. LCA enables comparing and quantifying the impacts of different waste solutions, acting as a support tool for decision making in waste management. If LCA is applied to anaerobic digestion of food waste (and sludges for Waste Water Treatment Plants), the following conclusions can be reached:

Mostly, all of the environmental impacts of AD are due to climate change. A large part are caused by methane leaks and other accidental emissions during the AD process. As methane is the major component of biogas and it is considered a greenhouse effect gas, these emissions should be taken into account. In order to reduce leaks and their impact, flaring systems and emergency torches are usually incorporated in biogas plants [33,266,267]. Other impacts are usually related to different gas leaks that cause acidification and eutrophication [268,269]. Mainly, because high ammonia or hydrogen sulphide biogas contents, which are important parameters used as control factors in biogas production with food waste as substrate, and digestate uses. Acidifications come from biogas combustion, resulting in nitrogen oxide and sulphur dioxide emissions [13,270]. Both are considered secondary particulate precursors, resulting in particulate matter formation. On the other hand, eutrophication can be a result of digestate management [271,272], as it contains a high level of N, and it is usually considered as fertilizer.

However, when comparing AD with other waste management solutions, it seems to be, if not the best, one of the most preferable environmental solutions. Studies have been carried out [4] when comparing different scenarios and their impacts, showing CoAD treatment as the most viable solution, in spite of its undesirable impacts, as it generates the highest amount of renewable energy in form of biogas turning this disposal method into an energy recovery system. Biogas can be used

in different forms: for electricity generation, heat production [14,273,274], and even for vehicle use through biogas upgrading [12,275]. Also, biogas is used in cogeneration, producing heat and electricity simultaneously. Biogas can supply energy in form of electricity to the principle industries, as well as to those close or nearby, excess is often delivered to the public grid. Heat can be used internally to maintain the anaerobic reactor temperature and to provide heat and steam to industries. It can also be connected to district heating systems. Moreover it will be upgraded and injected to the gas grid for household use, or used as fuel, meeting traditional fuel standards through purification processes. Environmental emissions from biogas utilization should also be considered, although methane is the cleaner hydrocarbon due to its lower carbon content.

7. Conclusions and Perspectives

AD and CoAD appear as reliable and feasible solutions and technologies for recycling and recovering both sewage sludge and food waste. In economic, social, and environmental terms, it seems to be the best waste management option, because it is a renewable energy source with low emissions. Although a more thorough knowledge of the process is needed in order to ensure the proper development and stability of the microbial degradation.

Addition of FW to SS anaerobic digesters enriches the nutrient content, dilutes inhibitors, increases the alkalinity, and reduces ammonia formation, so the stability of the process is enhanced.

However, due to the origin and composition diversity of FW, which gives specific properties to them, a well-known characterisation is needed to combine them in the correct proportion to enhance biogas production and stability of the process. Protein rich compounds show a fast conversion to biogas, but ammonia and sulphides can be released. On their behalf, carbohydrates show the fastest conversion rate, but methane yield is not so elevated. Lipids represent the highest biogas yield, but it can lead to process inhibition due to VFA and LCFA accumulation and foam formation. However, a buffer system between ammonia and VFA can be formed, as occurs when co-digesting FW and SS. In essence, AD challenges from the technical point of view, are related with the process stability and development, such as VFA accumulation, foaming, low buffer capacity, and fast acidification, with its consequent inhibition of methanogens. In this context, multi-stage systems arise as a feasible solution.

Pre-treating substrates constitutes a way of improving and increasing anaerobic degradation. In FW terms, pre-treatments mainly consist of size reduction for a better cell wall disruption, and this enables a better hydrolysis stage, as well as enhancing biogas rate and yield. However, an excessive pre-treatment can cause VFA accumulation and its subsequent inhibition due to hydrolysis overloading.

In light of this, a correct separation and characterisation of FW is needed, at both household and industrial levels, to help to predict biogas formation and the development of the anaerobic process, ensuring a correct nutrient balance, reducing lipid content, and achieving an appropriate C/N ratio. This objective can be reached with better planning and separation methods, by local authorities, who must keep in mind the importance of social awareness.

Economic cooperation for AD is also needed to improve and establish a circular economy. A distributed ion system for biogas production with many smaller plants, instead of few high capacity plants, could help to reduce transportation costs. This would lead to a continuous process making the digester less sensitive to input changes. Buffer capacity could be increased, along with the balance and stability between biogas/methane rates. Under these terms, wastewater treatment plants seem a perfect solution, because of their multiplicity and continuous operation. In addition to the benefits in waste management, previously mentioned, these plants, environmental and required installations, can be converted into energy generators.

Although the using already existing anaerobic digesters (such as WWTP anaerobic digesters for sewage sludge) for FW biodegradation is desirable as it increases the heat and electricity outputs, the adoption of co-digestion in these infrastructures will impose higher requirements for process control. This, in addition with the high cost of substrate transportation and the low value of the end products, develops a future scenario where AD is integrated with the production of value-added products.

As an example, on one hand, FW AD can be merged with biorefineries so high-value products are produced, and, in addition, the solid wastes are treated with a subsequent AD process. On the other hand, by-products from AD process can be used to produce another high-value products, as VFA are already used to produce biopolymers, like PHA.

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Abbreviations

AD	Anaerobic Digestion
AM	Animal Manure
BMP	Biochemical Methane Potential
CoAD	Anaerobic Co-digestion
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agriculture Organization
FL	Food Loose
FSC	Food Supply Chain
FW	Food Waste
HTG	Hydrothermal Gasification
LCFA	Long Chain Fatty Acids
LPCH	Lipids, Proteins and Carbohydrates
OFMSW	Organic Fraction of Municipal Solid Waste
OM	Organic Matter
TBMP	Theoretical Biochemical Methane Potential
TS	Total Solids
SS	Sewage Sludge
VFA	Volatile Fatty Acids
VS	Volatile Solids
WWTP	Waste Water Treatment Plants

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