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Pretreatment of Food Waste for Methane and Hydrogen Recovery: A review

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ABSTRACT

Food waste (FW) management by biological process is more attractive and eco-friendly approach than thermo-chemical conversion or landfilling. However, FW composition and physico-chemical and biological characteristics affect the overall biological process in terms of product yield and degradation rate. To overcome this major bottle neck, the pretreatment of FW is proposed. Therefore this review aims to provide a comprehensive summary of the importance of pretreatment of FW with respect to FW management by anaerobic digestion (AD) and dark fermentation (DF). It also reviews the existing knowledge gaps and future research perspectives for better integration of FW pretreatments for AD and DF, which should include (i) the preservation of carbon mass through freeze and thaw, or drying; and (ii) improve the carbon accessibility through particle size reduction and thermal pretreatments for high-rate bioenergy recovery.

Keywords: Biowaste; Anaerobic digestion; Biogas; Dark fermentation; Biohydrogen

1. INTRODUCTION

Globally, around 1.3 x 10^9 tonnes of food waste (FW) are disposed in landfills, contributing to 3.3 x 10^9 tonnes-CO_2-eq.year^{-1} of greenhouse gas emissions (GHG) (Salemdeeb et al., 2017; Fisgativa et al., 2017). In which, around 83% of FW were from Industrial Asia (IA), Europe (EU) and North America & Oceana (NAO) (Fig 1a) (Pliessner and Lin, 2013). The composition of different food products that will end-up as typical FW is depicted in Fig 1b. It is predicted that globally ~ 2.5 x 10^9 tonnes of FW will be generated by 2025, which need to be avoided, reduced or recovered, processed and recycled for a sustainable circular (carbon) economy. Recycling of FW will be beneficial for the economy as below:

(a) Option 1: FW to bioenergy and biofuels, which will greatly reduce the fossil fuel demand and associated fuel/energy production costs;

(b) Option 2: FW to biofertilizer, which will help to improve the soil quality, stability and reduce the fossil fuel based commercial fertilizer production/demand;

(c) Option 3: FW to new biomaterials and industrial biochemicals (e.g. pigments, bioplastics, etc), which will reduce the fossil fuel demand and utilization of base chemicals;

(d) Option 4: FW to animal feeds, which will reduce the arable land and water use that go for production of feeds for animals and fisheries.

Ultimately, FW recycling provides job opportunities, reduces GHG emissions, decreases the waste disposal costs, mitigate the negative environmental impacts and support sustainable waste management practices under circular economy.

Food waste contains natural fibers, carbons, proteins, fats & lipids, vitamins and minerals in a complex matrix that are readily biodegradable and reusable. But, the FW compositions are region specific that affect their overall bio-chemical characteristics and could mainly influence their management/disposal plans. For instance, vegetables, cereals and fruit waste components represent ~ 80% of the FW in China, while vegetable and fruit waste alone represent ~ 70% of the total FW volume in Turkey. In comparison, bakery waste and dairy products account for ~ 50% of the FW in western countries (Fig 1c). The meat components represent 3-5% of the FW in all regions. The fruit waste are characterized by higher C/N ratio (> 20) than meat products (< 5) and their mixing ratio with other food products influences the final C/N ratio of FW. The typical C/N of FW varies between 14 and 37 (Zhang et al., 2007). Also, dry solids contents vary between 10 and 25%. Therefore, FW is a heterogeneous substrate with unpredictable composition that makes it difficult to manage/treat them effectively (Cesaro and Belgiorno, 2014).

According to FW management hierarchy, prevention is the best option followed by biological treatment and thermal disintegration, and as a last alternative, landfill disposal. Nevertheless, landfilling of FW is a very common disposal method in developing countries e.g., India, China, Thailand, Bangladesh, Sri Lanka, etc. Compared with thermal treatment of FW, which requires more energy to remove the water contents, mineralize and recover energy, biological approaches are highly feasible, reliable and cost-effective as summarized in Table 1. Considering all the benefits, composting is the most commonly used option for FW recycling in developed countries (e.g. USA) followed by anaerobic digestion (AD). There are more than 300 composting facilities that are treating ≤ 3% of 28.8 x 10^6 tonnes of FW in USA (Levis et al., 2010), while more than 2000 facilities are treating biowaste (mainly including FW) in Europe (Boldrin et al., 2009). But, operational time and impacts of FW composting process on climate change are significantly higher than AD (Table 1). Moreover, the quick acidification of FW, high moisture contents, odorous volatile organic compounds (VOC) emissions and pathogen spread are the major concerns with FW composting (Wang et al., 2016). In contrast, the AD of FW provides both energy (i.e., 0.6 MWh t^{-1}) and biofertilizers (~ 40% of initial feed) from the same amount of input materials with a lead time and foot print lower than that of composting.

The first AD plant treating organic fraction of municipal solid waste (so-called OFMSW) was established in USA in 1939, while in Europe numbers of AD facilities were established only over the past few decades. It is projected that biogas production capacities will grow up to 20 x 10^9 m^3 by 2030. Especially, Germany and Switzerland are the pioneers for installing pilot scale biogas plants and their treatment capacities reached between 15 and 200 x 10^6 tonnes per year (Grando et al., 2017). The AD processes for FW and sewage sludge co-digestion are also commercialized in Italy, Germany, Denmark and Switzerland (Iacovidou et al., 2012; Chakraborty et al., 2017). China (~242 facilities) and Hong Kong (1 facilities) are also building the organic waste treatment facilities for FW management/treatment, in which AD is the primary technology. In South Korea, one-third of existing AD plants (out of 92 facilities) are treating FW or FW leachate for biogas production (De Clercq et al., 2017). Table 2 lists the FW-AD installation capacities and policy measures proposed by few developed and developing countries.

Compared to single-stage AD processes, two-stage processes that separate rate-faster hydrolysis-acidogenesis steps (fermentation) from rate-slower methanogenesis step is more attractive for FW treatment (Cavinato et al., 2012). The main advantages of two-stage processes are (i) better stabilization of the AD process under two different pH optima, (ii) regulate the methanogenic process from organic overloads, (iii) reduce the digestion time and buffering requirements; and (iv) increase the overall yield (carbon conversion up to 40%) of gaseous end-products i.e., H_2 and CH_4. (Schievano et al., 2014). Hydrogen is mainly produced from readily available sugars (~ 10% of total COD is utilized for H_2 production at first stage Dark Fermentation; DF), while the more complex unfermented materials are further digested to produce CH_4 (~ 80% of total COD is converted to CH_4) in second-stage methanogenesis reactor.

In this review, the basic knowledge of different pretreatment options for FW-AD and -DF are discussed. In particular, the effects of pretreatments on H_2 and CH_4 recovery from AD and DF systems are detailed, respectively. Based on the FW characteristics and compositions, the pretreatment technology needs to be carefully selected for AD or DF processes as detailed in below sections.

2. PRETREATMENT OF FOOD WASTE

Pretreatment of organic substrates (originally developed for fermentation process) started in the early 1920s' and was considered as the most expensive step due to an extensive use of energy/chemicals. More recently, pretreatment steps have been reconsidered and constitute now the most important step to improve CH_4 or H_2 yields from FW. From a Web of Science search with the keywords "Anaerobic digestion", "Food Waste" and "Pretreatment", the research papers that are related to FW digestion and pretreatment technologies were found to be exponentially increased between 3 and 200 folds by 2017 compared with that of 1990's data (Figure 2). High number of physico-chemical, mechanical, thermal and biological pretreatment methods are reported for FW in recent studies. The main objectives of using pretreatments are : (i) to improve the surface properties for better microbial interactions; (ii) to reduce/remove the toxic compounds that may affect the process; (iii) to improve the hydrolysis rate kinetics for proteins and lipids; (iv) to increase the accessibility of hardly accessible compounds and (v) to process the FW prior to AD or DF, while reducing the organic carbon losses during storage/transport (Kurian et al., 2013; Monlau et al. 2013; Karthikeyan et al., 2016; Fisgativa et al., 2016a). However, the pretreatment method should be selected on the basis of characteristics of the FW and subsequent bioprocess methods (Raud et al., 2015, Carrere et al., 2016). Four categories of pretreatment methods can be distinguished as follows:

(a) **Physical and mechanical pretreatments** are inevitable to improve the FW physical properties i.e., surface area. It is the most important process that facilitates easy handling and feeding of FW into the digesters for AD or DF. It also facilitates the digestion/fermentation in shorter retention time. Milling/chopping/grinding, screw press, lysis-centrifugation, liquid shear/collision and high-pressure homogenization methods can be alternatively used to improve the physical or mechanical properties of FW. They do not affect the original substrate composition, but energy requirements are high.

(b) **Thermal pretreatment** methods are classified as wet- type and dry- type (e.g. simple drying). Food waste is usually pretreated by wet-type prior to AD or DF. Since it is operated under elevated temperatures (and pressure), it helps to solubilize more sugars through better hydrolysis and provides a more homogenous pulp for feeding AD/DF. In addition, it is easier and quicker than other pretreatment techniques. Another important advantage is that the FW pulp is also sterilized and native unwanted microbes (e.g. lactic acid producing bacteria) that could affect CH_4 or H_2 yields are deactivated. The pH regulation may further improve the efficiency of thermal pretreatment of FW for AD or DF, which requires better understanding. But, the thermal pretreatment of FW also favors the formation of recalcitrant compounds (i.e., melanoidins) over 150^{o}C (with short retention time) or < 100^{o}C (longer retention time) that may affect the product recovery.

(c) **Chemical pretreatment** mainly relies on strong to mild chemical agents to modify the physico-chemical and biological properties of FW. It is a quick process that requires specific optimization depending on FW characteristics to avoid the accumulation of inhibitors such as furanic or phenolic compounds (Monlau et al., 2014), long-chain fatty acids or the production of recalcitrant compounds through Maillard or burnt sugars reactions, affecting CH_4 or H_2 recovery. Acid pretreatment is known to be efficient to solubilize carbohydrates, while alkali pretreatment is efficient in solubilization of proteins and lignin as well as lipid saponification. However, the chemicals used for acid pretreatment is corrosive (e.g. H_2SO_4, HCl etc.) and require non-corrosive coatings for the equipment used in the processes. For acid/alkali pretreatment, the FW to acid/alkali ratio needs to be optimized based on the total solids contents and strength of the acid/alkali used. The alkali pretreatment requires longer reaction time than acid pretreatment but salt formation is considered as the major drawback. There are few other pretreatment methods (i.e., such as ozone (Ariunbaatar et al., 2014a), hydrogen peroxide (Gundupalli and Bhattacharya, 2017) and etc., that are not suitable for FW pretreatment, while they are also been less investigated.

(d) **Biological pretreatment** is usually slow process that requires longer retention time and the microbes utilizethe free and readily available sugars as main carbon source during the pretreatment step. Optimization and maintenance of pure biological agents for pretreatment of FW are usually difficult, since they are competing with the indigenous microorganisms during the pretreatment process. There are only a few case studies using pure microbial enzymes for pretreatment of FW because enzymatic pretreatment is expensive and requires high concentrations of enzymes to achieve efficient pretreatment. Instead, crude enzymes produced from biomass lysate are also directly used for pretreatment to reduce the costs (Kiran et al., 2015; Yin et al., 2016). But only limited information is available from the literature and it is too early to conclude whether the biological pretreatments of FWs are viable technologies.

Aeration (and micro-aeration) of FW is also considered as an alternative pretreatment approach, which can improve the CH_4 yield. Aeration limits the quick accumulation of volatile fatty acids by altering the microbial community structure and hydrolyzes substrates that are more complex by excretion of mobilizing enzymes (Fisgativa et al. 2016b). Thus the aeration can modify the physico-chemical- and biological properties of the FW, but the success depends on the establishment of optimum biological conditions.

(e) **Combined pretreatment** is usually the combination of physical (e.g. grinding) and chemical (e.g. acid/alkali) or thermal (e.g. wet-type; low temperature) technologies for improving the FW properties prior to AD or DF. However, no efficient integration and pretreatment combination has been reported for FW yet. The available results are not directly comparable due to (i) heterogeneous characteristics of FW used in different research studies; (ii) the types of inoculum used; and (iii) the operating variables tested.

In summary, the purposes of FW pretreatment are to (i) reduce the carbon loss as CO_2 during storage/transport; (ii) improve the surface properties for easier access to microbes; (iii) reduce the accumulation of volatile fatty acids at early stage or during storage and transport; and (iv) alter biological properties to support microbiomes from AD/DF. Nevertheless, more specific objectives may differ for CH_4 or H_2 production as will be detailed in sections 3 and 4.

3. PRETREATMENT OF FOOD WASTE FOR CH_4 RECOVERY

3.1 Objectives of food waste pretreatment prior to anaerobic digestion

Anaerobic digestion of FW is a complex process, where FW is converted into biogas by sequential actions of fermentative bacteria and methanogenic archaea, while minerals are retained in the slurry as nutrients (Khalid et al., 2011; Karthikeyan and Visvanathan, 2013). The organic carbon conversion rate is directly proportional to the biogas yield under well operated conditions. A typical biogas contains 50-70% of CH_4, 30-50% CO_2 and other gases in traces. In addition the complex microbial metabolism requires essential nutrients such as nitrogen, phosphorus, magnesium, sodium, manganese, calcium and cobalt (Speece and McCarty, 1962). The excess or lack of any of the above nutrients in the AD process severely inhibits or affects the specific growth rates of the microbes, which can lead to poor biogas yield. Therefore, a better understanding of FW characteristics is important prior to optimization of the AD process. It is also equally important to understand the process inhibition at early stages by monitoring (a) a drop in daily CH_4 yield up to 10%; (b) an increase in volatile fatty acids concentrations > 250-500 mg L^{-1}; and (c) a drop in pH over the subsequent days.

The biogas productivities are usually expressed in terms of per unit digester volume, which are calculated using the following theoretical model (Contois 1959) as given below (eq. 1),

$$Vs = (M_o\,S_o / HRT)\,[1 - K / (HRT \times \mu_m - 1 + K)] \qquad \text{eq. 1}$$

Where,

Vs = specific productivity (rate of methane production in cubic meters per cubic meter volume of digester per day)

M_o = ultimate methane yield (cubic meter methane per kilogram of volatile solids added)

S_o = influent volatile solids (kg m^{-3})

HRT = hydraulic retention time (hours or days)

K = dimensionless kinetic co-efficient (it varies for different feed stocks)

μ_m = maximum specific growth rate of microbes (d^{-1})

The role of HRT (= SRT for low solids digesters) is a critical parameter for AD with 20 ~ 36 days being the optimal according to Komilis et al., (2017). Organic loading rate and operating temperature influence this parameter and subsequently the CH_4 recovery. Especially, the temperature influences the specific growth rate of microbes and affects the organic carbon removal rate, which is given in Equation 2.

$$\mu_m = 0.013\ (T^oC) - 0.129 \qquad \text{eq. 2}$$

The organic loading rate (OLR) alters the total solid contents of the reactors and thereby alters the microbial activity and carbon removal rates. The total solids content of the digester could be wet- (< 5% TS) or dry- (>20% TS) digestion, however, the C/N ratio should be 20-30, otherwise inhibition of the digestion process could be expected due to ammoniacal-N accumulation under continuous operation (Puyuelo et al., 2011; Leung and Wang, 2016; Chatterjee and Majumder, 2016). In contrast, a review by Zhang et al (2014) highlighted that the operation of digesters at low C/N ratios of 15-20 was feasible and concluded that the C/N ratio is not a critical factor in AD. The typical CH_4 yield from FW digestion ranges between 140 and 470 L kg^{-1} of volatile solids added or removed in the reactors. The differences in CH_4 yields are more related to the FW composition and characteristics (i.e., carbohydrates, proteins and lipid contents in FW), which are difficult to control due to their sources (Kondusamy and Kalamdhad, 2014). Also, the carbohydrates, proteins and lipids have different digestion rate and CH_4 potentials (Table 3). The start-up of the FW-AD process is rather difficult since the operations often encounter operational failures due to different mixing proportions of carbohydrates, proteins and lipids in FW from different seasons or sources and changing physiochemical and biological compositions (Zhang et al, 2014; Ariunbaatar et al., 2014b; Chiu and Lo, 2016). Moreover, most FW digestion studies are performed in batch experiments (and under mesophilic conditions), which does not represent the real life situation and so it may not provide realistic answer for the cause of poor digestion or the development of efficient strategy to mitigate operation failures. Komilis et al. (2017) reviewed that the mode of AD operation and the type of FW pretreatment are the two major factors that significantly affect the CH_4 yields. To more specific, the authors concluded that FW pretreatment is necessary to improve CH_4 recovery rate in continuous digestion systems. In contrast, several reports highlight that the pretreatment step provides negative correlation with the CH_4 yield, likely because of high number of variables that need to be optimized, i.e., choice of pretreatment, substrate composition, pretreatment conditions and etc., (Carlsson et al., 2012). Therefore, no standardized pretreatment scheme is proposed to handle the heterogeneous FW. Moreover, most studies are performed at lab scale that cannot be directly translated into full field scale operations.

3.2 Results of food waste pretreatment on methane production

Food waste pretreatment for CH_4 recovery should mainly aim to, (apart from carbon preservation): (i) improve the digestibility of lipids/proteins in short retention time; (ii) reduce the quick acidification rate in AD; and (iii) alter the physico-chemical and biological characteristics of FW to avoid process inhibition/low-rate CH_4 recovery. Many studies reported that FW pretreatment is improving CH_4 recovery as a function of the applied conditions, as compiled in Table 4. Thermal pretreatment is often reported as the best method, followed by alkali pretreatment of FW for AD. Under combined pretreatment selections, FW are often preprocessed (i.e., grinded) before subsequent pretreatment step, which may affect the efficiency of second stage process and overall net-energy balance. Physical pretreatment (i.e., grinding) to reduce the particle size is one of the most important pretreatment steps for FW-AD, through which the surface area is largely improved for microbial attachment and solubilization. Especially, particle size is reported to have a significant effect on methanogenesis process i.e., more particularly on methanogens functions (Obulisamy et al., 2016). As an illustration, FW particle size of less than 2.5 mm yields ~ 22-26% higher CH_4 recovery than 8 mm particle size under semi-solid digestion conditions (Agyeman and Tao, 2014). Also, the lower the particle size, the better the thermal or acid/alkali solubilization of sugars and the subsequent higher CH_4 yield. High-pressure pretreatment is another technique that can efficiently solubilize the sugars, decrease the particle size and subsequently improve the biogas yield by ~ 48% from kitchen waste (Ma et al., 2011). Li and Jin (2015) achieved a maximum of 32% higher biogas yield (over control) from FW following combined physical (grinding to 1-2 mm) and thermal (120^{o}C, 50 min) pretreatment. However, pretreatment temperature and duration were reported to have a significant impact, therefore, these parameters require optimization taking into account of FW composition (Li and Jin 2015 and Li et al., 2016). Low (55^{o}C for 70 min) or high thermolysis (160^{o}C for 50 min) was not favorable for the biogas recovery i.e., resulted with 3-5% lower yield than in the control. With a long thermolysis process, the oil and fat contents of FW might be solubilized into short chain fatty acids, which in return might be inhibitory to biogas production. Nonetheless, the thermal process might be beneficial to reduce the lactic acid bacteria, which can cause the quick acidification during FW-AD and alter the acid production pathways. In addition the thermal pretreatment (not including autoclaving or high-temperature) process helps to enrich the spore-forming bacteria in FW, which is beneficial to avoid quick accumulation of organic acids. The thermal pretreatment process also can inactivate or reduce the toxicity effects of some FW components, providing better hydrolysis of sugars, reducing the viscosity of the FW slurry, pathogens loads and improving the slurry pH (Nguyen-Hao et al., 2015). Hence, the thermal process with or without physical pretreatment (i.e., grinding) is the most reliable pretreatment option for FW prior to AD, as it could achieve up to ~ 75% higher CH_4 yield than in the control (Naran et al., 2016). The best option to subsidize the energy and cost factors related to thermal pretreatment of FW is to use the excess heat produced from gas turbines of the biogas plant.

Acid or alkali pretreatments are often preceded by physical grinding or combined with thermal pretreatment. Nevertheless, the CH_4 recovery was comparatively less than that in thermal pretreatment of FW (Naran et al., 2016; Ma et al., 2011). This could be due to several complex reactions i.e., acid pretreatment favors the Maillard reactions, which reduce the carbon source available for CH_4 conversion. In addition, grinding of FW for particle size reduction prior to chemical pretreatment may also alter the number of reactive sites in comparison to non-grinded FW, which may affect the acid/alkali requirements and also the yield of burnt sugars. As shown by Karthikeyan et al. (2017), acid pretreatment alone did not improve the carbohydrate solubilization from FW. Acid pretreated FW led to ~45% lower biogas yield (Ma et al., 2011), while alkali pretreatment improved the CH_4 yield by 25% in comparison to the control. However, combination of alkali and thermal pretreatment improved the methane yield ~32% over control (Naran et al., 2016).

Alternatively, microwave and high-voltage pulse discharge FW pretreatment techniques were also investigated. Improvement was less significant i.e., ~ 6% with FW and sewage sludge (Zhang et al., 2016) when compared with the FW only i.e., ~ 35% (Zou et al., 2016). In both studies, the particle size of the FW was less than 2 mm and therefore, the effect of physical pretreatment could be similar without considering the differences in FW compositions. When compared to high-voltage pulse discharge pretreatment, ~ 56% higher CH_4 yield was measured from ultrasonic pretreated FW (Naran et al., 2016). However, none of these pretreatments achieved higher CH_4 yields than thermal pretreatment technology.

Few recent studies used biological pretreatment techniques and compared them with the commercial enzyme pretreatment methods. As an illustration, a fungal mash hydrolysis was able to provide 40-136% higher CH_4 yields than the control (Yin et al., 2016; Kiran et al., 2015).

However, the enzymes were directly added from the production medium, which might also have additional sugars and carbon sources that are used for biomass cultivation. So, prior to conclude on biological pretreatment, carbon mass balances need to be carefully calculated especially when crude enzymes or spent medium are used for pretreatment of FW. Nonetheless, when compared with the commercial enzyme addition, crude enzyme addition is beneficial in terms of energy-economic point view for FW-AD.

Oddly, micro-aeration could also be considered as a pretreatment to improve the AD process. Lim and Wang (2013) found 10% increase in CH_4 yield with micro-aeration in comparison with the control. Micro-aeration provides selective pressure on specific groups of microbes that support efficient hydrolysis-acidogenesis process and also avoid VFA chain elongation reactions. But, no clear evidence of this hypothesis is reported, which therefore requires further investigation. Aeration of FW to reduce VFA contents is proposed as an alternative pretreatment option by Fisgativa et al. (2016b). Under low aeration condition and duration (2 days), CH_4 yield increased in spite of ~ 10% organic matter loss.

Freeze and thaw pretreatment is a process commonly found in food outlets where food items are stored under frozen conditions over a long period of time before they being disposed. The freeze and thaw method has some effects on FW properties and thereby positively affect the biogas and CH_4 yields (Ma et al., 2011). Even though the increase of CH_4 yield is often lower than 10%, it is highly desirable option because the overall carbon content of the FW is maintained until it is processed by AD or DF. Drying is also considered as an interesting alternative option to preserve the organic carbon from FW. Sotiropoulos et al. (2015) proposed to use an onsite domestic dryer, which prevented the biological decomposition and odor emissions without altering the CH_4 potential of biowaste.

From the detailed review, freezing and thawing or drying process are very useful pretreatment approaches to store the organic carbon and avoid natural degradation of FW. Nonetheless, the best pretreatment option for improving the CH_4 yields from FW seems to be a combination of physical and thermal processes i.e., grinding followed by thermal pretreatment.

4. PRETREATMENT OF FOOD WASTE FOR HYDROGEN RECOVERY

4.1. Objectives of food waste pretreatment for dark fermentation

In DF, equivalent to the early stages of the AD process, the conditions are principally set to avoid the methanogenic activity, i.e., short hydraulic retention time and high-acid conditions. The ability of the microorganisms to ferment organic carbon and produce hydrogen is widespread in the environment. Thus the range of microbial inoculum from different origins are used to produce H_2 by DF e.g. aerobic or anaerobic sludge from municipal wastewater plants, composts, landfill leachates and soils (Guo et al., 2010). Dark fermentation can also be carried out without any inoculation when microbial consortia are naturally present, which is the case in FW.

In DF processes, the growth of H_2-producing bacteria (HPB) should be favoured. The HPB include strict anaerobes such as clostridia or rumen bacteria, or facultative anaerobes such as enterobacteria (*E.Coli, Enterobacter sp., Citrobacter sp, etc.,*). Among them *Clostridium sp.* and *Enterobacter sp.*, are most widely used as a model species for DF. The two main pathways for H_2 production from glucose under dark fermentation are the acetate and butyrate pathways as shown in the equations below (eq. 3 and eq. 4),

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4\,H_2 \quad \text{(eq. 3)}$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2\,H_2 \quad \text{(eq. 4)}$$

Theoretically, 4 and 2 moles of H_2 are produced from 1 mole of glucose conversion through the acetate and butyrate pathway, respectively. Hawkes et al. (2007) proposed to consider the following reaction when dealing with mixed cultures, and in that case, a maximum of 2.5 moles of H_2 per mole of glucose is expected to be produced as shown in the equation below (eq. 5):

$$4C_6H_{12}O_6 + 2H_2O \rightarrow 3CH_3CH_2CH_2COOH + 2CH_3COOH + 8CO_2 + 10H_2 \quad \text{(eq. 5)}$$

On top of such metabolic limitations, ecological interactions are possible to occur with various H_2-consumers or other micro-organisms, which do not produce hydrogen (non-HPB) but are outcompeting HPB for the same organic substrate. All these limitations lead to lower the H_2 yield from FW under mixed culture DF conditions. Therefore, pretreatment of both the inoculum and FW are necessary prior to DF.

Among the main H_2 consumers, hydrogenotrophic methanogenic archaea that directly convert H_2 to CH_4 (eq.6) will co-exist with HPB in DF systems and may reduce the H_2 yield.

$$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O \quad \text{(eq. 6)}$$

However, the operating conditions of DF reactors are often set to be detrimental to their growth, i.e., low pH (5-6); low HRT (from few hours to few days), thermal shock pretreatment of the microbial inoculum, etc. Indeed methanogenic archaea are highly sensitive to acid, alkali or heat-shock treatments that are often carried out for their inactivation in inoculum for DF. Heat shock consists of thermal pretreatment of inocula at 90-110°C for 15 min and 2 h. It presents the dual advantages of eliminating non-spore-forming microorganisms (*e.g.* methanogenic archaea) and select spore forming HPB e.g., *Clostridia sp., (*Argun and Kargi, 2009). Methanogenic archaea can also be controlled using chemical inhibitors such as bromoethane-sulfonate, acetylene and chloroform (Guo et al, 2010). Considering that methanogens could be well avoided in DF by applying an initial inoculum pretreatment, other H_2 consumers are rapidly outcompeting with HPB (Cabrol et al., 2017). They are: (i) homoacetogenic bacteria (HAB) that directly convert H_2 to acetate (eq. 7).

$$4\ H_2 + 2\ CO_2 \rightarrow CH_3COOH + 2H_2O \quad \text{(eq. 7)}$$

(ii) Lactic Acid Bacteria (LAB) that convert glucose to lactate without producing H_2 via homolactic (eq.8) or heterolactic pathways (eq.9):

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH \quad \text{(eq.8)}$$

$$C_6H_{12}O_6 \rightarrow CH_3CHOHCOOH + CH_3CH_2OH + CO_2 \quad \text{(eq.9)}$$

and (iii) propionic acid bacteria (PAB) that accumulate propionate by consuming both the organic substrate and H_2, as follows (eq. 10):

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \quad \text{(eq.10)}$$

Alternatively, H_2 can also be consumed during the reduction of sulphate, nitrate or metals such as iron or manganese but at a lower extent in most cases with FW. Lactic acid bacteria are the most competitive bacteria if the FW is used as a feed substrate. The LAB could even further inhibit the growth of H_2 producers by producing bacteriocines (Rafrafi et al., 2013). Nonetheless, Kim et al (2011a) explained that their activity might be limited under thermophilic conditions. In continuous reactor systems, a strong competition can occur between HPB and LAB and low HRT favour the activity of HPB (Palomo-Briones et al., 2017).

Many substrates are suitable for H_2 production by DF, such as carbohydrates solutions or various effluents originated from food industries such as molasses, cheese whey that have been both extensively studied (Ntaikou et al., 2010). In the case of solid waste, H_2 yield was shown to be strongly linked with their initial contents in readily soluble carbohydrates (Monlau et al., 2012; Guo et al., 2014). Today, most of the review papers have dealt with inoculum pretreatment (Yasin et al. 2013, Kiran et al. 2014) but none on the DF substrate itself. In this below section the FW pretreatment possibilities for DF are detailed and discussed.

4.2. Results of food waste pretreatment on H_2 production

The pretreatment objective and strategy for FW-DF is different from that of FW-AD. In specific, pretreatment of FW-DF consider three factors: (i) solubilisation of complex carbohydrates to make them easily accessible for HPB; (ii) inactivation of hydrogen consuming microorganisms and non-hydrogen-producing (HAB, LAB and PAB) microbial communities; and (iii) selective enrichment of HPB for DF without any additional inoculum. Table 5 compiles the efficiency of different pretreatment options tested to improve the H_2 yield from FW-DF. Kim and al. (2009) studied the impact of FW pretreatment on their endogenous microbial consortia and H_2 yield by DF without any microbial inoculum additions. FW without pretreatment led to very poor H_2 yield (4.4 mL/gVS), and high carbohydrate removal (83.1%). Lactic acid was observed as the major soluble metabolites i.e., ~ 60% of COD and provided a clue that the HPB were dominated by LAB. Among the acid (pH=1 for 1 day), alkali (pH=13 for 1 day) and thermal (90°C for 20 min) pretreatment of FW, thermal pretreatment resulted in maximum H_2 yield (96.9 mL/gVS) and accumulated butyrate as the major soluble metabolite (i.e., > 80 % of COD). The *Clostridium sp.* was the most dominant species in thermally pretreated FW, which led to higher H_2 yield (Kim et al. 2009). The same group of authors investigated the impact of pH pretreatments i.e., acid (Kim et al. 2014) and alkali (Jang et al., 2015) of FW prior to DF. For acid pretreatment, the FW-slurry pH was adjusted to < 4. The best results were found at pH 1 or 2, where LAB in FW were inactivated and *Clostridium sp.*, was predominant (Kim et al. 2014). In alkaline pH range between 9 and 13, the best H_2 yield was achieved with the FW pretreated under pH of 11-12 (Jang et al., 2015). Indeed, LAB was predominant at pH 9 and 10, while *Clostridium sp.* and *Enterococcus sp.* predominated at pH 11-13. However, the H_2 yield in continuous fed batch reactors fed with pretreated FW (at pH 11) significantly dropped due to the increase activity of hydrogen-consumers or competitors such as HAB and PAB.

Elbeshbishy et al. (2011) highlighted that ultrasound pretreatment of FW led to higher H_2 yield than heat shock followed by acid and alkali pretreatment (Table 5). Combined pretreatments of FW such as sonication followed by acid pretreatment perfomed better than just sonication. Although maximum H_2 yield corresponded well with a maximum carbohydrate solubilisation yield, H_2 yields did not correlate well with carbohydrate solubilisation underlining the different mechanisms involved during the DF process. Kim et al (2009) explained that the specific role of any pretreatment technique for DF is to support the selection of beneficial microbial population rather than a real enhancement of FW hydrolysis.

However, several other studies investigated the effect of various pretreatment methods on FW-DF and with external source of inoculum on H_2 yield (Table 5). Pagliaccia et al. (2016) reported that the thermal pretreatment at 134°C for 20 minutes improved the H_2 production by 360% assuming a substantial increase of substrate availability. In contrast, Li et al. (2014) found no significant improvements in H_2 yield after pretreatment of FW at 150°C to 200°C. Consequently, no correlation was established between COD solubilisation and H_2 yield. The oil contents in FW could have inhibited the growth of the H_2 producing bacteria in the latter study. This observation is supported by Bundhoo (2017), who studied the effect of sonication and microwave pretreatment of FW mixed with yard waste for DF. Although the solubilisation of sugars was found to be significant, the pretreatments led to low H_2 production due to the accumulation of propionic acid and ethanol. Similar observation was also reported by Wongthanate et al. (2014), who assumed that sonication led to the suppression of the activity of HPB and mechanisms are still unclear. In contrary, the sonication pretreatment of FW was successfully used in another study with 53-75% enhancement of H_2 yield (Gadhe et al. 2014).

Considering a two-stage AD process fed with synthetic FW at various proportions of carbohydrates, proteins and lipids, Rafieenia et al. (2016) tested the effect of aeration as a pretreatment approach to improve the H_2 yield in the first stage of the digestion process. In contradiction with AD process, they showed a decrease of H_2 production in the first stage for all synthetic waste which was due to the loss of some readily available carbon as CO_2 during aerobic pretreatment (for 24 h). As compared with the FW-DF with no inoculum addition, a minimum dose of acid or alkali pretreatment is required before FW-DF with inoculum addition. For tofu residues, Kim et al (2011b) showed that an optimum pretreatment of 1% HCl resulted in 316 % increase or 1% NaOH with 263 % increase in H_2 production as compared to the control, which was likely due to the reduction in the LAB and PAB populations. In addition, denaturing gel gradient electrophoresis analysis of fermented tofu residue pretreated with 1% HCl showed *Clostridium thermosaccharolyticum* as dominant species (Kim et al.2011b), supporting the conversion of soluble and insoluble carbohydrates such as starch, xylan, cellulose and pectin into H_2.

However, Kim and Shin (2008) performed a long-term H_2 production from FW in a sequencing batch reactor (3 cycles per day). They showed that pretreatment at pH 12.5 for 1 day was more efficient for stable production of H_2 than acid pretreatment (pH=2 for 1 day). Indeed, alkali pretreatment showed a 4.9 log CFU/gVS reduction of HPB against a 2 log CFU/gVS reduction for the acid pretreatment, which may be due to the acclimation of some indigenous bacteria to such a low pH condition. Thus, in contrary to reactors treating raw FW or acid pretreated FW, reactors fed with alkali pretreated FW could be operated for a long period of time up to 50 days at a 1 day HRT with a stable H_2 production of 62.6 mL/g VS corresponding to 0.87 mol_{H2}/mol hexose added.

In addition, most studies on FW-DF are BHP tests, except two studies that used CSTR (Jang et al.

2015) or SBR (Kim and Shin 2008) for continuous H_2 productions. In both cases, long term H_2 production using FW was failed when no pretreatment was applied, highlighting the issue of reactor stability under long-term operations. The use of alkali pretreatment could be an option to overcome this issue as suggested by Kim and Shin (2008). Therefore, it is suggested that the use of pretreatments, such as alkali or thermal, which have been shown to enhance H_2 production in batch reactor studies, could be considered as an option in a continuous process for optimal H_2 production in FW-DF.

5. FUTURE RESEARCH PERSPECTIVES

Based on the detailed literature review, the following recommendations and research directions are proposed:

(i) Preservation of carbon is a major issue when FW is processed by AD or DF. This can be overcome by freezing or drying of FW as usual storage as reported in a number of lab-scale studies, but seldomly in pilot scale operations. Further work on pretreatment techniques to improve the storage of carbon is essential and will be highly beneficial for the development of AD and DF plants to optimally recover energy in the forms of CH_4 and H_2, respectively.

(ii) Unlike that of other organic substrates, carbohydrate release after pretreatment does not directly correlate with CH_4 or H_2 production for FW-AD or FW-DF, respectively. This could possibly be due to the changes in indigenous microbial composition of FW and to the effect of organic molecules released, which require further investigations.

(iii) There is no unique composition of FW as their carbohydrate, protein, lipid and mineral contents vary according to several parameters such as source, regions and the seasons. Proposing a unique pretreatment that would be optimal for all kinds of FW is thus unrealistic and pretreatment optimization studies should put the heterogeneous composition of FW into consideration.

(iv) Elimination of unwanted indigenous microorganisms is also essential for better H_2 production and makes the pretreatment step (either thermal, alkali or acid) mandatory. In particular, better understanding of the equilibrium and the dynamics, which exist between HPB and competitive populations (methanogens, LAB, PAB, HAB), will provide better solutions to avoid reactor instability, while it may favor the optimal bioprocess conditions for treating FW.

(v) The physical reduction of particle size is an important pretreatment step for FW to improve the process of AD or DF and product recovery. Although particles < 2 mm are in favour of high CH_4 recovery, the effective particle size that is required for better fermentative H_2 production using FW as substrate is unclear and warrants further investigation.

(vi) Physical pretreatment process step could be integrated with any other pretreatment steps to improve the availability of substrates for CH_4 or H_2 recovery. It is also obvious that thermal pretreatment is the most feasible technology for integrations, but the temperature and pretreatment time still need to be optimized under such integrated mode.

(vii) Also, alkali pretreatment could be considered for highly acidic substrate like FW to improve the process efficiency. The alkali requirements will also vary with the FW type and particle size and hence, optimization and testing are necessary for optimal operation.

It is also found that most of the studies on pretreatment have been performed in a batch mode at laboratory scale and the data obtained may not be reliable for scale-up and/or does not provide similar yields during pilot-scale operations. Further studies should be performed at pilot scale to establish more reliable data for accurate energy and mass balance calculations. Longer AD or DF operations will also provide a clear impact of FW pretreatment on CH_4/H_2 yields, which will eventually help enhance the process stability. Current literature does not provide such knowledge.

In addition, results obtained in BMP/BHP studies use quite diluted reactive media and cannot predict the results of full-scale batch process where media will be much more concentrated, in particular in the case of high solids content AD systems. The start-up of such reactors can encounter difficulties due to too high VFA concentrations that may have been produced during FW storage. Therefore, more detailed research work should focus on pretreatments that will limit VFA production while avoiding any carbon loss.

CONCLUSIONS

It is very clear that the freeze and thaw or drying pretreatment of FW could be considered to provide a total un-degraded carbon for AD or DF. In addition, physical (i.e., grinding) pretreatment in combination with thermal and/or alkali should be considered means to improve CH_4 and H_2 yields. All of them regulate the indigenous microbial communities, reducing LAB activity and supporting spore-forming HPB that are highly favourable for H_2 and CH_4 production. However, there is a lack of energy-economic calculations for integrated FW pretreatment methods that requires more detailed study and analysis prior to commercial applications.

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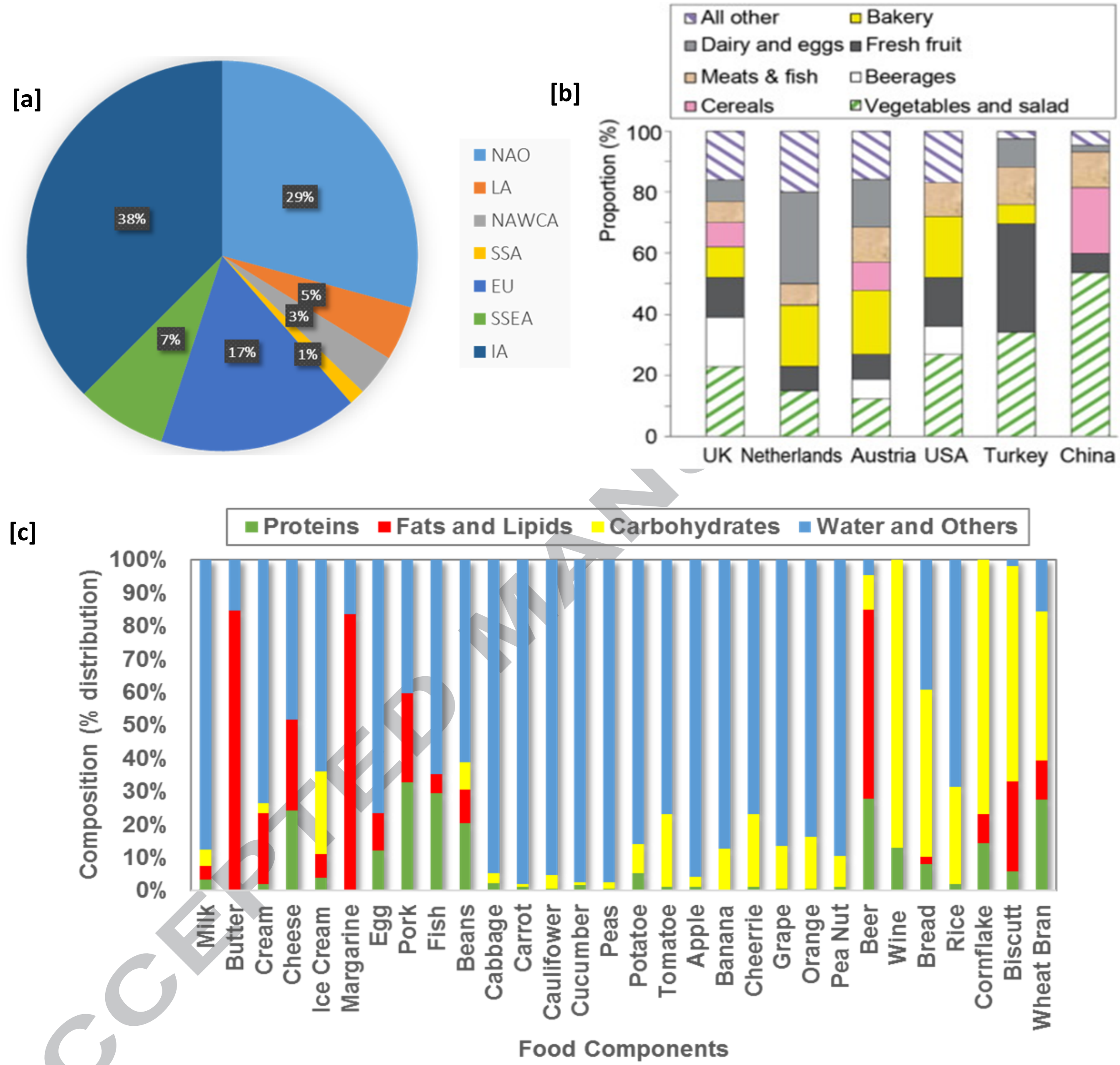
Figures and Tables :



Note : NAO-North America & Oceana ; LA – Latin America ; NAWCA – North Africa, West & Central Asia, SSA – Sub-Saharan Africa ; EU – Europe and UK ; SSEA – South & South East Asia ; IA – Industrial Asia
source : Pliessner and Lin, 2013 ; Song e tal., 2015

Fig 1. Global distribution of Food Waste and their composition differences. [a] repartition of total FW production by different countries; [b] chemical composition of individual food components; [c] the country specific FW composition

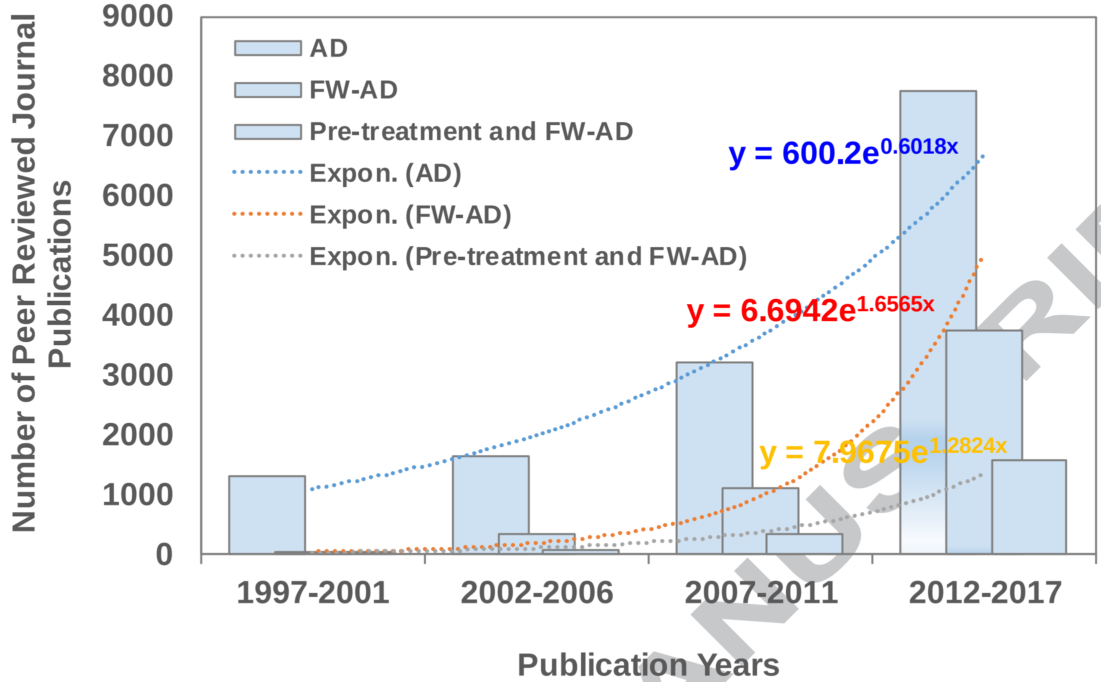


Figure 2. Research trends in anaerobic digestion of food waste with pretreatment over last 20 years (Source: Web of Science)

Table 1. Food waste disposal methods and facts to consider for selection

Treatment options	**Cost (€/t)[@]**	**Climate change impact range (kg CO_2-eq/t)**	**Process considerations**	**Merits**	**Demerits**
Composting	40-110	-50 (min.) 850 (max.)	- Centralized or decentralized designs - Open or in-vessel composters - Process acceleration by special culture or bulking agent additions, etc.	Recycling of essential nutrients and carbon	Long process time and critical care required
Anaerobic Digestion	45-140	-400 (min.) 400 (max.)	- Pre- and post- treatment requirements - Single or two or multi-staged processes - Operational variables e.g. temperature, pressure regulations, pH, etc.	Recycling of organics into energy and bio-fertilizers	Technical knowledge and process failures under poor operation conditions
MBT	40-100	-	- Pretreatment and processing - Easy to combine with AD or composting facility	Resource recovery and restoration of essential nutrients	Technical knowledge, market requirements, energy consumptions.
Incineration	50-250	-250 (min.) 600 (max.)	- With or without energy/heat recovery - Pre-processing and post-disposal of materials - Air-quality and regulations	Quick process and mass destruction ; space requirements	Cost and highly skilled operation
Landfills	40-65	400 (min.) 1200 (max.)	- With or without methane recovery - Engineering landfills or open dumping	Cheap and easy to execute ; simple equipments	Land requirements, GHG emissions and environmental contaminations

Note : *@ data adapted from Germany food waste management case report ; sources Bernstad and la Cour Jensen, (2012) and Frohnmaier et al., (2013)*

Table 2. Anaerobic digesion facilities for food waste treatment and related policies from selected countries

Country	**Number of AD plants treating FW**	**% total biogas plant operations in the country**	**FW treated (t/y)**	**Methane / Electricity Yield**	**Policies / Action Plans**
China	183 (capacity ~ 200 t/d) & 118[a] (pilot plants)	76	13426160[#] and 7847500	~	The fifth-recommended food kitchen waste recycling and safe disposal alternative pilot cities, 2015.
Hong Kong	2	33	182500	~	40% reduction of FW by 2022.
South Korea	31	33	~	68.59 million N m^3/y	2020 target is for 100% of the FW effluent currently being dumped in the sea to be converted into biogas for electricity generation or vehicle fuel; and increase the mandatory supply quantity of biogas to 10% of total power generation in 2022.
Germany	180[b]	2	3800000	850 GWh/y	Federal Environmental Agency (UBA) recommends to focus on the use of organic waste and biowaste in biogas plants and to gradually phase out bioenergy crops. By 2025, around 4-5 million tonnes[c] of biowaste AD plants is expected.
France	11[d]	2.2	~	~	Reduce food waste by 50% by 2025.
United Kingdom	30	32	397893	1529 kWe	5 TW h by 2020.
United States	44[d]	17			50% reduction of FW by 2030.
Brazil	2	~	~	0.9 MW	~

Note: [a] actual number of plants that will be installed by 2017; [b] biowaste - mixture of food waste and garden waste; [c]Prediction; [d]Co-digestion of FW with other organic resources (e.g. manure, sludge, etc.); [#] average of 200 t/d FW treatment capacity was considered. Source: De Clercq et al., 2017.

Table 3. Hydrolysis rate constant and methane potential of individual components of organic materials under anaerobic digestion process

Component (Chemical formula)	**Hydrolysis constants (Kh values (d^{-1}))**	**Hydrolyzing Enzymes**	**Methane potential (under mesophilic temperature)**			
			Methane content in biogas (%)	**Time required for 50 % methane production (days)***	**Time required for of 80 % methane production (days)***	**Methane potential ($Nm^3 CH_4$ /tonne VS)@**
Lipids and Fat ($C_{57}H_{104}O_6$)	0.005-0.7	Lipases	72	14.8	57	1014
Proteins ($C_5H_7NO_2$)	0.015-0.8	Proteases	63	5.9	23	496
Carbohydrates ($(C_6H_{10}O_5)_n$)	0.025-2.0	Carboxylases	50	3.0	30	415

*Note: * theoritical value for simulated food waste reported by Neves et al., 2008; @ theoritical value calculated based on Buswell's formula; Source: Karthikeyan and Visvanathan, 2013.*

Table 4. Table Synthesis of results of different kinds of food waste pretreatment for CH_4 production by anaerobic digestion

Substrate	Inoculum	Anaerobic digestion conditions	Substrate Pretreatment	Methane Recovery *(enhancement towards control)*	Remarks	Reference
Kitchen waste (14%TS)	Anaerobic sludge	Batch, 36°C, 140 rpm, 1.8 L	Physical = 2.5 mm	510-630 mLCH_4/g VS	The effects of particle size on biogas production are attributed to the larger specific surface area provided by smaller particles for enhanced hydrolysis, Lower particle size also improves digestate dewaterability.	Agyeman and Tao, 2014
			Physical = 4 mm	470-560 mLCH_4/g VS		
			Physical = 8 mm	460-470 mLCH_4/g VS		
Food waste (ground < 2.38 mm)	Heat treated sludge	Batch, pH of 7.0, at 35°C, 100 rpm.	Control	234 mL CH_4/g CODrem	COD removal rate of FW pretreated with HVPD were more than 100%, which was higher than the control. Also, the higher ammonia concentration in the reactor with HVPD pretreatment would neutralize more VFAs	Zou et al., 2016
			High voltage pulse discharge at 40 kV, electrode distance of 5 mm, pulse frequency of 400 Hz and pretreatment time of 30 min.	315 mL CH_4/g CODrem *(+ 35%)*		
Food waste (pre-homogenized and crushed to particle size of 2 mm	anaerobic sludge	Batch, 37± 0.5 °C, 0.4 L	Control	297 mLCH_4/g VSadd	Proteiniborus and Parabacteroides were responsible for proteins and polysaccharides degradation, respectively, while Bacteroides only dominated in co-digestion system. Methanosphaera dominated in microwave treated during the active methane production phase.	Zhang et al., 2016
			Microwave = 100 °C, 600W	316 mLCH_4/g VSadd *(+ 6%)*		
Kitchen waste (KW)	anaerobic sludge	Batch, 250 mL glass bottles, at 35°C	Thermal = 120°C, 10 min	112 mLCH_4	Thermal treatment of KW is beneficial for floating oil recycling and improved the CH_4 recovery rate.	Li et al., 2016
			Thermal = 120°C, 30 min	152 mL CH_4		
			Thermal = 120°C, 40 min	168 mL CH_4		
			Thermal = 120°C, 50 min	161 mL CH_4		
			Thermal = 120°C, 60 min	129 mL CH_4		
Kitchen waste (KW) (pre-grinded to 1-2 mm)		Batch, 5.5-L airtight Plexiglas reactors, at 35°C,	Control	911 mL_{biogas}	This finding suggests that both low and high thermal hydrolysis temperatures cannot effectively promote biogas production. At 90 and 120°C, with treatment durations of 70 min and 50 min, a large	Li and Jin, 2015
			Thermal = 55°C, 70 min	939 mL_{biogas} *(+ 4%)*		
			Thermal = 70°C, 70 min	1135 mL_{biogas} *(+ 25%)*		
			Thermal = 90°C, 70 min	1173 mL_{biogas} *(+29%)*		
			Thermal = 120°C, 50 min	1200 mL_{biogas} *(+ 32%)*		
			Thermal = 140°C, 50 min	885 mL_{biogas} *(-3%)*		

			Thermal = 160 °C, 50 min	909 mL_{biogas} *(-1%)*	fraction of VS, crude fats and proteins was degraded and a large amount of methane was produced during digestion.	
Food wastes (pre-grinded to 6 mm)	Anaerobic microbial sludge	Batch, at 35°C (14 days)	Control	26.0 dm3	According to the analysis of methanogens, thermal pretreatment of food waste increased the population densities of methanogens, which favored methane recovery	Wang et al., 2006
			Thermal = 70°C, 2 h	26.7 dm3 *(+ 3%)*		
			Thermal = 150°C, 1 h	29.1 dm3 *(+ 12%)*		
Food waste	anaerobic sludge,	Batch, 35 ± 1°C, pH=7 (controlled), 20 days at 80 rpm	Control	271.7 $mLCH_4$/g VSrem	Better VS and COD solubilization achieved with pretreatment that subsequently improved the CH_4 recovery	Naran et al., 2016
			Alkali = 0.4 N NaOH, pH=12.7, 1 h	339.2 $mLCH_4$/g VSrem *(+ 25%)*		
			Alkali-thermal = 0.4 N NaOH and autoclave at 120 °C for 30 min	360.7 $mLCH_4$/g VSrem *(+ 33%)*		
			Thermal = 120°C for 30 min	480.8 $mLCH_4$/g VSrem *(+ 77%)*		
			Ultrasonic = energy intensity of 360 kJ/L, 30min	423.6 $mLCH_4$/g VSrem *(+ 56%)*		
Kitchen waste	thermophilic anaerobic sludge	Batch, 0.25 L reactor, at 55°C, 100 rpm. (40 days)	Control	350 mL_{biogas}/g CODrem	Pressure–depressure pretreatment physically break-up the particles, and its effect depends on the mode of pressurization and the pressure applied.	Ma et al., 2011
			Acid = 10 N HCl, pH 2, 24h	160 mL_{biogas}/g CODrem *(-46%)*		
			Thermal = 120°C (1 bar)	360 mL_{biogas}/g CODrem *(+ 3%)*		
			thermo-acid = 10 N HCl, pH 2, 24h, at 120 °C (1 bar)	300 mL_{biogas}/g CODrem *(-24%)*		
			Pressure = 10 bar with CO_2, few minutes	520 mL_{biogas}/g CODrem *(+ 49%)*		
			Freeze–thaw = 80°C, 6 h, and thawed at 55 ± 2°C, 30 min.	380 mL_{biogas}/g CODrem *(+ 9%)*		
Food waste	anaerobic sludge	Batch, 35°C and 150 rpm.	Control	197.9 $mLCH_4$/g VS	Fungal mash rich in glucoamylase and protease was produced from cake waste and was applied without enzymes purification steps found promising pretreatment option, which provided more than 80% VS removal and more CH_4 recovery	Kiran et al., 2015
			Commercial enzymes = 10 U/g dry FW for glucoamylase, at 60°C, 100 rpm, 24 h.	457.3 $mLCH_4$/g VS *(+ 131 %)*		
			Fungal mash = 10 U/g dry FW for glucoamylase, at 60° C, 100 rpm for 24 h	468.2 $mLCH_4$/g VS *(+ 137%)*		

Food waste (pre-homogenized by blender)	anaerobic sludge	Batch, 160 mL serum bottles, At 35°C, 150 rpm	Control	610 $mLCH_4$/g VS	Fungal mash hydrolysis addition improves the rate kinetics faster than control and thereby improve the CH_4 recovery rate.	Yin et al., 2016
			fungal mash hydrolysis at 100 rpm, 60°C for 24 h	817 $mLCH_4$/g VS *(+ 34%)*		
Food waste (pre-grinded to 2 mm)	Mesophilic anaerobic sludge	Batch, 0.25 L bottles, at 35 °C, 100 rpm. (40 days)	Control	233±17 $mLCH_4$/g VS	The micro-aeration pretreatment was sufficient to increase the degree of solubilization but not enough for the subsequent VFA oxidation, thus resulting in higher methane yields.	Lim and Wang 2013
			Microaeration = 37.5 mL O_2/L reactor/d	256±9 $mLCH_4$/g VS *(+ 3-9%)*		
Food waste rich in carbohydrates	anaerobic sludge	Carried out after hydrogen tests. Batch, 1 L bottles, 35 °C. (75 days)	Control	201 $mLCH_4$/g VS	Aeration increased AD rate of carbohydrate-rich FW, it decreased the rate of protein-rich FW but led to a significantly higher CH_4 yield. Aeration was not efficient on lipid-rich FW .	Rafieenia et al. 2016
			Aeration 5L/h, 24 h	223 $mLCH_4$/g VS *(+6%)*		
Food waste rich in proteins			Control	241 $mLCH_4$/g VS		
			Aeration 5L/h, 24 h	352 $mLCH_4$/g VS *(+46%)*		
Food waste rich in lipids			Control	263 $mLCH_4$/g VS		
			Aeration 5L/h, 24 h	240 $mLCH_4$/g VS *(-9%)*		
Food waste stored at -20°C	anaerobic sludge	Batch, 0.57 L bottles, at 38 °C, 40 days	Control	500 $mLCH_4$/g VS 130 $mLCH_4$/g WW*	Up to 10% VS losses after 4 days aeration, reduction of VFA, simple sugars and low weight organic molecules. Methane potential of pretreated waste ($mLCH_4$/g VS) was maintained but reduction of methane potential reported to initial amount of waste after long aeration time	Fisgativa et al. 2016b
			Aeration in 10 L reactor, 40°C, 50 L/h, 21% O_2 2 days	500 $mLCH_4$/g VS *(0%)* 130 $mLCH_4$/g WW *(0%)*		
			Aeration in 10 L reactor, 40°C, 50 L/h, 21% O_2 4 days	500 $mLCH_4$/g VS *(0%)* 121 $mLCH_4$/g WW *(-7%)*		
Source separated food waste	anaerobic sludge	Batch, 0.167 L bottles,	Household dryer, 8 L capacity, 75°C, 8 h	400 $mLCH_4$/g TS	Moisture removal led to around 70% reduction of FW mass. Drying preserved sugar content thanks to avoiding biodegradation within storage time.	Sotiropoulos et al., 2015

*Note: * WW wet weight*

Table 5. Synthesis of results of different kinds of food waste pretreatment for H_2 production by dark fermenatation

Substrate	**Inoculum**	**Dark Fermenation conditions**	**Substrate Pretreatment**	**Hydrogen yield mL H2/gVS$_{fed}$ *(enhancement towards control)***	**Remarks**	**Reference**
Food waste Shredded <5mm	none	Batch, 35°C, 30g COD$_{carbohydrates}$/L at t0 pH$_{init}$=7 then controlled at 5	Control (no pretreatment)	1.4 (-)	Selection of hydrogen producing bacteria by pretreatments and inactivation of lactic acid bacteria	Kim et al. 2009,
			Thermal 90°C, 20 min	96.9 *(+6821%)*		
			Acid, pH=1, 1 d	89.5 *(+6293%)*		
			Alkali, pH=13, 1 d	50.9 *(+3536%)*		
Food waste Shredded <5mm	none	batch 35°C, 30g COD$_{carbohydrates}$/L at t0 pH$_{init}$=8 then controlled at 6	Control	54 (-)	Pretreatment at pH 1-3 suppressed lactic acid bacteria and *Clostridium sp* was predominant. After pH 4, *Lactobacillus* and *Streptococcus* were the dominant genus.	Kim et al. 2014,
			Acid, pH=1, 12 h, 20°C	152 *(+181%)*		
			Acid, pH=2, 12 h, 20°C	158 *(+193%)*		
			Acid, pH=3, 12 h, 20°C	125 *(+131%)*		
			Acid, pH=4, 12 h, 20°C	27 *(-50%)*		
Food waste Shredded <2mm	none	batch 37°C, 30g COD$_{carbohydrates}$/L at t0 pH$_{init}$=8 then controlled at 6	Alkali, pH=9, 6 h	63	Lactic acid bacteria were predominant after pH 9 and 10, *Clostridium genus* predominant after pH 11 and 12, *Enterrococus* was major after pH=13.	Jang et al. 2015,
			Alkali, pH=10, 6 h	82		
			Alkali, pH=11, 6 h	156		
			Alkali, pH=12, 6 h	162		
			Alkali, pH=13, 6 h	88		
		CSTR, 37°C , pH=6 HRT : 0.7 and 1 d	Alkali, pH=11, 6 h	Decreased after 3 d	In CSTR, H_2 production shifted to acetate and propionate production	
Food waste	none	Batch, 37°C, pH$_{init}$=5.5	Control	41 (-)	Highest H_2 yield when highest increase in soluble carbohydrates (sonication + acid). Highest COD and protein solubilisation (sonication + alkali) led to a decrease in H_2 yield towards sonication alone.	Elbeshbishy et al 2011
			Sonication 79 kJ/gTS,	97 *(+136%)*		
			Heat 70°C 30 min	70 *(+70%)*		
			Acid pH=3, 4°C, 24 h	55 *(+34%)*		
			Alkali pH=11, 4°C, 24 h	46 *(+12%)*		
			Sonication + heat	78 *(+136%)*		
			Sonication + acid	118 *(+90%)*		
			Sonication + alkali	67 *(+63%)*		
Food waste Ground < 2.38 mm	Heat treated sludge	SBR, 3 batch/d pH controlled at 5.3 HRT =30 h	Control	Max 25 decreased to7.1	Alkali pretreatment showed a 4.9 log reduction in CFU/gVS; less impact was observed after acid pretreatment	Kim and Shin 2008
			Acid, pH=2, 35°C, 1 d	Max 48 decreased to 5		

			Alkali, pH=12.5, 1 d	24.5 stable for 25 d		
		SBR, 3 batch/d pH controlled at 5.3 HRT =24 h with biomass retention		62.6 stable for 50 d		
Tofu residue thawed	anaerobic sludge, 90°C, 15 min	Batch, 35°C, pH_{init}=7 then controlled at 5.5	Control	0.30 mol $H_2/mol_{hexose\ fed}$	Pretreatments did not directly contribute to carbohydrate solubilisation but increased H2 yield. *Clostridium thermosaccharolyticum sp* allowed the fermentation of insoluble carbohydrates	Kim et al 2011
			Acid 0.5% HCl	0.64 *(+113%)*		
			Acid 1% HCl	1.25 *(+316%)*		
			Acid 2% HCl	1.10 *(+266%)*		
			Alkali 0.5% NaOH	0.49 *(+63%)*		
			Alkali 1% NaOH	1.09 *(+263%)*		
			Alkali 2 % NaOH	0.97 *(+223%)*		
Food waste thawed and ground	Anaerobic sludge	Batch, 35°C, S/I=0.6 pH_{init}=7	Control	5 (-)	Enhancement of substrate availability	Pagliaccia et al. 2016
			Thermal 134°C, 20 min	23 *(+360%)*		
Food waste ground,sieved <5mm mixed with water ratio 3:1 (vol)	anaerobic sludge, 90°C, 10 min	Batch, 35°C, pH_{init}=6.5	Control	2.9 mL H_2/g_{COD}	Sonication may have altered hydrogen producing bacteria.	Wongthanate et al. 2014
			Thermal 134°C, 20 min	3.5 *(+20%)*		
			Sonication, 20 min	2.2 *(-32%)*		
			Acid pH=3 $HClO_4$	3.0 mL *(+3%)*		
Starch waste ground,sieved <5mm mixed with water ratio 3:1 (vol)			None	1.8 mL H_2/g_{COD}		
			Thermal 134°C, 20 min	2.2*(+22%)*		
			Sonication, 20 min	1.4 *(-22%)*		
			Acid pH=3 $HClO_4$	2.2*(+22%)*		
Kitchen waste 14%TS	Anaerobic sludge	Batch, 35°C, , S/I=1 pH_{init}=6	Control	35.0	Inactivation of hydrogen consuming bacteria, no correlation between COD solubilisation and H2 yield. Lowest hydrogen yield corresponded to the highest amount of floatable oil (150°C).	Li et al., 2014
			Thermal, 90°C , 30 min	76.1 *(+117%)*		
			Thermal, 120°C , 30 min	53.7 *(+53%)*		
			Thermal, 150°C , 30 min	34.2 *(-2%)*		
			Thermal, 200°C , 30 min	81.3 *(+132%)*		
Food waste ground (slurry),	Anaerobic sludge, 90°C 20 min	Batch, 37°C, S/I=4 (COD/VSS°) pH_{init}=5.5	Control	85	Decrease of fermentation lag phase from 42 h to 26-22 h after sonication	Gadhe et al., 2014
			Sonication, 5 min	130 *(+53%)*		
			Sonication, 10 min	146 *(+72%)*		

8%TS T<30°C			Sonication, 15 min	149 *(+75%)*		
Food waste mixed with yard waste 50/50 (wet weight) Ground through 2 mm screen TS=6%	Anaerobic sludge pretreated by microwave	Batch, 35°C, pH_{init}=6.5	Control	21.3 (-)	Both microvawe and sonication induced waste solubilization, sonication being more effective, but no technique improved H2 yield. Production of inhibitor was suspected as ethanol and proponiate yield also decreased.	Bundhoo, 2017
			Sonication 149 kJ/kgTS	18.8 *(-12%)*		
			Sonication 1789 kJ/kgTS	7.9 *(-63%)*		
			Sonication 4210 kJ/kgTS	18.9 *(-11%)*		
			Sonication 6946 kJ/kgTS	11.2 *(-47%)*		
			Microwave 149 kJ/kgTS	7.0 *(-67%)*		
			Microwave 1789 kJ/kgTS	15.6 *(-27%)*		
			Microwave 4210 kJ/kgTS	10.5 *(-50%)*		
			Microwave 6946 kJ/kgTS	16.8 *(-21%)*		
Food waste rich in carbohydrates	Anaerobic sludge 80°C, 15 min	Batch, 35°C, S/I=16 pH_{init}=6	Control	55.3 (-)	Part of readily available carbon (mainly sugars) was converted to CO2 or used for biomass growth during aerobic pretreatment	Rafieenia et al. 2016
			Aeration 5L/h, 24 h	44.4 *(-19%)*		
Food waste rich in proteins			Control	27.9 (-)		
			Aeration 5L/h, 24 h	21 *(-25%)*		
Food waste rich in lipids			Control	7.96 (-)		
			Aeration 5L/h, 24 h	5.27 *(-33%)*		

S/I substrate/Inoculum ratio (VS/VS if not specified)

Highlights

- Freeze and thaw and drying pre-treatments preserve the carbon for future processing.
- Grinding pre-treatment of FW improves the surface property and bio-accessibility.
- Combined grinding and thermal pre-treatments improves the digestibility.
- Energy-economics of integrated FW pre-treatment require to be established.