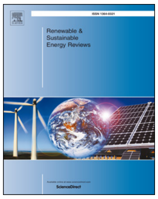
Renewable and Sustainable Energy Reviews 90 (2018) 583–604

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Biological pretreatments of biomass for improving biogas production: an overview from lab scale to full-scale

Ulysse Brémond[a,b], Raphaëlle de Buyer[a], Jean-Philippe Steyer[b], Nicolas Bernet[b], Hélène Carrere[b,*]

[a] Air Liquide, Centre de Recherche Paris Saclay, 1 Chemin de la Porte des Loges, 78354 Jouy-en-Josas, France
[b] LBE, Univ Montpellier, INRA, 102 avenue des Etangs, 11100 Narbonne, France

ARTICLE INFO

Keywords:
Anaerobic digestion
Biological pretreatment
Enzyme
Two-stage digestion
Aerobic consortium

ABSTRACT

Recent shifts in European countries biogas policies tend to limit the use of energy crops and encourage the use of manure, lignocellulosic feedstocks and bio-waste. The need to use feedstocks that are more difficult to handle (displaying either too low or too high biodegradation rates) is calling for the development of adapted pretreatments. Among them, biological pretreatments are very promising due to their reasonable cost, environmental friendliness and possible application to a wide spectrum of feedstocks. They can be divided into three categories: enzymatic, anaerobic and aerobic ones. This review aims at providing some guidelines on which type of biological pretreatment to apply for a given feedstock. To deliver such recommendations we considered the full range of technological readiness level. We gathered an analysis of the recent literature data obtained at lab or pilot scale focusing on methane yield enhancements and the description of some full-scale commercialized technologies. For lignocellulosic feedstocks, both enzymatic pretreatments using lignin-modifying enzymes or carbohydrases and aerobic pretreatments using consortia or simple aeration appear as promising. For bio-waste, anaerobic pretreatment via two-stage digestion seems to be an efficient biological pretreatment. For landfill, enzymatic treatment may be an interesting solution. Finally, for sludge digestion, both aerobic and anaerobic pretreatments favouring autohydrolysis may be recommended. Full-scale applications already exist but their use remains scarce. Indeed, each biological pretreatment features technological issues. Enzymes have high production costs and limited activity in time. Anaerobic pretreatments, notably two-stage digestion, are more expensive and complex to handle than a single stage. Finally, aerobic pretreatments need fine tuning and control due to respiration mass loss. Research and development conducted toward these specific issues may allow these pretreatments to become more cost-effective as well as practical and thus facilitate their development at full-scale.

1. Introduction

In Europe, France and the United Kingdom have a similar strategy for their biogas industry: a progressive development based both on co-digestion of a wide range of substrates and on a limited use of energy crops [1]. Similarly, Germany has shifted, since 2012, from an intense use of energy crops toward a more diverse use of substrates. This new state of affairs in Germany, the biogas European leader, emerged from the quick growth between 2000 and 2012 of an industry that was technologically based on a "standard" liquid CSTR plant using energy crops (especially maize) coupled with cattle liquid manure that permits to ensure high and resilient biogas production [2]. However, this strong appetite for energy crops led to agricultural distortions such as the increase of land rental prices, the increase of energy crops prices (also

---

Abbreviations: AD, Anaerobic Digestion; ADT, Advanced Digestion Technology; BMP, Bio-Methane Potential; COD, Chemical Oxygen Demand; CSTR, Continually Stirred Tank Reactor; DM, Dry Matter; DSM, Dutch State Mine; EPS, Extracellular Polymeric Substance; FW, Food Waste; GE, General Electric; HRT, Hydraulic Retention Time; HTP, HydroThermal Pretreatment; IPF, Inverted Phase Fermentation; LCFA, Long Chain Fatty Acid; LFD, Liquid Fraction of Digestate; LiP, Lignin Peroxidase; MCHCA, Microbial Consortium with High Cellulolytic Activity; MnP, Manganese Peroxidase; MSW, Municipal Solid Waste; OFMSW, Organic Fraction of Municipal Waste; OLR, Organic Loading Rate; RPM, Revolution Per Minute; RURAD, RUmen Derived Anaerobic Digestion; s-COD, soluble Chemical Oxygen Demand; SRT, Solids Retention Time; SS-AD, Solid State Anaerobic Digestion; TAD-MAD, Thermophilic Aerobic Digestion coupled with a Mesophilic Anaerobic Digestion; TMP, Thermophilic Microaerobic Pretreatment; TPAD, Temperature Phased Anaerobic Digestion; TRL, Technological Readiness Level; UASB, Up-flow Anaerobic Sludge Blanket; VFA, Volatile Fatty Acid; VP, Versatile Peroxidase; VS, Volatile Solids; WAS, Waste Activated Sludge; WRF, White Rot Fungi; WWTP, Waste Water Treatment Plant

[*] Corresponding author.

E-mail address: helene.carrere@inra.fr (H. Carrere).

https://doi.org/10.1016/j.rser.2018.03.103
Received 7 June 2017; Received in revised form 3 October 2017; Accepted 31 March 2018
1364-0321/ © 2018 Elsevier Ltd. All rights reserved.

used for cattle feeding) and therefore the difficulty for smaller farms or biogas exploitations to thrive [3]. Furthermore, “maizification” (wide spreading of maize monoculture) diminished both beneficial environmental impact of biogas production and public acceptance of the technology [4]. Thus, nowadays in Europe, to handle the higher diversity of substrates required by biogas policies, biogas plant model is shifting from a “standard” to a more versatile conception. Pretreatments are identified as a key tool that requires more investigation [5–7].

From a given organic substrate and in absence of oxygen, anaerobic digestion (AD) is a natural occurring phenomenon. AD can be divided in four different steps happening in the following order: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Depending of the substrate composition and its structure, hydrolysis or methanogenesis can be considered as limiting steps. In the case of complex organic substrates, the hydrolysis step is often the limiting step. Indeed, the production rate, the amount and the variety of hydrolytic enzymes released by hydrolytic microorganisms are often not sufficient to adequately degrade a given substrate [8]. On the other hand, in the case of easily degradable organic substrates, a quick and important acidogenesis step can lead to a rapid acidification of the environment, inhibiting the pH sensitive methanogenesis step [9]. Therefore, pretreatments are needed to handle and reduce substrate limitations toward their optimal use in AD.

At lab scale, evaluation of pretreatments on substrates is mainly carried out using bio-methane potential (BMP) tests. It is a batch method that permits to obtain, from a given substrate, its maximal biogas yield by using a high ratio of substrate to inoculum, a diluted environment and a long incubation time. Curves of BMP tests are usually modelled by using first order kinetic relations but it cannot be used to evaluate kinetics of continuous reactors except if more sophisticated modelling procedure is used [10]. Indeed, at pilot or full-scale the conditions are totally changed. Continuous operation, lower dilution and lower ratio of substrate to inoculum are the main differences. Concerning biogas yield in continuous systems, despite a better adaptation of the inoculum to substrate and the fact that endogenous methane production is included, it is likely that biogas yield will be lower than results of BMP tests due to a lower degradation time. This point concerns both raw and pretreated feedstocks. For pretreatment assessments, BMP tests can also be used to compare kinetic of degradation between raw and pretreated feedstocks via curve shapes [11]. This additional information can be used to forecast pretreatment effect on AD in a continuous system, which takes into account both impacts on methane yield and degradation rate. For low hydraulic retention time, continuous system enhancements on AD rate may prevail over biogas yield enhancements. From that, it can be considered that the most promising BMP results for pretreatments are the one displaying both a positive effect on degradation rate and biogas yield. Ideally, to clearly evaluate the interest of a pretreatment, both BMP and continuous reactor results have to be taken into account.

Four different types of pretreatments can be distinguished: thermal, mechanical, chemical and biological. If the first two ones are already applied at full-scale for a variety of substrates (animal by-products, sludge and lignocellulosic biomass), their high demands in heat or electricity are restricting their benefits [12]. Concerning chemical pretreatments, they are for the moment limited at lab scale due to their cost and their environmental consequences even though some alkaline treatments (lime notably) displayed promising results, especially with lignocellulosic substrates and animal by-products [13]. Finally, like all other pretreatments, biological pretreatments are progressively gaining in interest over time as it can be seen in Web of Science® where “anaerobic digestion” and “biological pretreatment” as topics, display both an increasing scientific production over years and a stable 15% ratio of the total “pretreatment” literature from 2011 (Table 1). This can be due to their potential lower energy consumption and promising results, especially with lignocellulosic materials [12,14].

Table 1
Web of Science® bibliometric study with the topics "biological pretreatment" or "pretreatment" and "anaerobic digestion" (January 2017).

Period	2009–2010	2011–2012	2013–2014	2015–2016
Number of papers about “biological pretreatment”	54	48	72	136
Number of papers about “pretreatment”	141	324	544	830
Ratio biological/all types of pretreatment	38%	15%	13%	16.5%

Prior to detail biological pretreatments, it is important to clearly distinguish them from another current research topic in AD, which is bioaugmentation [15]. This practice was recently defined as the direct addition of selected strain(s) or mixed cultures to AD to improve the catabolism of refractory compounds such as lignocellulosic materials and to increase the methane yield [16]. Despite the fact that bioaugmentation is targeting similar aims as pretreatments, it will not be addressed further in this review as it cannot be considered as a pretreatment but more as an improved inoculation. However, it can be interesting to combine bioaugmentation with pretreatments due to several advantages of this practice (e.g. environment-friendly, cost effective) [16] and it can be noticed that commercial solutions provided by several companies already exist, such as Bioplus by General Electric Water & Process Technologies (Boston, the USA) or Hycura products (Calgary, Canada) for instance.

Biological pretreatments can be divided in three parts: enzymatic, anaerobic and aerobic. The aim of this review is to give an overview of what is done in this field from lab scale to full-scale in function of the substrate. This review will concern agricultural waste, bio-waste that are gathering food waste and organic fraction of municipal solid waste, municipal solid waste and sewage sludge. Concerning animal by-products, as they generally require thermal pretreatment due to sanitary reasons, literature on the application of biological pretreatment is scarce. For this reason, this feedstock will not be included in this review. Promising and recent research results will be presented, with a special focus on methane yield enhancements. Furthermore, non-exhaustive examples of associated full-scale products sold by companies will be described in order to provide to the reader a first insight in existing industrial applications of such pretreatments.

2. Enzymatic pretreatments

Exogenous enzyme additions during AD in order to improve the hydrolytic step of complex organic substrates have been investigated with a growing interest since the mid-1980s. From this literature, it is important to distinguish the four ways to practice enzyme addition as shown in Fig. 1: (1) in a dedicated pretreatment vessel (2) directly in the digester vessel (single-stage process) (3) directly in the hydrolysis and acidification vessel (two-stage process) (4) in the recirculated AD leachate. Besides, it is also worthy to underline that to obtain an increase in biogas production via enzyme addition, parameters such as enzyme activity, specificity to the substrate, quantity, temperature, pH and enzyme stability need to be optimized and are often keys parameters in the economic assessment [17]. This section will give an overview of enzymatic pretreatments with a special focus on results of available commercial solutions. It can be already mentioned that Dupont (Wilmington, USA), Novozymes (Bagsvaerd, Denmark) and DSM (Delft, the Netherlands) are the three key players in the enzyme market. Therefore, enzyme products that will be presented are mostly commercialized by these companies.

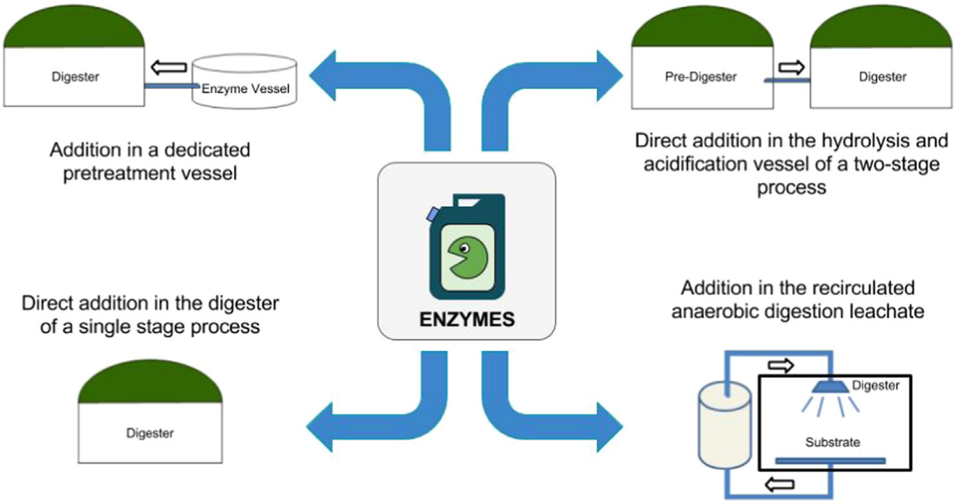


Fig. 1. The different ways to practice enzyme addition in order to enhance anaerobic digestion.

2.1. Agricultural waste

Agricultural waste can be summarily separated between crop residues and livestock manure. The former are mainly made of cellulose, hemicelluloses, lignin and proteins in little amount, the latter is composed of lignocellulosic biomass (straw in some manure) and feces composed of proteins and undigested lignocellulosic rich biomass. Linked to this composition several types of enzymes have been used to pretreat agricultural waste obtaining various results (Table 2).

Proteases have been recently evaluated in studies working on co-digestion of agricultural substrates where direct addition of proteases in the digester was applied. Muller et al. [18] by applying different proteases (alkaline, serine and aspartic types) to a mix of maize silage, chicken dung and cow manure in a 2 L BMP test obtained interesting results. Indeed, proteases increased methane yield between 9% and 52%. Following these results, similar experiments in semi-continuous 12 L digesters were carried out. After digesters stabilization, daily addition of enzymes did not lead to any increase in biogas yield. In addition, when the quantity of enzymes was increased tenfold, the biogas yield decreased between 13% and 36%. Here, the scale up from BMP to semi-continuous AD was not successful, demonstrating that promising BMP results are not ensuring higher scale results. Besides, negative results with BMP were also obtained by Wang et al. [19] where direct addition of a protease from Novozymes to a mix of cow manure and straw did not lead to any increase in biogas yield. Several reasons are given in these studies to explain these negative results regardless of the scale: (1) proteases degrade some essential enzymes such as hydrolases which are important in the hydrolytic phase or enzymes related to acidogenesis and methanogenesis; (2) they favour accumulation of intermediates such as phenyl acetate and propionate leading to inhibition of microorganisms; (3) proteases can attack microorganisms at their surfaces. Overall, it seems that positive effects are cancelled by negative effects of proteases addition in the case of agricultural residues. Therefore, proteases might be appropriate only for the pretreatment of protein-rich material.

Enzymes targeting lignin, such as laccases and peroxidases, have been recently explored as separated pretreatment before BMP tests of agricultural lignocellulose rich substrates. Frigon et al. [20] applied lignin and manganese peroxidases (LiP and MnP) to switch grass and obtained a significant increase in methane yield of 29% and 41%, respectively. Similarly, laccase pretreatment of corn stover by Schroyen et al. [21] showed a 17% increase in methane yield. However, more recent trials on various agricultural feedstocks with laccases and versatile peroxidases (VP) have shown that the higher the lignin concentration of the substrate, the lower the efficiency of this pretreatment [22]. Indeed, large release of phenolic compounds from lignin degradation can strongly inhibit the anaerobic digestion as it can be seen for the miscanthus case. From these results, the use of LiP, MnP, VP and laccases seems to be promising for some types of lignocellulosic agricultural waste. However, at the moment, this kind of enzyme is only tested at lab scale and not yet used for AD industrial purposes. Indeed, their production costs remain high and limit their application to high added value fields such as food and pharmaceutical industries [23]. One potential advantage of AD in comparison to the controlled environment of industrial fermentation is that expensive cofactors/redox mediators may naturally be found in the complex AD environment. Because lignin and links between lignin and carbohydrates have been shown to be the main bottleneck to lignocellulosic biomass AD [24], further research may focus on how to improve the use of lignin-modifying enzymes in AD systems.

Finally, cellulases, hemicellulases, amylases and pectinases which are targeting carbohydrates have been extensively tested on agricultural waste. If Romano et al. [25] did not show any significant increase in methane yield of wheat grass using Novozymes cellulase solutions whatever the way they were applied, recent studies have shown more promising results at lab scale. Sutayro et al. [26] worked on dairy cattle manure on which, a mix of pectate lyases and cellulases was added in equal proportion (w/w). Three days pretreatment at 50 °C followed by an anaerobic digestion permitted a 4.5% increase in methane yield whereas a direct addition did not have any positive impact. Using Novozymes products, Wang et al. [19] showed that pretreatment of a mix of cow manure and corn straw by a cellulase blend at 55 °C for 18 h permitted a 103% increase in the methane yield. Furthermore, in this work, direct addition of amylase to the anaerobic digestion permitted an increase of the methane yield by 111%. The use of Ultraflo® L, another cellulolytic enzymatic cocktail from Novozymes, in pretreatment of corn cobs (3 h at 40 °C and pH 6) also displayed positive results on subsequent AD as methane yield was increased by 14% [27]. Finally, by directly adding a mix of endoglucanase, xylanase and pectinase (CeluStar XL) formerly proposed by Dyadic (Jupiter, the USA), Zieminski et al. [28] succeeded in increasing by 28% the methane yield during co-digestion of sugar beet pulp silage and vinasse.

From these lab scale results, it can be suggested that the application of carbohydrates degrading enzymes can enhance both production rate and yield of methane but a careful attention has to be paid to process optimization such as enzyme selection for a given substrate, type of application, incubation time, pH, temperature; otherwise results can be negative [25]. Cellulases, hemicellulases, amylases and pectinases can be considered as promising enzymes due to their positive impact on biogas yield if well applied and no antagonist interference with

Table 2
Effect of enzymatic pretreatment on biogas and methane yield in function of feedstock.

Feedstock	Enzyme/Product and/or suppliers	Type of application	Enzymes application conditions	AD scale / AD process conditions	Methane yield (L/g VS)		References
					Control	Treatment	
Maize silage, chicken dung and cow manure	Alkaline, serine and aspartic Protease / not available	Direct	Lab scale 2 L BMP / triplicate − 39 °C − 43 days		0.265	0.29 – 0.405	[18]
			Lab scale 12 L semi-continuous / 39 °C − 100 days (among which 17 days of enzyme daily addition)		No influence and even some decrease in the biogas yield between 13% to 36%*		
Cow manure (95%) and corn straw (5%)	Cellulase blend / Novozymes	Pretreat	30 mL − 55 °C − 18 h at pH 5–6	Lab scale 600 mL BMP / Triplicate − 37 °C − 30 days - pH 7	0.179	0.364	[19]
	Alpha-amylase / Novozymes	Direct	Lab scale 600 mL BMP / Triplicate − 37 °C − 30 days - pH 7		0.179	0.377	
	Protease/Novozymes	Direct	Lab scale 600 mL BMP / Triplicate − 37 °C − 30 days - pH 7		0.179	0.181	
Switch grass	Lignin Peroxidase + cofactors / Sigma Aldrich	Pretreat	40 mL − 22 °C − 8 hours - pH 7.4	Lab scale 500 mL BMP / 35 °C − 37 days - pH neutral	0.157 ± 18%	0.202 ± 9%	[20]
	Manganese Peroxidase + cofactors / Jena Bioscience GmbH	Pretreat	40 mL − 37 °C − 8 hours - pH 7.4	Lab scale 500 mL BMP / 35 °C − 37 days - pH neutral	0.157 ± 18%	0.222 ± 22.5%	
Corn Stover	Laccase + cofactors / not available	Pretreat	180 mL − 30 °C − 24 hours - pH 4.7	Lab scale 200 mL BMP / 30 days	0.293	0.344	[21]
Corn Stover	Laccase and Versatile Peroxidase + cofactors / not available	Pretreat	180 mL − 30 °C − 6 hours - pH 4.5	Lab scale 200 mL BMP / 30 days	0.192	0.238	[22]
Miscanthus					0.139	0.138	
Wheat grass	Endoglucanase - Xylanase and β-glucanase/Novozyme 342	Pretreat	150 mL − 50 °C − 7 days - pH 7	Lab scale 1 L batch / Triplicate − 50 °C − 14 days -pH 7	0.15 ± 7%	0.16 ± 10%	[25]
		Direct	Lab scale 1 L batch / Triplicate − 50 °C − 14 days -pH 7		0.17 ± 4%	0.16 ± 9%	
	Cellulase and β-glucosidase / 85% Celluclast 1,5 L − 15% Novozyme 188	Direct 2nd	Lab scale 1 L batch / Triplicate − 50 °C – Hydrolysis: 7 days at pH 5 – methanogenesis: 14 days at pH 7		0.22 ± 3%	0.29 ± 13%	
Dairy Cattle manure	Mix of Pectate lyase - Cellulase in equal proportions (w/w) / Novozymes	Pretreat	50 °C − 3 days - pH 7.8	Lab scale 10 L semi-continuous / 50 °C − 42 days (HRT 14 days) - pH 7.8	0.135	0.146	[26]
		Direct	Lab scale 10 L semi-continuous / 50 °C − 42 days - pH 7.8		0.135	0.136	
Corn cob	Endoglucanase - Xylanase - Cellulase - Cellobiase - Feruloyl esterase / Ultraflo® L - Novozymes	Pretreat	30 mL − 40 °C − 3 hours - pH 6	Lab scale 500 mL BMP / 35 °C − 32 days - pH neutral	0.25	0.29	[27]
Sugar beet pulp silage (75%) vinasse (25%)	Endoglucanase - Xylanase and pectinase / CeluStar XL - Dyadic	Pretreat	50 °C − 7 days	Lab scale 1 L batch / 37°C-30 days-pH 7.2	0.35	0.465	[28]
Various agricultural waste (not given)	Xylanase - Endo-glucanase - exo-glucanase and β-glucosidase / Methaplus® L 100 - DSM	Direct	Full-scale tests in 30 agricultural plants from 55 kW to 1022 kW / Various conditions of operation. HRT varying from 35 to 221 days and OLR ranging from 1.5 to 15.1 kg(m^{3}d)$^{-1}$		Biogas yield increased in average of 18%*. Biogas quality not affected by the enzyme addition		[29]
Various (manure, corn, sugar beet, oat meal, shea nut meal)	Probably mix of cellulases / Optimash 100-AD - Dupont	Direct	Full-scale - Biogas plant type plug-flow 2000 kW / 40–44 °C – 60 days HRT - loading of 110 t/day of fresh matter		Methane production increased by 8%		[31]
Co digestion of whole plant Rye silage, maize silage	Pectinase - cellulase and hemicellulase / Axiase™ 100 - DSM	Direct	Full-scale - Test in a 2000 m^3 digester / 63 days of HRT - other information not given		Energy** increased by 4.7%		[33]
FW	Blend of carbohydrase, protease and lipase (ratio 1:2:1)/ Viscozyme® L - Novozymes & Amano products	Pretreat	500 mL − 50 °C − 10 h - pH 4.5	Lab scale UASB reactor 2.7 L / 75 days - pH 8.3 to 7.6	/	0.35 L/g s-COD	[37]
FW	Rich enzyme fungal mash (mainly a wide spectrum of carbohydrases)	Pretreat	60 °C − 24 h	Lab scale 1 L BMP / Triplicate − 35 °C − 30 days	0.198	0.468	[38]
MSW	Cellulase and Amylase / Mix of Celluclast and 1.5 L and Liquozyme SC DC - Novozymes	Pretreat	Pilot scale 50 kg batch − 55 °C − 16 h after 30 min at 95 °C	Not performed	/	/	[41]
Landfill waste (5–20 years old)	Cellulase / CEL 30 - Sinobios (China)	Recircu	Lab scale 7 L batch / Duplicate − 130 days		0.43*	0.6*	[45]
Landfill waste (30 years old)	Lignin Peroxidase + hydrogen peroxide / Sigma Aldrich	Direct	Lab scale 125 mL batch / 30 days		Methane production increased 23 times		[46]
	Manganese Peroxidase + hydrogen peroxide / Sigma Aldrich	Direct	Lab scale 125 mL batch / 30 days		Methane production increased 36 times		

(*continued on next page*)

Table 2 (*continued*)

Feedstock	Enzyme/Product and/or suppliers	Type of application	Enzymes application conditions	AD scale / AD process conditions	Methane yield (L/g VS)		References
					Control	Treatment	
WAS	Rich enzyme fungal mash (mainly a wide spectrum of carbohydrases)	Pretreat	60 °C – 24 h	Lab scale 160 mL BMP / Triplicate – 35 °C – 30 days	0.24	0.367	[47]
Primary sludge	Mixture of amylase and protease (3:1) / Jiehui biotechnology Ltd.	Direct	Lab scale 250 mL / 50°C- 14 h		/	/	[48]
WAS	Mix of sludge endogenous enzymes mainly amylases and proteases	Pretreat	37 °C – 28 h	Lab scale 250 mL BMP / Duplicate – 37 °C – 30 days	Biogas production increased by 23.1%*		[49]
Digested mixed sludge	Amylase / Sigma Aldrich	Direct	Lab scale 600 mL BMP / 38 °C – 24 h at pH 7.7		No effect on biogas yield*		[51]
	Cellulase /Sigma Aldrich	Direct	Lab scale 600 mL BMP / 38 °C – 120 h at pH 7.7		No effect on biogas yield*		
	Lysozyme /Sigma Aldrich	Direct	Lab scale 600 mL BMP / 38 °C – 120 h at pH 7.7		Biogas yield increased by 9%*		
	Protease /Sigma Aldrich	Direct	Lab scale 600 mL BMP / 38 °C – 120 h at pH 7.7		Biogas yield increased by 37%*		
Grease (5%) - Primary sludge (57%) -WAS (38%)	Lipase / Biolipasa L - Biocon S. A.	Direct	Lab scale 60 mL BMP / Duplicate – 35 °C – 60 days		0.292 ± 1%	0.452 ± 1%	[52]

Type of application: Direct: Direct addition in the digester – Pretreat: Addition in a specific vessel before digestion – Direct2st: Addition in the hydrolysis digester of a two-stage process – Recircu: Addition in recirculated leachate.

Methane yield:

* Biogas yield (L/g VS) is given instead of methane yield.

** Energy coming from the cogeneration (kWh/t of fresh matter) of the plant is given instead of methane yield.

anaerobic microorganisms or endogenous enzymes. Currently, carbohydrases are the only enzymes commercialized at full-scale for biogas applications. One hypothesis might be that carbohydrases are easier and cheaper to produce at industrial scale than lignin-modifying enzymes. Furthermore, due to its higher simplicity for implementation, direct addition can be seen as the most promising way to apply enzymes even though during AD operations, acidic pH that is optimum to certain enzyme activities cannot be applied. Thus, commercial products currently used are based on direct addition of carbohydrases.

On the market, several enzyme products to boost biogas yield are proposed by Novozymes, DSM, Dupont. It can be observed that other smaller enzyme producers or plant constructors are offering dedicated solutions for biogas production such as for instance Metzyme® Forci™ by Metgen (Kaarina, Finland) or Enzymaxx by Agrikomp (Merkendorf, Germany) but these products will not be further described as existing literature on their use is scarce. A similar remark can be drawn for Novozymes, which is offering a range of product called BG Max® 5005/5105/5205 targeting agricultural waste via blends of cellulases, hemicellulases, amylases and pectinases. However, the lack of information on these products, both from Novozymes itself and from the scientific literature, seems to indicate that Novozymes is not currently focusing on this specific market. On the contrary, DSM and Dupont appear to be more active in the field.

DSM Methaplus® L 100 was formerly a product of Biopract GmbH before the company was taken over by DSM in 2009. In 2007, a full-scale study carried out by Biopract on 30 agricultural plants showed that the direct addition of this enzyme blend had an average positive effect of 18% on the biogas yield without any effect on the biogas quality. Thus, Methaplus® L 100 addition was proved to be financially beneficial to all the 30 plants [29]. A precise composition of the DSM Methaplus® L 100 was given; it is composed of xylanase, endo-glucanase, exo-glucanase and β-glucosidase [30]. More recently, linked to the purchase by Dupont of the solid advanced fungal fermentation platform technology, called "C1", of Dyacid in 2016, a new product named Optimash® AD-100 was announced mid-2016. This enzyme blend from *Trichoderma reesei* and *Myceliophthora thermophila* has not been used in laboratory studies yet. Only Dupont data are available, showing that a direct addition in a 2000 kW full-scale plant led to an 8% increase in the methane yield and a 10% decrease in costs for digester operatorion [31]. However, more data will become available thanks to a new European funded project called Demeter. Started in October 2016, this public-private project aims to demonstrate economic benefits of using Dupont C1-enzyme product in biogas industry [32].

From these available products, two points can be highlighted. Firstly, it can be noticed that studies not provided by the supplier on these particular products are very seldom. That is why both lab and full scale academic studies would be very valuable to evaluate and compare the efficiency of these different products. The Demeter project, by its public-private partnership, is a promising example. Secondly, this review mainly focuses on methane yield improvement but enzyme products can offer other advantages. For instance, DSM Axiase™ 100 can lower viscosity of substrates mix rich in whole crop cereal silage [33]. This quality is given as the major feature of Axiase™ 100 product. Similarly, the addition of Fibrezyme® G4 of Dupont to MiaMethan® ProCut, a biogas powder optimizer from MIAVIT (Essen, Germany) is firstly presented as a viscosity reducer. From that, it is important to understand that enzyme application to agricultural waste has actually a wider range of applications than biogas yield improvement such as: reduction of digester viscosity, improved digester mixing, increase of anaerobic digestion rate which implies shorter hydraulic retention time, better use of feedstocks and a wider range of possible feedstocks. Nevertheless, if these features can be observed at full-scale, they are less commonly studied at lab scale as they are more complicated to carry out than methane potential tests at this scale. Thus, pilot research and full-scale trials would facilitate better evaluation of the technology [34].

2.2. Food waste, OFMSW and municipal solid waste

Food waste (FW) can be defined as very variable substrates for anaerobic digestion. However, recent statistical analysis of FW literature has permitted to obtain the main features of FW such as an average high carbohydrate content (36.4% VS) and proteins content (21% VS), as well as a pH around 5 [9,35]. Linked to these features, FW has a good potential for AD treatment but a careful handling is needed to avoid inhibitions by rapid acidification. This drawback is due to the combination of the quick hydrolysis of the carbohydrates and the release of high quantity of ammonium as well as ammonia from protein hydrolysis that inhibits methanogenesis and consequently leads to the accumulation of a high quantity of volatile fatty acids (VFA). These VFA acidify the AD medium and methanogens microorganisms are even more inhibited (generally at a pH below 5.5). Thus, in the case of FW, one of the main objectives of pretreatment is to reduce the quantity of VFA [9,36]. By doing so, secondary objectives of pretreatment such as reducing the hydraulic retention time or improving the biogas yield may also be reached.

Recent literature on the enzymatic pretreatment of FW is relatively scarce and the few existing articles are focusing on improvement of the hydrolysis and methane production (Table 2). Moon and Song [37] carried out an enzymatic pretreatment of 10 h at 50 °C on FW mixing carbohydrases, proteases and lipases from commercial solutions. Following this step, FW was diluted and digested in an up-flow anaerobic sludge blanket (UASB) reactor. High methane yield and reduced HRT were obtained for a loading rate of 9.1 g s-COD/L/d. Higher loading rates decreased the methane yield due to slow acidification of the environment showing that digester input coming from an enzymatic pretreatment has to be carefully managed to avoid any inhibition of the methanogenesis step. More recently, Kiran et al. [38] developed at lab scale a low-cost pretreatment based on enzyme-rich fungal mash. In this study, fungal mash is obtained from waste cakes incubated with *Aspergillus awamori* that notably produces carbohydrases among other enzymes. The pretreatment consisted of a mixing of fungal mash to FW for 24 h at 60 °C. Hydrolysis was improved leading to a 2.3-fold increase in the biogas yield and a 3.5-fold increase in the production rate without any problem of acidification. Out of these results, fungal mash seems to be a promising complement for pretreatment, which combines both reduced cost and improved AD. A larger scale study based on this principle would be valuable. Besides, no enzymatic commercial products, specifically dedicated to food waste pretreatment, are clearly emerging after enzyme suppliers offer analysis.

The lack of examples of enzyme use for FW pretreatment both at lab and full scales can be explained by several factors: (1) natural high hydrolysis rate of the FW is already sufficient to ensure high biogas production at full-scale; (2) increase of this natural hydrolysis rate could jeopardize the future AD by acidification; (3) efficient VFA regulation in FW via enzyme addition has not been proved yet. From that, it can be assumed that enzyme addition to food waste in order to boost methane yield will stay limited to very specific food waste that are difficult to digest.

Similar assessment can be drawn for OFMSW. Literature on enzymatic pretreatment of OFMSW is very scarce [39]. Complexity and composition variability over time of OFMSW are limiting efficiency of a standard enzymatic cocktail. It would be necessary to adapt its composition in function of OFMSW composition shifting, which is difficult to carry out both at lab and full scales. Besides, it was also observed that acceleration of anaerobic digestion rates can be obtained rather than improved yields in terms of methane production [40].

An emerging and very promising application for enzyme treatment concerns the field of Municipal Solid Waste (MSW). For MSW AD, source sorting of municipal solid waste would be the ideal case. However, it needs higher operational cost, it is difficult to apply in dense urban area and it makes the process reliable on community goodwill. Because of these reasons; mainly unsorted municipal solid waste are currently collected and their sorting before AD remains an issue. Today, mechanical pretreatments are principally used in waste plants to separate the organic and the inorganic fractions. Still, they have several drawbacks such as: difficulty to extract glass and plastics that can hamper both AD and digestate quality, losses of a large part of the organic fraction. These drawbacks make mechanical pretreatment of municipal solid waste controversial and alternatives have been explored. The use of enzymes as a liquefaction pretreatment of the organic fraction for the sorting of municipal solid waste has emerged as a very promising technology, which is mainly supported by Dong Energy (Fredericia, Danemark). A first academic study published on this topic was using cellulase and amylase from two industrial Novozymes solutions (Celluclast 1.5 L and Liquozyme SC DC). By combining a step at 95 °C for 30 min followed by an enzyme addition at 55 °C for 16 h, they succeeded in obtaining very good liquefaction results from 50 kg MSW pilot scale experiments [41]. In parallel, a pilot plant was started in 2009 in the Danish incinerator Amagerforbraending and has been operated with success since then by Dong Energy. The relatively low enzyme addition, the efficient and easy sorting by sieving and the promising results at pilot scale have paved the way to a technology scale up. Therefore, Dong Energy will start operating in spring 2017 the first industrial plant based on this technology. Located in Northwich (UK), it will have an annual capacity of 144, 000 t of waste and an energy production forecast of 5 MW. All enzymes used on-site will be provided by Novozymes following an exclusive partnership. Dong Energy under its project entity Renescience A/S has published several patents permitting to have some insights in the full-scale technology. According to Jensen et al. [42], MSW will be heated at temperature up to 75 °C by warm water addition, and then enzymatic hydrolysis and microbial fermentation will be carried out in a long cylindrical tank that slowly rotates to mix all of the waste with enzymes and microorganisms. Temperature is maintained between 45 °C and 50 °C, pH is below 6, HRT is lower than 24 h, influent has a dry matter content ranging between 10% and 45% and enzymes added were only cellulases. More recently, a new patent has underlined the importance of using a blend of enzymes to ensure better liquefaction [43]. Thus, a cellulolytic background of enzymes (between 40% and 99% w/w of the total enzyme protein) can be complemented with proteases (0–20%), lipases (0–10%), beta-glucanase (0–30%), pectate lyase (0–10%), mannanase (0–10%) and amylase (0–10%) to obtain an optimal efficiency blend. Concerning the combined microbial fermentation, lactic acid bacteria and cellulase producing microorganisms are inoculated at the same time that enzymes to enhance the bioliquefaction and probably decrease the enzyme cost [44]. If Dong Energy succeeds with its full-scale demonstration plant, several others may be constructed (a new one is already ordered and will be located in Eindhoven) ensuring a promising prospect for enzyme applications in MSW sorting pretreatment.

Landfill is another emerging field of application for enzymatic pretreatment via leachate recirculation. Indeed, it has been shown that 40 to 50% of the waste composition of landfill sites is composed of paper and cardboard rich in lignocellulose that are degraded with difficulty in this type of system [45]. To illustrate that, Hettiaratchi et al. [46] showed that direct addition of LiP or MnP with hydrogen peroxide in BMP, permitted respectively a 23 times and 36 times increased in methane yield of MSW coming from a 30-year-old landfill. These results clearly illustrate the potential methane leftovers that old landfill contains. They also show the interest to use enzymes to release them. An ingenious way to apply them to existing landfill is to add lignocellulose targeting enzymes directly into the recirculated leachate. This was recently successfully done at lab scale. The addition of a blend of cellulases to a recirculating leachate passing through an MSW coming from a 25-year-old landfill permitted to increase by 50% the biogas yield [45]. Subsequent economic analysis showed that enzymes addition, despite their high cost, created strong benefits of 7–9 euros/tons of waste, ensuring a positive return on investment. From our knowledge, it has not been done yet, but it would be of high interest to test this type of enzyme treatment on full-scale landfill sites and to evaluate both its effect on long-term biogas production and its profitability.

2.3. Sludge

Sludge produced from wastewater treatment plants (WWTP) can be divided into settled primary sludge and waste activated sludge (WAS) coming from the biological treatment. If the former can be readily digested, the latter is less biodegradable leading to a 30–35% conversion efficiency of total sludge organic matter in biomethane [47]. WAS is made of flocs rich in microbial biomass and exopolymeric substances, which are mainly proteins and carbohydrates. Lipids are found in lower quantities in sludge as they are generally captured in grease trap. Several types of enzymes can be applied to enhance sludge hydrolysis in order to both reduce the amount to dispose and improve the amount of biogas produced (Table 2).

Due to the sludge composition, mainly carbohydrases and proteases have been used in literature until now. For primary sludge, direct addition of enzymes was carried out and hydrolysis improvement has been evaluated. By directly adding a mixture of one amylase and one protease to a primary sludge, Yang et al. [48] observed both an enhancement in sludge solubilization by 70% and in its hydrolysis rate by tenfold. However in this study, biogas measurement during AD following enzyme addition was not done. Despite this lack of results, it can be assumed that improvement of the hydrolysis step will at least increase AD rate. But an increase in biogas yield and a reduction in final sludge volumes remain highly uncertain and further studies have to be done. Proteases and carbohydrases have also been used efficiently as a pretreatment step for WAS before their AD. For instance, a 28-h pretreatment at 37 °C using amylases and proteases isolated from the fermentation of endogenous sludge microorganisms permitted a 23% increase in biogas production compared to control [49]. According to the authors, this increase was due to a better solubilization of the sludge, even though flocs disintegration was not observed. More recently, application of a fungal mash, mainly rich in carbohydrases, as WAS pretreatment also led to a 50% increase in methane yield and a three times higher hydrolysis rate than the control [47]. No information was given on the evolution of the flocs structures in presence of the fungal mash. At higher scale, very rare trials are reported. Rademacher et al. [50] added a mix of proteases and carbohydrases during the digestion of sludge resulting in a 10% increase in biogas yield. However, a high dosing of 0.5–0.7 kg/tons of sludge was needed to reach such positive effect.

Aside from proteases and carbohydrases, lipases are generally less studied due to the fact that lipids are not one of the main components of sludge and that the release of long-chain fatty acids (LCFA) from their hydrolysis could cause inhibitory conditions for AD [51]. This can be well illustrated by the direct addition of lipase to the co-digestion of grease with a mix of primary sludge and WAS [52]. In this study, optimum lipase addition led both to an increase of 50% in the methane yield and of 25% of the hydrolysis rate. However, too high concentration in lipase strongly hampered that improvement, probably due to high and inhibitory concentration in LCFA. In this particular case, reasonable addition of lipase is of interest as anaerobic digestion needs to handle lipids coming from a grease trap, but this application is not widely used.

If proteases and carbohydrases have been shown to be the most suitable enzymes for primary sludge and WAS pretreatment, the important question of their lifespan and activity in the sludge after addition remains. To answer this question, Odnell et al. [51] followed at lab scale both activity and lifetime of several types of enzymes during AD of Waste Water Treatment Plant (WWTP) digested sludge. Surprisingly, cellulase addition did not show any biogas yield improvement due to an immediate inhibition of its activity by an endogenous component of the sludge. Similarly, amylase did not increase biogas yield and its lifetime was shorter than 24 h due to endogenous proteases that hydrolyse it. Lysozyme showed the longest effect as methane yield was still increasing 48 h after addition for a final net increase of 9% in comparison with the control. Lysozyme effect was prolonged over 24 h (its lifetime in the sludge) due to the release of intracellular enzymes that probably favour autohydrolysis. Finally, proteases such as subtilisin displayed the highest increase in methane yield (37% increases after 24 h) with an activity that was shorter than 24 h. From this study, activity lifetime of all types of added enzymes in sludge was very limited in time (generally less than 24 h). It can be explained by both inhibitions due to unknown sludge compounds and enzyme degradation by endogenous proteases. Despite this short period of activity, proteases and lysozyme succeeded in increasing biogas yield and the production rate at high dosage. From this high dosage, the cost/benefit ratio is likely too high. To favour the implementation of such pretreatment, enzymes with higher activity or longer lifetime have to be developed in order to lower dosages.

Carbohydrases and proteases have shown to give some good technical results at lab and full scales but their high cost and short lifetime strongly limit their application at industrial scale for sludge pretreatment. Thus, from our knowledge, no product is available on the market as a specific enzymatic pretreatment to enhance biogas yield and reduce sludge volume. However, technologies focusing on enhancing activity lifetime or reducing cost of enzymes in sludge are being developed. For instance, Veolia (Paris, France) in order to reduce membrane clogging of Memthane® and Biosep® processes, has developed a patented technology called Memzyme™. Before reaching the filtration step, sludge coming out from the anaerobic digester is passing through an enzymatic reactor, where enzymes are fixed on a three-dimensional support that enhances their activity lifetime and therefore reduces their dosage need [53]. From this idea, similar fixed enzyme technology could be imagined that would permit the implementation of a large-scale cost effective pretreatment of sludge before AD. Another example that is studied at lab scale is garbage enzymes, a low-cost crude enzyme solution made of fruit peels fermentation. The pretreatment of WAS using this type of enzyme solution successfully improved its solubilization and its subsequent AD [54]. Garbage enzymes due to their low production cost, environmental advantages, and positive lab scale results may also be a promising option to explore for biocatalytic sludge pretreatment.

2.4. Assessment of enzymatic pretreatments

Experiments that follow a careful selection of the pretreatment enzyme type in function of the substrate composition have generally shown good results in biogas and methane yield improvement. However, most of these data are obtained at lab scale and in batch BMP tests. At higher scale, main issues hindering widespread use appear to be the enzyme cost and the enzyme activity lifetime after addition. To solve these issues, several tracks appear: (1) advance in enzyme engineering using recent molecular tools may permit to obtain more robust enzymes having a higher activity and less sensitivity to specific inhibitions (phenol for instance in the case of lignocellulose degradation). Speda et al. [55] recently improved lab scale AD of ensiled forage ley by using an enzymatic cocktail (previously obtained from an AD environment) that displays long-lasting activities and stability during the digestion but full characterization of this enzyme cocktail for its production in recombinant systems remains challenging; (2) development and use of highly productive genetically modified microorganisms by companies should permit to reduce the enzyme production cost; (3) on-site production of enzymes for large biogas plant can be a solution to reduce enzyme cost, a company called Greenmove technologies (Leeuwarden, the Netherlands) is developing this kind of solution in plug-in containers; (4) the addition, in complement of enzymes, of highly productive enzyme microorganisms under solid (fungal mash for instance) or liquid form could permit both to reduce the cost of downstream process for enzyme purification and to increase enzyme activity as they are produced in situ; (5) finally, enzyme fixation on a three-dimensional support is a promising way to enhance the activity lifetime of the enzyme and thus reduce dosage.

Besides, it is important to underline that enzymatic pretreatment is a versatile technology that should not only be economically evaluated through the prism of biogas yield increased. For instance, a cheaper substrate use, a reduced HRT or a lower mixing cost would be very profitable in certain full-scale plants and should be considered in the future. Even more disruptive application such as liquefaction of MSW for sorting may soon succeed at full-scale. For all these reasons, enzymatic pretreatments remain a very promising tool for anaerobic digestion enhancements that may continue to develop.

3. Anaerobic pretreatments

In this part, existing anaerobic pretreatments, whatever their predominant aim is (storage or enhancing AD yield), will be described. Thus, three anaerobic pretreatment types can be distinguished: basic two-stage digestion that can be applied to a broad range of feedstocks, enhanced two-stage digestion using specific hydrolytic anaerobic consortia that are focusing more on lignocellulosic biomass and ensiling that is used for agricultural waste or crop storage. Each of them has its own degree of development ranging from lab scale trials to widely used.

3.1. Two-stage digestion

Two-stage digestion is based on the separation in time and space of the hydrolytic and acidogenic steps from the acetogenic and methanogenic steps [56]. This is generally made by using two separate vessels, the first step can thus be considered as pretreatment of the methanogenic step. Based on this primary principle several technologies can be distinguished in function of the temperature applied in these vessels: thermophilic two-stage digestion, mesophilic two-stage digestion and temperature Phased Anaerobic Digestion (TPAD) where the first vessel is thermophilic (or hyper-thermophilic) and the second vessel is mesophilic. Ariunbaatar et al. [39] listed both the advantages and drawbacks of these technologies that are given in Fig. 2.

If this technology already exists at full-scale, it is not yet very common depending on the feedstock and continues to be developed at lab scale. Thus, for each feedstock, focus on recent research projects and examples of available commercial technologies will be given.

3.1.1. Agricultural waste

It is commonly accepted that two-stage digestion technology is valuable for easily biodegradable waste that can generate acidification issues [12]. Agricultural feedstocks, often rich in lignocellulose, are rarely easily biodegradable and application of two-stage digestion is in this case very questionable. Indeed, if pH does not drop and hydrolysis is a long process, methanogenic activities will appear and a single vessel will be sufficient. To support this theory, Lindner et al. [57] recently showed that two-stage anaerobic digestion fits better to sugar rich feedstocks. They evaluated the most suitable feedstock for a continuous two-stage process at pilot scale, among maize silage, sugar beet and a mix of hay/straw. After 50 days experiments, it appears that OLR and substrate degradation were respectively 5 times and 4 times higher for sugar beet than hay/straw. Besides, in comparison to their respective BMP, methane yield was 70% lower for hay/straw whereas sugar beet was only 8% lower.

Besides, a distinction must be made with the other type of two-stage anaerobic digestion that is commonly found in agricultural biogas plant, which consists of a digester and a maturation or post-digester. Indeed, in this particular set-up, hydrolysis and methanogenesis are taking place in both digesters and the pH of the first digester is neutral. In this case it is not a hydrolytic pretreatment but rather a way to increase HRT and to recover more biogas from a given feedstock.

Some biogas plant manufacturers are selling two-stage digestion systems for agricultural waste such as Bioplex Ltd (Stockbridge, the UK) or Snow leopard projects GmbH (Reisbach, Germany). However, regarding the two previous conclusions, full-scale applications at farm scale of a “hydrolytic” two-stage digestion remain very seldom as it generates both higher complexity and costs without clear benefits compared to a single stage digester. To reduce costs for farm scale, innovative compartmented vessels can be used such as Linear Vortex™ by DVO Inc. (Chilton, the USA) that displays a very specific “U” design or Arkometha™, by Arkolia Energies (Mudaison, France), a highly productive, small size and multi-step vessel digester dedicated to solid digestion. However, these innovations can be considered as process configuration or bioreactor design improvement and therefore are outside the scope of the current pretreatment study. Another option is to enhance first step hydrolysis using specific consortia as it will be developed thereafter (Section 3.2).

3.1.2. Food waste, OFMSW and municipal solid waste

Contrary to agricultural feedstocks, food waste are easily biodegradable substrates on which two-stage digestion is highly recommended and therefore often applied. For instance, a recent pilot study using food waste in 5 m^3 digesters showed that two-stage mesophilic performed better than a single stage. It ensured both a better methane yield (460 vs 380 L CH_4/ kg VS) and a better digester stability over time [58]. Aside from higher methane yield, concomitant hydrogen production from the pre-digester is another reason that makes two-stage digestion very valuable. Thus, Cavinato et al. [59] successfully obtained a stable hydrogen production from food waste in a two-stage thermophilic pilot set-up and Gioannis et al. [60] showed that two-stage AD of food waste yielded 20% more energy than one stage AD mainly due to hydrogen production (5% of the total energy) in the first stage together with a subsequent higher methane production due to lower inhibition. According to Sen et al. [61], hydrogen can be recovered from the pre-digester with a yield ranging from 10% to 20% of the total substrate energy potential. This hydrogen can be further used to produce biohytane, electrical power or heat. Thus, in this article a

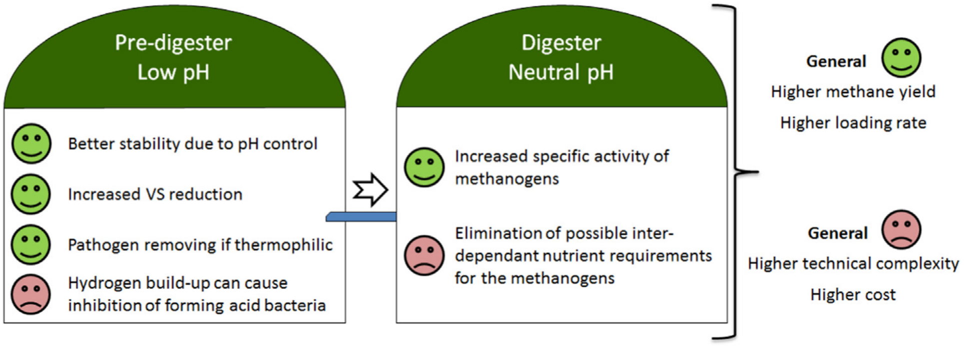


Fig. 2. Advantages and drawbacks of two-stage digestion.

promising biorefinery model proposed for food waste is including a temperature phased anaerobic digestion, from which both hydrogen and methane production are maximized and can be then valorized. Similar results were obtained for OFMSW in a recent study where TPAD displayed better results than single stage process. Both COD removal and methane yield were increased up to 15% and 60% respectively, in comparison to a single-stage process [62].

At full-scale, several two-stage technologies dedicated for bio-waste are commercially available. Without being exhaustive, some examples are listed below. The Gicon® process proposed by Gicon Group (Dresden, Germany), is a two-stage dry-wet digestion that can be used for feedstocks rich in impurities and unwanted compounds such as unsorted MSW. Firstly, a dry digestion is performed. Then, hydrolysis percolates are recovered and further digested in a liquid digester to produce methane-rich biogas. A plant based on this technology and handling 27, 000 t of organic waste per year has been operated since 2012 in Richmond (BC, Canada). Veolia is also offering two-stage anaerobic plants under the trademark Biomet™. In this technology, two CSTR digesters are used in series. A territorial plant using this technology, named Artois Methanisation (Pas-de-Calais, France), treating 25, 000 t/year of waste has been operated by Veolia's business unit SEDE since 2012.

3.1.3. Sludge

Several types of two-stage anaerobic digestion processes have been applied to sludge in order to improve the hydrolysis step of its digestion. Temperature phased anaerobic digestion (TPAD) has been extensively tested at lab scale and is given as an effective strategy that promotes solid destruction, sanitation of pathogens and higher methane production [63]. However, it is also outlined that TPAD is still in its infancy due to its complexity and needs further optimization especially for up-scaling. Two-stage thermophilic AD is another promising option. Recent pilot trials (CSTR of 0.15 and 0.23 m^3), showed that WAS high rate (OLR close to 2 kg VS/m3 per day) thermophilic AD was better in the case of a two-stage than a one-stage set up [64]. Biogas production was increased by 32%, digestate sanitary quality met all requirements to be used in agriculture and economic analysis showed that additional hydrolysis reactor can be paid back in about 3 years. Finally, another option which is being developed at lab scale is a two-stage process called inverted phase fermentation (IPF). This method consists of a preliminary 2 days anaerobic digestion at slightly thermophilic conditions (42 °C), from which gas bubbling, separate sludge into a top layer enriched in solids and a liquid clarified bottom layer. Subsequent separation of the two phases and respective anaerobic digestion showed interesting results. Negral et al. [65] by applying this technique to sludge showed that digestion time in a 2.5 L CSTR was lowered as the organic loading rate could be increased between 3 and 6 fold thanks to phase separation.

From these different sludge two-stage processes, similarities are coming from the use of higher temperatures that favour endogenous hydrolytic enzyme activities and accelerate the hydrolysis reaction rates. Common benefits are: higher biogas production, lower HRT, final sludge volume reduction and pathogen reduction (in the case of an adequate time and temperature exposure).

Due to these given benefits, full-scale technologies based on a two-stage process have been developed. An English company called Monsal that was taken over by GE Water & Process Technologies in 2014 (and lately has become a business unit of Suez), has developed an advanced digestion technology (ADT) for sludge. According to Hacking [66], this technology is based on biological hydrolysis that is carried out in six reactors in series (first stage) leading to the digester (second stage). Total HRT of the first stage is about 3 days. Sludge is heated between 42 °C and 55 °C and only a portion of each reactor vessel is transferred forward, leaving a concentration of endogenous enzymes behind in each of the 6 vessels. Hydrolysis mechanisms of this method were recently explored showing that improvement of AD was, at these temperatures, due both to a better depolymerization of extracellular polymeric substances (EPS) into smaller organic compounds as well as VFA and to the release of EPS bounded proteins and carbohydrates [67]. Twelve Monsal plants using this technology have been commissioned since 2002 mainly located in the United Kingdom. Their operations are given as successful leading to higher sludge digestion capacity, higher biogas production and reduced final biosolids mass. This technology is very promising as it permits to enhance WWTP energy production.

3.2. Enhanced two-stage digestion

To manage lignocellulose rich substrates in a two-stage digestion set-up, several ways to enhance the first hydrolytic step were explored. The shared idea of these different ways is to bring to the system anaerobic hydrolytic microorganisms that would degrade more efficiently and more quickly lignocellulose. In other words, bioaugmentation is applied to the first hydrolytic step. These exogenous microorganisms can come from different origins that permit to define several ways to enhance two-stage digestion.

3.2.1. Rumen derived anaerobic digestion

Rumen is one of the most efficient microbial ecosystems in nature to carry out degradation of lignocellulosic biomass. This ecosystem is made of bacteria, fungi, protozoa and archaea that can grow rapidly on lignocellulose and can secrete high quantity of hydrolytic enzymes. Thus, in this environment lignocellulose is quickly degraded into VFAs that can be further metabolized by ruminants [68]. It can be noticed that production of methane is not the aim of this ecosystem therefore; methanogens content is naturally low in rumen fluid. To make it short, rumen ecosystem is foremost a super hydrolytic consortium and secondarily a methane producer.

Pretreatments using rumen ecosystem have been widely tested at lab scale on several lignocellulosic feedstocks to increase their methane production. One of the underlying aims is to recreate an efficient artificial rumen system. This kind of pretreatment can be gathered under the name rumen derived anaerobic digestion (RURAD) [69]. Here, focus is made only on two-stage AD but it has to be noted that several other experimental set ups using rumen fluid have been tested up to now such as continuous-flow culture reactor, dual-flow continuous culture reactor, anaerobic sequencing batch reactor and modified UASB reactor [70]. Zhang et al. [71] pretreated rice straw with rumen fluid at 39 °C, for 24 h under anaerobic conditions and then digested it with sludge inoculum at 35 °C for 30 days. At the end, biogas production from AD was increased by 66.5%, its methane yield was improved by 82.6%, and the digestion time was 40% shorter than control. This better digestion can be explained by biomass structural changes during pretreatment such as an increase of the specific surface area, the removal of the hemicelluloses, a decrease in cellulose crystallinity and in lignin content [70,72].

Rumen fluid addition pretreatment displays very interesting results showing that lignocellulosic biomass can be efficiently hydrolysed. However, several points strongly hinder its application at full-scale for methane production: (1) the understanding of the rumen ecosystem is still limited; (2) the reproduction of an efficient and long-lasting artificial rumen system is for the moment kept out of research hands; (3) promising lab scale results are based on the application of a high ratio of rumen fluid on solid biomass (ratio of 10 to 20) that indicates the need to use a large amount of rumen fluid in case of a current scale up; (4) rumen fluid is produced in limited quantity from slaughterhouses, its extraction has a cost and it is better to use it fresh. Therefore, from our knowledge, there is no example of industrial two-stage AD plant using rumen fluid as pretreatment in the first stage. Research still needs to advance on rumen understanding and on ways to maintain in a hydrolytic digester an efficient rumen ecosystem over time. From these advances, promising potential pretreatment scale-up for biogas production might emerge.

3.2.2. Pure culture or designed anaerobic hydrolytic consortia

Microorganisms isolated from other environments than rumen can be used to enhance the hydrolytic first stage of a two-stage digestion. Pure culture of hydrolytic microorganisms was explored with contrasting results. A first study using *Caldicellulosiruptor lactoaceticus*, a thermophilic anaerobic bacterium isolated from hot springs, was carried out on a laboratory two-stage continuous thermophilic (68 °C/55 °C) digestion treating fibre rich cattle manure. Bioaugmentation of the first stage with *C. lactoceticus*, led to a 10% higher methane yield than the control [73]. However, results can be very different from one strain to another and it is needed to carefully select the strain to obtain positive results. For instance, Nkemka et al. [74] used an anaerobic hydrolytic fungus, *Piromyces rhizinflata* YM600, to pretreat corn silage and cattails in a laboratory two-stage digestion system. In this study, bioaugmentation of the first stage did not increase the methane yield from both corn silage and cattail due to the competition for growth between the fungus and methanogens microorganisms.

Consortia are another option that can be more efficient and robust than pure culture for bioaugmentation of the hydrolytic first stage. Martin-Ryals et al. [75] tested at lab scale a commercialized cellulolytic culture of anaerobic bacteria (mainly from the genus *Clostridium*) on corn lignocellulosic residues in a two-stage continuous digestion. Daily bioaugmentation increased hydrolysis and VFA concentrations that led to a final methane yield 56% greater than the control. Furthermore, economic analysis showed that daily bioaugmentation was economically feasible and could improve the economics of AD by 27–34 dollars/dry ton for this specific feedstock. Similarly, Poszytek et al. [76] designed a Microbial Consortium with High Cellulolytic Activity (MCHCA), made of 16 selected strains, that was used to treat maize silage in a two-stage digestion system. MCHCA addition succeeded in significantly enhancing the biogas yield by 38% and increased the methane content by 14%.

From these results, it seems clear that bioaugmentation using anaerobic hydrolytic consortia would be preferred to pure culture as they adapt better to environmental changes (pH, T°) and tend to show higher resistance to the presence of toxic organic compounds, heavy metals or contamination by other strains [76]. Several hydrolytic anaerobic consortia have been developed and it would be interesting to test them in full-scale applications [77]. One of the impediments for a technology scale up is probably lying in the lack of a market. Indeed, nowadays full-scale “hydrolytic” two-stage digesters dedicated to lignocellulosic substrate are very seldom. Bioaugmentation scale-up will be part and concomitant with the development of a reliable hydrolytic two-stage digestion solution at full-scale dedicated to lignocellulosic feedstocks.

3.2.3. Hydrolysis using the liquid fraction of digestate

Another possibility for the hydrolytic first stage consists in submerging the lignocellulosic feedstock into the liquid fraction of digestate (LFD). Then, the feedstock and the LFD are transferred into the second stage digester. This strategy is based on the recirculation of the LFD and has several interests that make it a very interesting solution to pre-degrade lignocellulosic feedstocks: (1) LFD is a microbial medium that contains abundant hydrolytic microorganisms; (2) LFD is an additive agent that provides abundant nutrition substances for the AD under the form of inorganic (nitrogen and phosphorus) and organic molecules (remaining carbohydrates, proteins, etc.); (3) it is a low-cost solution as LFD is readily available on biogas plant and it can be environmentally friendly in the case of LFD overproduction [78].

Two recent lab scale studies applied with success this pretreatment. Hu et al., [79] pretreated corn stover for 3 days at ambient temperature with LFD and obtained 70.4% more biogas production, 66.3% higher methane yield and a 40% shorter digestion time compared to the control. Similarly, Wei et al. [78] applied to a mix of cattle manure and corn stover LFD for 5 days at ambient temperature and also obtained a better subsequent AD, where methane yield was 25% higher, buffer capacity was improved and digestion time reduced. But the most interesting result in this study is that LFD pretreatment performed as well as a chemical pretreatment (e.g. caustic soda or ammonia solutions) but for a lower cost (in average 60% less costly). Recirculation of LFD is a method which is widely applied within agricultural plants at full-scale in order to ensure a proper and homogenous microbial activity. However, LFD pretreatment, where feedstocks is in a first stage only in contact with LFD is not yet applied at full-scale from our knowledge. Regarding the lab scale results, it would be very interesting to scale up this technology. A low-cost pretreatment solution under the form of a two-stage anaerobic digestion treating lignocellulosic feedstocks may emerge from this concept.

3.3. Ensiling

Ensiling is a very conventional and widely applied method for efficient storage of crops at farm scale. It is based on the application of anaerobic and wet conditions that favour lactic and acetic acid fermentations, transforming free sugars, hemicelluloses and cellulose mainly into organic acids. It results in an environment acidification that inhibits most of the activities of microorganisms that would otherwise degrade the biomass. An important feature of ensiling is that it does not permit to degrade lignin efficiently [80]. Montgomery et al. [56] underlined that ensiling cannot be considered as a pretreatment to enhance biogas production, due to its minimal effect reported on methane yield. However this statement can be discussed.

Indeed, ensiling is a complex biological process that needs a careful tuning. To ensure its success, the following parameters need to be optimized: particle size, moisture, storage conditions, storage duration, temperature and additives [81]. Each of these parameters has an impact on the storage quality but also on the future methane yield of the feedstock. Only a few studies that took into account organic matter loss succeeded in showing an increase in methane yield using ensiling. For instance, Pakarinen et al. [82] reported a 50% increase in methane yield of hemp after ensiling. More recently, ensiling of giant reeds permitted to obtain an increase in methane yield ranging from 4% to 14% [83] and ensiling of switchgrass also improved subsequent AD despite a 6% mass loss [84]. According to Teixeira Franco et al. [81], these results may be explained by gains in biochemical accessibility that overcame the potential organic matter loss during storage. In this regard, if anaerobic conditions are well applied, the most critical parameter to ensure an increase in methane yield appears to be the feedstock biochemical characteristics. Therefore, results are strongly feedstock dependent and that might explain why ensiling of some feedstocks (mainly energy crops) have shown no effect or negative effects on the methane yield [85,86].

Even if it remains very challenging, future research may find out for dedicated promising feedstocks and with optimized ensiling conditions a way to enhance biogas production. Furthermore, its combination with other biological pretreatments may be very interesting in the case of lignocellulose degradation and it will be developed thereafter [87]. Over time, ensiling may not only be a storage process but also become a potential low-cost pretreatment to enhance subsequent digestion of specific feedstocks.

3.4. Assessment of anaerobic pretreatments

Anaerobic digestion as a pretreatment to enhance biogas production is developed at full-scale under the form of two-stage digestion to treat easily degradable substrates (for instance food waste) and sludge. However, this process is less promising for lignocellulosic biomass. With this kind of substrate, two anaerobic solutions are currently explored: an enhancement of the first hydrolytic stage by bringing under different forms efficient anaerobic consortia or an ensiling step for certain specific biomass. This may enhance biogas production but further research and scale-up need to be carried out. From our knowledge, no full-scale example currently exists for these hydrolytic pretreatments.

4. Aerobic pretreatments

In the case of aerobic pretreatments, the presence of oxygen permits to take full advantage of decomposition capacities of facultative anaerobic and aerobic microorganisms. These microorganisms degrade organic matter using oxygen as a final electron acceptor in order to ensure their growth. Through their metabolism, they mainly produce CO_2, water, nitrate and sulphate [8]. These types of pretreatments can be very interesting in the case of lignocellulosic substrates. Indeed, they can offer better subsequent accessibility to organic matter during AD by specifically degrading lignin polymers [80]. In the case of municipal solid waste and sludge, they can also be of interest as they can permit to warm up waste before AD, to speed up AD start up and to reduce waste volume. An increase in methane yield can also be obtained if pretreatment is finely tuned as it will be seen thereafter.

Aerobic pretreatments can be divided into three categories. The first one is simple aeration where substrate is only subject to aerobic conditions. The second one is aerobic pure culture pretreatment where preaeration is complemented by the inoculation of a given aerobic microorganism featuring interesting degrading properties. The last category gathers aerobic consortium pretreatments where aerobic consortia under liquid or solid forms are inoculated instead of a pure culture. Micro-aeration during AD and aeration of the digestate are out the scope of this review but it can be noticed that several works displaying interesting results have been published on these topics [88,89].

4.1. Simple aeration

Simple aeration can be operated under solid state. In this case, it is important to make a distinction between simple aeration and composting. Indeed, in the first case, feedstock is shortly exposed to aerobic conditions, it may eventually reach thermophilic phase but never the maturation phase. While in the case of composting, according to the classical definition, feedstock is subject to a long aeration time, including mesophilic, thermophilic, cooling and maturation steps [90]. Duration, temperature and organic matter stabilization are the main criteria to distinguish between both processes. Besides (micro-)aeration prior AD can also be applied. It generally consists in injecting air or oxygen in the system for a given period before to shift to anaerobic conditions. Simple aeration is taking advantage of endogenous aerobic or facultative anaerobic communities' hydrolytic activities. This pretreatment can be relatively easy to implement for all kinds of organic feedstocks; therefore, a wide range of results at lab scale have been obtained. Recent or highly interesting literature results are gathered in Table 3.

4.1.1. Agricultural waste

Simple aeration is particularly interesting in the case of lignin rich substrates as oxygen favours ligninolytic activities of endogenous fungi and bacteria populations. Thus, some studies have recently evaluated at lab scale the impact of micro-aeration prior AD or aeration on lignocellulosic agricultural waste and their subsequent biogas production. For the former case, Fu et al. [91] injected a small amount of oxygen (5 mL/g VS) in bottles flushed beforehand with nitrogen and containing corn straw as well as anaerobic inoculum. After total depletion of oxygen, substrate received additional inoculum and water, and then AD was carried out. The pretreatment had a notable disruptive effect on the structure of corn straw. Besides, methane yield was 16% higher than untreated group due to improved hydrolysis efficiency (11% higher VS removal). For aeration under solid state, Zhou et al. [92], applied a 20 days pile pretreatment to corn stover that was beneficial to hemicellulose, cellulose and lignin depolymerization (up to 5.7% lignin degradation for the pile middle layer). Consecutive 5L anaerobic codigestion of the pretreated corn stover with cow dung had a biogas yield enhanced up to 29% (for the middle part of the pile) in comparison to the control. This improvement was due to a higher cellulose and hemicelluloses degradation during the AD, that can be explained by a higher accessibility to these polymers by anaerobic microorganisms thanks to lignin removal. Similarly, the aeration of rice straw showed that cellulose, hemicelluloses and lignin were decreased by 7.5%, 64.5% and 13.6% respectively [93]. Besides, total solids also showed a significant decrease of 63.6% after pretreatment. No biogas measurement was carried out to measure the efficiency of the pretreatment but it can be assumed that such mass loss during pretreatment was detrimental for methane production.

The question of mass loss during aerobic pretreatments is of the utmost importance in order to fully evaluate their impacts on methane yield. Indeed, during aerobic degradation reactions, carbon can be relocated under different forms that are soluble carbonated molecules, aerobic biomass and CO_2. If for the former two, they can be potentially used as carbon sources during following AD, it is not the case of CO_2, which is a carbon loss that will directly impact the methane yield. From this point, the main challenge for efficient aerobic pretreatment dedicated to agricultural waste can be raised: finding a trade-off between a better accessibility to hemicelluloses and cellulose and the loss of organic matter. Therefore, pretreatment optimization and measurement of the matter loss under the form of CO_2 are critical to ensure and fully validate a gain in methane yield. Until now, the question of mass loss has often been neglected in literature and it is highly recommended to take it into account in future studies [94].

At full-scale, aerobic pretreatment of agricultural waste can be easily carried out. Simple aeration under the form of stacks, piles, pits or bins are commonly carried out in farms. If no results are published on the subject, it is likely that farmers already tested them for specific lignocellulosic feedstocks. Fully detailed full-scale studies would be interesting to evaluate the impact of short aeration on methane production with respects of the substrate characteristics and following process optimization. If it proves to be efficient and easily implementable, it may generalize this pretreatment method for lignocellulosic feedstocks similarly to ensiling for crop storage. An important drawback of such pretreatment that can arise is its potential long duration (several days) that may necessitate a more complex substrate management on-site.

Another interesting feature of short aeration that can only be observed at pilot or full-scale is organic material temperature rising similarly to a thermophilic composting phase. This process specificity can be used to avoid a high energy requirement for substrate heating in the case of subsequent thermophilic AD. Historically, such principle was applied to solid manure, in the Ducelier-Isman process. A demonstration plant of 15 m^3 in France, in 1986–1987 showed that pre-aeration of 24–45 h can increase manure temperature up to 72 °C and thus, reduce the lag phase of the subsequent AD from 6 to 2 days [95]. Nonetheless, this pretreatment application remains confidential on farm plants probably due to the fact that efficient warming of digesters can be ensured by heat surplus from cogeneration or by on-site boiler using biogas excess production in injection plant.

4.1.2. Food waste, OFMSW and municipal solid waste

Application of aerobic pretreatment to food waste or OFMSW can have in a short time an important impact on mass loss of organic matter as these substrates are easily degradable. Brummeler and Koster [96] applied to OFMSW strong and long aeration (12.5 L/h/kg of OFMSW − 10 days) and at the end of the treatment, volatile solids were reduced by 23.5%. Easily degradable parts of the substrate were degraded. Despite an accelerated start-up of the AD, the loss of organic matter decreased the potential methane yield by 40%. Similarly and even with a lower flow and reduced time of aeration (1 L/h/kg of OFMSW – 5

Table 3
Effect of aerobic pretreatment on biogas and methane yield in function of feedstock.

Feedstock	Type of aerobic pretreatment	Pretreatment conditions	AD scale / AD process conditions	Methane yield (L/g VS)		DM loss taken into account in Methane yield	References
				Control	Treatment		
Corn stover (pile middle part)	Simple aeration	Aeration using 1 m pile set up – density of 5 kg/m3 – ambient temperature (25–30 °C) – 20 days	Lab scale 5 L co-digested with cow dung (1:1) / 60 days	0.315*	0.45*	No	[92]
Corn straw	Simple aeration	AD conditions in bottles and then pure oxygen was added 5 mL/gVS – 55 °C – until total oxygen depletion	Lab scale 500 mL batch / 37 °C – 60 days – 130 rpm	0.28	0.325	No	[91]
Wheat straw	Fungal pure culture	Column autoclaved - *Polyporus brumalis* BRFM 985 (1: 166) – 120 mL/min 100% moisture air – 28 °C – 21 days	Lab scale 600 mL BMP / 36 °C	0.217	0.28	Yes	[94]
Tall wheatgrass	Fungal pure culture	250 mL Erlenmeyer 65% moisture autoclaved – *Flammulina velutipes* – cotton plugs – 28 °C – 4 weeks	Lab scale 2 L digester / 37 °C – 23 days – pH 7	0.125	0.169	Only calculated (up to 29%)	[113]
Rice straw	Fungal pure culture	1 L Erlenmeyer 75% moisture autoclaved – *Pleurotus ostreatus* (1:4)– cotton plugs – 28 °C – 20 days	Lab scale 500 mL batch / 37 °C – 45 days – pH neutral	0.12	0.263	Only calculated (up to 13%)	[114]
Hazel branches	Fungal pure culture	250 mL Erlenmeyer autoclaved – *Ceriporiopsis subvermispora* ATCC 96608 (1:15) – 28 °C – 28 days	Lab scale 500 mL BMP / 35 °C	0.105	0.185	Yes	[115]
Sugarcane bagasse				0.230	0.220	Yes	
Corn stover (4.5–9 mm)	Fungal pure culture	250 mL Erlenmeyer autoclaved – *Pleurotus eryngii* (2:1) – 82% moisture air – 30 °C – 30 days	Lab scale 250 mL BMP / 35 °C – 40 days	0.355*	0.279*	Yes	[116]
Corn stover (0.5–4.5 mm)		250 mL Erlenmeyer autoclaved – *Pleurotus eryngii* (2:1) – 82% moisture air – 30 °C – 30 days	Lab scale 250 mL BMP / 35 °C – 40 days	0.302*	0.360*	Yes	
Corn stover (0.5–4.5 mm)		250 mL Erlenmeyer autoclaved – *Pleurotus ostreatus* (2:1) – 82% moisture air – 30 °C – 30 days	Lab scale 250 mL BMP / 35 °C – 40 days	0.294*	0.301* ± 2%1	Yes	
Corn Straw	Aerobic consortium from retted corn straw composting	1 L bottle – retted and composted corn straw (7:1) – 5 mL of O_2/g $VS_{substrate}$ was injected then bottles were closed – 55 °C – 20 h	Lab scale 200 mL batch / 37 °C – 45 days – 130 rpm	0.277	0.343	No	[120]
Sisal pulp	Aerobic consortium from WAS	500 mL Erlenmeyer – Aerated WAS (14:1) – open flask permits surface aeration – 37 °C – 9 hours – 135 rpm	Lab scale 500 mL BMP / 37 °C – 32 days – 70 rpm	0.19	0.24	No	[122]
Rice straw	Aerobic consortium from sludge	10 L bioreactor – aerobic sludge supernatant (2:1) – moisture 60% – aeration 30 L/h/kg DM – 35 °C – 2 days	Lab scale BMP type AMPTS / 37 °C – 55 days – 160 rpm	0.306	0.355	No	[123]
Cassava residues	Aerobic consortium from soil	250 mL flask – designed hydrolytic consortium (aerobic & anaerobic bacteria) (1:20) – Loose caps – 55 °C – 12 h	Lab scale 250 mL batch / 55 °C – 10 days – pH 7.2	0.132	0.259	No	[124]
Rotted silage maize	Aerobic consortium from compost	300 mL flask – designed consortium (MC1) – static aerobic conditions – 50 °C – 5 days	Lab scale 600 mL batch / 35 °C – 16 days	0.173*	0.304*	No	[125]
Sawdust	Aerobic consortium from rotten sawdust	5 L Erlenmeyer flasks – designed consortium (1:2) – Cotton stoppers – 30 °C – 10 days	Lab scale 5 L batch / 30 °C – 35 days	0.09	0. 15	No	[126]
Wheat straw	Aerobic consortium from compost and dairy manure	1.5 L bottle autoclaved – designed hydrolytic consortia (mainly facultative anaerobic bacteria) (1:20) – sealed with plastic film open periodically – 37 °C – 3 days	Lab scale 600 mL BMP / 37 °C – 23 days	0.137	0.246	Only calculated (up to 25%)	[127]
OFMSW	Simple aeration	Column reactor $0.2m^3$ – 60 kg of OFMSW – airflow 750 L/h (20 °C) – 10 days	Lab scale 6 L batch / 30 °c – 6 days	Methane yield decreased by 40%		Yes (up to 23.5% VS) 23.5% VS)	[96]
OFMSW	Simple aeration	10 L reactor – 6 kg of OFMSW – minimum 6 L/h to maintain O2 content above 12% – 5 days	Lab scale 1 L BMP / 37 °C – 28 days	0.518	0.43	Yes	[97]
Sugar rich FW	Simple aeration	1 L bottle – airflow 5 L/h – 24 h	Lab scale two-stage 1 L BHP-BMP / 35 °C – 4 & 73 days	0.22	0.22	No	[98]
Synthetic MSW	Simple aeration	Column reactor 8 l – 3 kg of MSW – periodic airflow with a total of 30 L/h – 35 °C – 8 days	Lab scale SS-AD batch 2.5 kg MSW – 35 °C – 100 days	Methane yield increased by 192%		Yes (30% loss)	[99]
Mechanically sorted OFMSW	Simple aeration	900 m^3 DICOM^{TM} bioreactor – Pressurized aerobic conditions alternating with loadings – 55 °C – 3 days	Full-scale 900 m^3 DICOM^{TM} bioreactor/ 55 °C – 10 days	/	0.44*	No	[100]
MSW/Landfill	Simple aeration	Column reactor $0.2m^3$ – 18.4 kg of MSW – 12 h/day aeration at 4.1 L/h – 39–42 °C – 35 days	Lab scale column reactor $0.2m^3$ / 39–42 °C – 270 days	0.042	0.102	No	[101]
MSW/Landfill	Simple aeration	Column reactor $0.02m^3$ – 2 kg of MSW – 2 h aeration at 9 L/h four times a day – 30 °C – 50 days	Lab scale column reactor $0.02m^3$ / 30 °C – 80 days	0	0.062	No	[102]
Water diluted OFMSW (1:5)	Fungal pure culture	250 mL flask – *Trichoderma viride* (1:7) – natural aeration through cotton stoppers – 25 °C – 4 days	Lab scale serum bottle batch / 52 °C – 18 days	Methane yield increased by 400%		No	[118]
OFMSW	Compost addition	1 L reactor let open ensuring surface aeration - Mature compost (1:40) – room temperature – 24 h	Lab scale 5 L fed-batch / 55 °C – 15 days SRT – pH 6.5-8	Methane yield increased by 141.6%		No	[119]

(*continued on next page*)

Table 3 (*continued*)

Feedstock	Type of aerobic pretreatment	Pretreatment conditions	AD scale / AD process conditions	Methane yield (L/g VS)		DM loss taken into account in Methane yield	References
				Control	Treatment		
WAS & primary sludge (40/60)	Simple aeration	5 L bioreactor –72 L/h continuous airflow – 100% moisture – 35°C – 2 days	Lab scale 5 L digester / 35 °C – 23 days – pH 7	0.180	0.4	/	[106]
WAS	Simple aeration	500 mL flask – micro aerobic conditions with open flask and rotating stirrers (12 rpm) – 55 °C – 12 h	Lab scale 300 mL BMP / 35 °C – 25 days – 150 rpm	Methane yield increased by 23%		/	[107]
WAS & primary sludge (70/30)	Simple aeration	2 L bioreactor – 300 L/h airflow – 55 °C – 24 h	Lab scale 7 L fed-batch / 35 °C – 19 days – pH not controlled	0.255	0.290	/	[108]

Methane yield:

* Biogas yield (L/g VS) is given instead of methane yield.

days), another study demonstrated that, due to aerobic degradation, methane production from OFMSW was 18% lower than without aerobic pretreatment [97]. On carbohydrate-rich food waste, Rafieenia et al. [98] applied even lower aeration and shorter time than previous studies (5 L/h – 24 h). If mass loss was not calculated in this article, it can be noticed that methane yield after 77 days two-stage AD was not affected by the pretreatment despite a quicker methane production. Finally, on synthetic MSW, a short-term pre-aeration was carried out before solid-state AD (SS-AD) and carbon balance was followed all along the experiments [99]. Here again, carbon loss under the form of CO_2 after 8 days of pretreatment represented 30% of the total carbon. Methane yield was highly increased (by 192% in comparison to the control) but such impressive result was due to total and initial inhibition of the AD without pre-aeration.

From lab scale experiments, it can be drawn some conclusions about application of aerobic pretreatments to OFMSW, food waste and MSW. Accelerated start-up of the AD observed in the literature was due to two effects of aeration: removal of inhibition from excess of easy degradable carbon such as VFA and degradation of proteins that release ammonia acting as a buffer. These two phenomena are both limiting acidogenesis risk and thus initial AD inhibition [98,99]. But this removal negatively impacts the final methane potential since easily accessible carbon is lost under the form of CO_2. Thus, it can be hypothesized that, for these kinds of carbohydrates-rich substrates, the quick loss of large amount of easily degradable organic matter will hardly be compensated by an increase in matter accessibility. Therefore, results on methane yield are likely to be negative even with process optimization.

What can emerge from above is that to enhance methane yield of bio-waste, two-stage digestion can be more profitable than an aerobic pretreatment. Indeed, two-stage digestion is also accelerating AD start-up without any loss of potential methane due to aerobic respiration. Despite that, several full-scale technologies have been developed using aerobic pretreatment. Their main purposes are different from methane yield enhancement. It can be distinguished two different goals of these full-scale technologies.

As for the Ducellier-Isman process, bio-waste can be aerated shortly in order to use generated heat for the subsequent SS-AD. Such technology already exists at full-scale under the trademark Smartferm® dry AD technology developed by Zero Waste Energy LLC (Lafayette, the USA). In garage set-up, 12 h forced aeration is applied to reach an OFMSW temperature of 50–55 °C and then, AD is started. This technology has been used for instance since 2014 in a 90, 000 t/year organic waste facility own by Zero Waste Energy Development Co. (San José, the USA). Similarly, a company called Anaeco (Bentley, Australia) has developed a system named DICOM™ bioconversion facility where a high biogas production for such substrates (0.44 m^3/kg VS) can be reached in a short time digestion of 15 days [100]. In a unique reactor, OFMSW is first subject to efficient aeration thanks to a patented pressure aeration method, which is applied over 4 days in order to increase temperature up to 55 °C. Then, AD is carried out in batch mode for 12 days. After AD, a post aeration step is carried out in the same digester for 5 days, which permits to obtain in a short duration (21 days) and reduced space (only one digester) a stabilized OFMSW digestate that can be directly used as organic fertilizer. A full-scale plant of 60, 000 t/year MSW, based on sorting and this technology was built in 2014 in Perth (Australia). Unfortunately, the first years of exploitation were not successful and the plant is currently stopped.

A second aim is to apply aerobic conditions in order to sort, reduce and homogenize MSW. A technology called MYT™, developed by "ZAK" (Zweckverband Abfallbehandlung Kahlenberg, a German waste managing company based in Kahlenberg), is centrally based on an aerobic mixed process. After a mechanical sorting, MSW are sent in plug-flow type reactors where they are mixed with water in aerobic conditions between 2 and 3 days at 35 °C. Subsequent solid press permits to recover a homogenous liquid rich in organic matter that can be used in AD. Liquid AD is easier to operate and volumes are reduced in comparison to SS-AD. Here, aeration and mixing permit to quickly make soluble organic matter and thus extract a large part of the potential methane from MSW that can be then easily digested. The first plant based on this technology is a 100, 000 t/year facility. It has been running in Kahlenberg (Germany) with success since 2006. As technology robustness and efficiency have been shown, it was licensed and now starts to spread internationally. For instance, at the end of 2016, Tiru, a business unit of EDF (Paris, France) opened, in the north of France, a new 100, 000 t/year waste treatment facility called TVME, which is based on this technology.

In the case of landfill MSW disposal, several types of bioreactors exist: anaerobic landfill, aerobic landfill and hybrid landfill. The latter is in the scope of the present review when aerobic conditions are applied first and then, anaerobic conditions are set up. Several lab scale studies, applying this protocol, have been carried out in order to produce faster and more methane by reducing VFA concentration and increasing pH. Recently, Cossu et al. [101] applied to MSW an alternated aeration (12 h/day) for 35 days and then AD was carried out for 270 days. AD lag phase was reduced by three as methane production started two weeks after the end of the pretreatment (50 days in total), whereas 150 days were necessary in direct AD. Besides, methane yield was increased by 142% but mass loss after aeration was not taken into account. Likewise, sequential aeration (2 h 4 times a day) of MSW for 50 days permitted to reach after a subsequent 80 days AD, a methane yield of 62 L/kg VS whereas even after 130d of anaerobic conditions, untreated MSW did not produce any methane due to acidogenesis [102]. Interestingly, in another similar experimental set-up, aeration was controlled according to oxygen consumption in order to manage mass loss during aeration. Progressive decrease in aeration permitted to reach a higher methane yield of 75 L/kg VS probably due to a lower mass loss. If methane yield was increased in both studies, applications at full-scale of this technology are unlikely due to several points. First, hybrid landfill reactors at full-scale are still very seldom due to higher operational cost and complexity. Secondly, at full-scale homogenous pressurized air injection in bioreactors is difficult and costly, hampering both good technical and financial efficiencies. Finally, concerning methane yield, if benefits on the short term are certain as AD start up at full-scale will be faster and methane production higher, it remains unclear on the long term. Indeed, landfills are operated over several years (up to 30 years), duration that lab scale cannot reproduce. Initial potential mass loss during aeration could diminish long term methane production of the landfill despite a quicker start-up. To conclude, pre-aeration and more generally combination of aerobic and anaerobic conditions is of interest in landfills to enhance site remediation [103] or shorter lifetime operation but its positive impact on long-term methane yield remains highly uncertain.

4.1.3. Sludge

Aeration pretreatment was mainly tested at lab scale to enhance WAS degradability via autohydrolysis. Combination of high temperature (up to 70 °C) and oxygen stimulates WAS endogenous hydrolytic microorganisms that release their enzymes (notably proteases) [104]. These enzymes will subsequently enhance sludge solubilization and it is accepted that materials that do not degrade under anaerobic conditions can, in this case, be degraded [105]. Besides, unlike to previous feedstocks, mass loss due to microbial respiration is not considered here as an issue as sludge volume reduction is also one of the pretreatment aims. In the literature, two set-ups to carry out sludge aeration can be distinguished: either directly in the digester under the form of aerobic conditions before AD start-up, either in a pretreatment step where (hyper-)thermophilic aerobic conditions are applied before mesophilic AD.

To illustrate the former set-up, in a same digester, a mix of WAS and primary sludge (40/60) was subject to an optimized 48 h pre-aeration with a 72 L/h airflow and mesophilic conditions [106]. Methane yield of the subsequent AD was enhanced by 210% in comparison to the blank. This was notably due to an 82% increase in soluble COD thanks both to pre-aeration and to high content of primary sludge. Concerning the latter set-up, trials using separated thermophilic aerobic reactors are conceptually close to temperature phased anaerobic digestion (TPAD) except that aerobic conditions are applied in the thermophilic reactor. Thus, the process is generally called in the literature, thermophilic aerobic digestion coupled with mesophilic anaerobic digestion (TAD-MAD). Carvajal et al. [107] applied such treatment to WAS for 12 h at lab scale. A 39% increase in organic matter solubilization was obtained and methane yield during the subsequent BMP tests was 23% higher. Jang et al. [108] also obtained positive results at lab scale by using this method on a mix of WAS and primary sludge. In this study, TAD consisted in a 1-day HRT, at 55 °C and with a forced aeration at 300 L/hour that proved to enhance both enzymatic activity (especially protease) and sludge biodegradability. After 19 days, MAD displayed a 13% increase in methane yield and a methane production rate 42% higher in comparison to the control. Recently, a comparison study between TAD, alkali as well as ultrasonic pretreatments before mesophilic sludge AD showed that TAD performed better than the two other pretreatments [109]. Besides, it can be mentioned that Dumas et al. [110] obtained a 30% higher COD degradation of WAS by using a system composed of a mesophilic anaerobic digestion reactor which was coupled in parallel with a reactor under microaerobic conditions at 65 °C (here called MAD-TAR). However, in this case, aerobic conditions were applied all along AD in the separated reactor via recirculation system and it cannot be really considered as a pretreatment but more as an inner treatment. Similarly, the recent use by Rennuit et al. [111] of TAD as inter-stage treatment of WAS appears to be promising, slightly increasing methane yield and substantially improving COD removal.

Such pretreatment may be interesting at full-scale as it requires less energy than a high temperature CambiTHP™ (Cambi) or Biothelys™ (Veolia) processes. At full-scale, a process to reduce sludge amount called Biolysis® E, based on endogenous enzyme stimulation via aerobic and thermophilic conditions, was commercialized by Ondeo-Degremont (Suez) from early 2000 [105]. However, no full-scale examples of this technology exist and it is not available on the market any more. Despite that, technologies inspired by GE Monsal process but with aerobic conditions may be developed in the future.

4.2. Aerobic pretreatment using pure culture of microorganisms

Pure culture of hydrolytic microorganisms can be used in addition to aerobic conditions in order to favour accessibility increase over mass loss. White rot fungi (WRF) in particular have drawn a lot of interest due to their ability to specifically target lignin polymers, consequently an abundant literature exists on the topic [80,112]. A few recent and selected studies using pure cultures and measuring mass loss are given in Table 3 for agricultural waste and OFMSW.

4.2.1. Agricultural waste

WRF strains that are using lignin for their growth instead of cellulose and hemicelluloses are of high interest to decrease the recalcitrance of lignocellulosic biomass while increasing the hydrolysis of carbohydrates. Therefore, an increase in biogas production of different substrates was found in several lab scale studies following WRF pretreatment. Lalak et al. [113] applied, after sterilization of tall wheat grass, a 4-week pretreatment using the WRF, *Flammulina velupites*. This pretreatment increased by 134% the methane yield of the subsequent AD. However, mass loss during the pretreatment was around 29% due to degradation of cellulose (20.5%), hemicelluloses (29%) and lignin (35.4%). Despite a higher degradation in lignin than cellulose and hemicelluloses, as mass loss is not taken account in calculation, it is unclear if the final methane yield is really improved. Similarly, Mustafa et al. [114] obtained a 120% increase in methane yield after 20 days pretreatment using the WRF *Pleurotus ostreatus*. Lignin degradation was still higher (33%) than cellulose (7%) and hemicelluloses (16%), resulting in higher structural decomposition. But mass loss, that was lower in this study (around 11%), was not taken into account leading again to an uncertain improvement. When mass loss was taken into account results on methane yield were less impressive and even negative. For instance, Rouches et al. [94] after Basidiomycetes strain screening, selected *Polyporus brumalis* BRFM 985 to pretreat wheat straw. Non-optimized 21-day pretreatment, led to an increase of 21% in methane yield with mass loss (14%) taken into account this time. Alike, a recent study including mass loss (10%) in calculations, displayed a 60% increase in methane yield of hazel branches after a 28-day pretreatment using *Ceriporiopsis subvermispora* ATCC 96608 [115]. However, identical pretreatment on acacia branches, barley straw and bagasse did not show any effect and even at some point a decrease in methane yield. For instance, bagasse had its methane yield lowered by 5%. These results can be explained both by the incapacity of the strain to efficiently degrade lignin for this substrate and by the too high mass loss. Similar results were observed on corn stover, where strains and even chopped size of the straw had an impact on pretreatment efficiency [116]. Among the three strains tested and two chopped size conditions only a treatment with *Pleurotus eryngii* at small size stover (between 0.5 and 4.5 mm) led to a 19% increase in biogas yield, all the others had lower or unchanged yields.

Once mass loss is taken into account, it is clear that positive impact of WRF pretreatment on methane yield is uncertain. Result is highly depending on feedstock, cultivation parameters (temperature, moisture and duration), nutritional supplementation and fungal strain [80,115,116]. Therefore, pretreatment design and fine optimization are required in order to obtain an increase in methane yield. Besides, one of the main drawbacks of such pretreatment apart its relative long duration is the necessity to carry out sterilization of the pretreated substrates. It is required both to ensure efficient colonization of the substrate by the selected microorganisms and to avoid consumption by endogenous microorganisms of the release sugars during pretreatment. At full-scale, sterilization is highly expensive, energy consuming and difficult to put into practice. For this reason, a full-scale application of such pretreatment does not exist yet. A possible solution to this problem would be to practice inoculum propagation, inspired by back-slopping methods of food industry. It consists of the sterilization and colonization of a small amount of substrate that is used to colonize and treat a larger amount of unsterile identical substrate. Then, this colonized material can be used as inoculum for a larger mass of the same unsterile substrate and so on and so forth. This solution was recently explored and promising results were obtained using miscanthus as feedstock [117].

4.2.2. Organic fraction of municipal solid waste

In the case of OFMSW, literature is very scarce. This is probably due, both to a low interest in hydrolytic pretreatment as OFMSW is already relatively easily biodegradable and to the fact that sterilization of OFMSW is economically unrealistic as for agricultural waste. Wagner et al. [118] applied a different strategy than sterilization at lab scale to pretreat OFMSW with *Trichoderma viride*. OFMSW was five times diluted and then waste suspension was inoculated with *T. viride* at a ratio of 1:20 v/v. Aerobic conditions were applied for 4 days at 25 °C and then AD was carried out for 18 days. Mass loss was not measured. Organic acid concentrations were increased during pretreatment leading to a 400% increase in methane yield. Despite this strong increase, OFMSW diluting and subsequent liquid AD (instead of SS-AD) can be seen as important drawbacks for scale up. Here again, no full-scale application exists as it is not economically attractive.

4.3. Aerobic pretreatment using consortia

The use of consortia or mixed cultures is a promising alternative to pure cultures due to several advantages: (1) greater quantity and variety of enzymes are produced that can act synergistically and thus enhance hydrolysis efficiency; (2) more tolerance with environment changes (pH, temperature) causing a gain in process robustness; (3) capacity to thrive and develop in unsterilized environment [16]. For these reasons, a large number of studies using consortia were carried out at lab scale. A selection is given in Table 3 where solid inoculum addition before the aerobic step can be distinguished from liquid inoculum addition.

4.3.1. Consortium addition from solid inoculum

Compost is a solid material rich in microorganisms with hydrolytic enzymes that are able to efficiently solubilize hardly biodegradable organic matter. Therefore, it can be considered as an interesting inoculum to enhance hydrolyse efficiency of an aerobic pretreatment step. At lab scale, such strategy was applied on OFMSW by Fdez-Güelfo et al. [119]. Mature compost made of OFMSW and digested sludge was mixed with fresh OFMSW at a ratio of 2.5% v/v. Then, the mixture was let for 24 h at room temperature with natural aeration. Subsequently a thermophilic 5 L fed-batch SS-AD was performed. The methane production was increased by 141% in comparison to the control and the final organic matter removal was also improved (e.g. VS removal was increased by 35%). These results demonstrate that a small addition of compost in aerobic conditions can efficiently hydrolyse and solubilize OFMSW in a short time. An alternative method was recently tested on corn straw, where Thermophilic Microaerobic Pretreatment (TMP) was combined with retted and composted corn straw as aerobic inoculum [120]. Twenty hours pretreatment at 55 °C with 5 mg of O_2 per VS of substrate initially injected led to a 21% increase in methane yield in comparison to the control. However, in this article, inoculum was mixed with corn straw at a high ratio of 700% w/w. Such amount of inoculum would be unrealistic at higher scale. According to that, the first feature of a promising aerobic solid inoculum would be to have a positive impact despite a small or reasonable quantity mixed with feedstock, such as for instance the compost used by Fdez-Güelfo et al. [119].

At full-scale, a solution based on compost addition exists for agricultural waste under the trademark Bacteriometha™ sold by a French company called Sobac (Lioujas, France). It is an additive made of compost rich in hydrolytic microorganisms. It has to be mixed with substrates (such as cow manure) between 3 and 15 days before AD in a ratio of 0.5–1 kg/m^3 of substrate. Mixture remains in aerobic conditions such as stacks, piles or open tanks. According to Sobac, biogas yield can be increased between 10% and 30% and trials on two full-scale plants displayed higher energy production and an easier mixing in the digester that ensured economic interest despite the additive cost [121].

In addition to compost, wood can also be used as inoculum especially for fungi, but this research track remains unexplored. Fungal mash is another option as already seen before [38].

4.3.2. Consortium addition from liquid inoculum

Other types of aerobic consortia under liquid form have been used to pretreat lignocellulosic feedstocks. They can be aerobic sludge or a solution containing a designed or isolated consortium. In the former case, Mshandete et al. [122] used an activated sludge mixed culture as inoculum for an aerobic pretreatment of sisal pulp. Inoculum was brought in large quantity to the system in comparison to sisal pulp with a ratio of 14:1 v/v. After optimization, surface aeration for 9 h at 37 °C appeared to be the most efficient as longer duration did not lead to higher methane yield. After AD, methane yield was enhanced by 26% in comparison to the control. High VFA concentration and high activity of hydrolytic enzymes were obtained at the end of the short pretreatment that can explain this positive result. Similarly, Zhou et al. [123] mixed rice straw with aerobic sludge supernatant and applied an optimized 2 days continuous aeration (30 L/h/kg DM) pretreatment. Subsequent BMP showed a 16% increase in methane yield compared to the control.

Several hydrolytic consortia have been constructed and tested at lab scale. It can be noticed that the method, often used to select efficient hydrolytic microorganisms, is based on the speed at which a filter paper is degraded; the faster the degradation is, the higher is the hydrolytic capacity of the isolated consortium. Zhang et al. [124] designed from soil samples a microbial consortium with high cellulose degradation ability. Then, the consortium was applied to cassava residues for 12 h in aerobic conditions at 55 °C. Subsequent AD of the cassava residues displayed a 97% higher methane yield than the control. Another hydrolytic consortium which is called MC1 was constructed from compost in 2002 and since then, has been regularly used to pretreat agricultural waste. For instance, it was recently used in the aerobic 5-day pretreatment of non-sterile rotten silage maize straw [125]. Following that, biogas yield was enhanced by 75% compared to the control. Rotten sawdust was used to screen microorganisms displaying both high cellulolytic and ligninolytic activities [126]. After isolation and identification, selected microorganisms were gathered to form a consortium displaying high lignocellulosic degradation activity. Its application for 10 days as a pretreatment to sawdust improved methane yield of the subsequent AD by 73%. Finally, Zhong et al. [127] designed a microbial hydrolytic consortium from compost and cow manure. It was used to pretreat wheat straw for 3 days in aerobic conditions and led to a methane yield 80% higher than control in BMP tests.

Enhancements of methane yield between 16% and 97% are reported herein above. However, these very positive results have to be put into perspectives. First, mass loss was not taken into account in calculations to obtain these results, even when it was measured. It can be assumed that for short duration (hours) it remains too low to negatively impact results. But when it comes to several days, it is likely that the calculated increase in methane yield will be lower; for instance, 3 days already led to a 25% mass loss under CO_2 form in the case of Zhong et al. [127]. Secondly, mainly BMP or small batches were performed, which limits lab scale evaluation of such pretreatment as it will probably be used in continuous or fed-batch mode at full-scale. Thirdly, to obtain positive results, this pretreatment has to be strongly optimized. CO_2 emission, VFA concentration, s-COD and in particular lignin degradation are criteria that can be used to determine the optimum duration beyond which enhancement will be lower or even non-existent.

At full-scale, a semi-aerobic hydrolytic pretreatment was developed by Bionova Biogas GmbH (Wernsdorf, Germany) for liquid CSTR agricultural biogas plants. It consists in a closed vessel, where air is injected uniformly through feedstocks in a liquid state. HRT is short (order of days in function of the plant) and a liquid aerobic inoculum is added once at operational start. It is dedicated to lignocellulose rich substrates to enhance their degradation before to enter the digester. According to the supplier up to 20% extra biogas can be obtained. Aeration is performed here using a compressor which is energy consuming. This pretreatment is currently implanted mainly in Germany and France in more than ten plants.

4.4. Assessment of aerobic pretreatments

Aerobic pretreatments are interesting for feedstocks that are difficult to degrade such as lignocellulosic ones or WAS. For these substrates, mass loss during aeration can be compensated by an increase in accessibility or matter degradability. But this is almost never happening for easy to degrade feedstocks, limiting therefore aerobic pretreatments interest in this case. Consortia and simple aeration are the most promising due to an easier and cheaper implementation at full-scale in comparison to pure cultures. Finally, few products based on aerobic pretreatments already exist for agricultural feedstocks but they are not yet widespread. Simple aeration is also likely to be already used in some agricultural plants but feedback on such trials are from our knowledge unknown.

5. Combination of pretreatments

As each type of pretreatment has its own functioning mode and as pretreatment effects are often complementary, an option to obtain even more efficient pretreatment is to combine them [128]. However, it is important to underline that if very interesting results can be obtained at lab scale, additional costs due to combination may be economically unacceptable at full-scale. Therefore, fine economic analysis comparing gain and cost should be carried out before any scale up. Some recent examples of literature on this topic will be given herein below and gathered in Table 4. Additionally, Sindhu et al. [129] reported earlier examples of biological pretreatment combinations for lignocellulosic feedstocks.

Biological pretreatments can be combined to keep low energy demand features. Thomsen et al. [130] applied first an ensiling step to wheat straw with *Lactobacillus buchneri* followed by a washing step and finally a WRF treatment with *Ceriporiopsis Subvermispora* before AD in BMP tests. Here, ensiling and washing were used as a conditioning method that eliminates waxes, fats and toxic compounds, thus facilitating subsequent feedstock colonization by *C. Subvermispora*. Only a minor 5% mass loss was observed after the combined pretreatment but it was not taken into account in calculation. If methane production rate was faster, methane yield did not significantly increase after this combined pretreatment. Here, the use of ligninolytic consortia instead of pure culture might be an interesting alternative to obtain an increase in methane yield. Another example at lab scale of combination of biological pretreatments was carried out on agave bagasse [131]. After an enzymatic treatment, hydrolysate was anaerobically digested in a two-stage process. In comparison to a single-stage process, energy recovery obtained from the enzymatic hydrolysate was 3.3 fold higher due to hydrogen production and no inhibition during methanogenesis step (neither VFA nor LCFA accumulation). This result is particularly interesting as it shows potential advantages of using two-stage AD for lignocellulosic substrates after their hydrolysis.

Biological pretreatments can also be combined with mechanical, chemical or thermal pretreatments to ensure higher methane yields. Wheat straw grinding followed by a 180 days ensiling showed a 36% increase in methane yield whereas grinding only led to a 26% increase [132]. Nevertheless this strong increase has to be nuanced as mass loss during ensiling was not taken into account in this study. Mustafa et al. [133] applied on rice straw a 30-day WRF pretreatment using *Pleurotus ostreatus* that was followed by a milling step. Despite a 12% mass loss that was not taken into account in subsequent calculations, the methane yield was increased. Indeed, 500 mL SS-AD displayed a methane yield 165% higher in comparison to the control. Alkaline treatments were applied in combination with enzyme or WRF pretreatments. Alexandropoulou et al. [134] applied the WRF *Abortiporus biennis* for 30 days to willow sawdust and then carried out a 24-h NaOH alkaline treatment. Here, mass loss during WRF was taken into account and despite a 17% DM loss, subsequent BMP displayed a 115% increase in methane yield due to high lignin removal during pretreatment. Similarly, NaOH pretreatment was carried out on miscanthus followed this time by an enzymatic pretreatment with cellulase and cellobiase [135]. Delignification and higher accessibility to cellulose were observed again, as well as, a 94% methane yield enhancement in comparison to sole enzymatic pretreatment. Finally, thermal pretreatment was applied before two-stage AD at lab scale on sugarcane bagasse [136] or on MSW [137]. Autohydrolysis of bagasse was carried out at 182 °C for 40 min that released sugars but also inhibitory phenols and furans. Here, the interest of the first AD stage was to biodetoxify the hydrolysate, as acidogenic microorganisms appeared to be able to decrease the concentration of toxic compounds for methanogenic microorganisms. This led to a higher energy yield in comparison to a one-stage process, as methanogenesis step was less inhibited. In the later paper, Li et al. applied a hydrothermal pretreatment (HTP) to MSW at 170 °C for 60 min. Subsequent, hydrolysis step of the AD had here the advantage to cope with recalcitrant molecules formed during thermal pretreatment (here melanoidins) and thus enhance methanogenesis step. In comparison to a single step AD of MSW and by taking into account the

Table 4
Different combinations of biological pretreatment strategies adopted in function of feedstocks.

Feedstock	Strategy*	Results	References
Wheat straw	Ensiling/washing + WRF	No significant increase in methane yield / Increase in methane production rate	[130]
Agave bagasse	Enzyme + 2-stage AD	3.3 fold higher energy recovery vs. Enzyme + 1-step AD	[131]
Wheat straw	Grinding + ensiling	36% increase in methane yield vs. untreated	[132]
Rice Straw	WRF + milling	165% increase in methane yield vs. untreated	[133]
Willow Sawdust	WRF + alkaline (NaOH)	115% increase in methane yield vs. untreated	[134]
Miscanthus	Alkaline (NaOH) + enzyme	94% increase in methane yield vs. enzyme treatment	[135]
Sugarcane bagasse	Thermal + 2-stage AD	14 times higher methane yield vs. thermal + 1 step AD	[136]
MSW	HTP + 2-stage AD	Higher mass reduction and 97.4% increase in energy output (HTP energy comprised) vs. 1 step AD	[137]
Miscanthus/Hemp straw	Thermal/chemical “like” + enzyme (laccase)	No significant increase in methane yield / Increase in methane production rate (reduced inhibition)	[138]

* Treatments are given by order of applications.

energy needed for HTP, the net energy output was almost two-fold increased. This was due to a combination of a slightly higher methane yield and especially a reduced amount of waste to dry and handle after AD. Likewise a detoxifying role was recently identified by Schroyen et al. [138], where laccase enzymes were used to remove high concentration of AD inhibiting phenolic compounds. A 24 h laccase treatment step was applied to miscanthus and hemp straw supplemented with different concentrations of p-Coumaric acid (up to 2000 mg/L), that simulated phenolic compounds that could be released following a harsh pretreatment (thermal or chemical). Interestingly, laccases were able to reduce p-Coumaric acid concentration and therefore improve initial hydrolysis rate of subsequent AD.

It has been shown that the use of biological pretreatments in combination with other pretreatments displays very interesting and promising results at lab scale. However, from our knowledge, they are not yet applied at full-scale. Besides, combination of pretreatments is almost always applied to lignocellulosic substrates in literature. Work on WAS or MSW may also be promising.

6. Guidelines on the selection of a biological pretreatment for a given feedstock

Biological pretreatments, as for other types of pretreatment in general, are feedstock dependent. In function of the feedstock features, their impact can be very variable, ranging from positive to negative effects on the subsequent AD. Therefore, selection of a biological pretreatment for a given feedstock has to be done cautiously. Recommendations will mainly be based on Table 5 that is gathering the effect of each pretreatment on methane yield in function of the feedstock. Besides, even if they were not reviewed in detail in this article, it can be underlined that additional potential positive effects, different from methane yield enhancement, can be obtained: an increase AD rate, the use of new or cheaper substrates, limitations in AD inhibitors concentration and reduction in viscosity as well as in the energy requirement for plant operations (mixing, floating layer). These additional specificities are given for each biological pretreatment in Table 6. As already mentioned, a full economic assessment of a biological pretreatment for a given feedstock has to take into account not only methane yield increase but also these additional advantages that can be observed at full-scale.

Enzymatic pretreatments can be interesting in the case of agricultural waste, MSW landfill and sludge. Agricultural waste already have full-scale commercialized carbohydrases cocktails displaying positive effects on methane yield. Application of carbohydrases and lignin-modifying enzymes in landfill lixiviate recirculation system is another promising topic still at research scale. For sludge digestion, application of enzymes displayed positive results at lab scale (notably proteases and carbohydrases). However their short lifespan after addition strongly hampers their full-scale application. For bio-waste that can be considered as easy to degrade substrates, enzyme application appears not to necessarily enhance methane yield but often accelerates hydrolyse kinetic that can generate acidification problems. Therefore, enzyme application for bio-waste is not recommended and commercial dedicated products do not exist.

Anaerobic pretreatments under the form of two-stage process are mainly recommended for bio-waste and WAS. For these feedstocks, full-scale technologies exist and are displaying higher methane yield than single stage process. In the case of bio-waste, this is due to a better control of the acidification risk, while in the case of WAS, this is due to autohydrolysis via endogenous enzyme stimulation. At lab scale, TPAD was identified as the most promising way to proceed due to additional benefits coming from thermophilic conditions. Full-scale processes may appear in the near future. Concerning lignocellulosic substrates, a basic two-stage process does not have much interest as anaerobic conditions will not favour lignocellulosic degradation. Enhanced two-stage process, notably via specific hydrolytic consortia, was identified as a promising anaerobic way to enhance methane yield at lab scale of such feedstock. Ensiling for certain lignocellulosic feedstocks and with optimized conditions also appears as a way to slightly enhance biogas production.

Aerobic pretreatments are mainly recommended for feedstocks in the case where either gain in accessibility will be superior to mass loss or either mass loss is not considered as a problem as waste volume reduction is sought. Following these two observations, it can be applied to lignocellulosic substrates and WAS. The former has already several full-scale applications. Indeed, it is relatively easy to put into practice and very positive results on methane yield can be obtained after optimization to limit mass loss, as lignin and crystalline cellulose are degraded. For the latter, aeration is stimulating endogenous enzymes that enhance sludge solubilization. Full-scale application does not currently exist on the market. For landfill MSW, aerobic set-up does not clearly enhance methane yield and full-scale applications remain scarce. Finally, in the case of bio-waste or easily biodegradable agricultural feedstocks, the mass loss will not be compensated by a gain in accessibility. Therefore, simple aeration pretreatment will definitely not be recommended. Full-scale applications exist but they have other aims such as for instance waste self-heating. Nevertheless, it can be noted that compost addition combined with aerobic treatment enhanced OFMSW methane yield. Therefore, aerobic consortium addition remains an option to explore for OFMSW due to cardboard, paper and other recalcitrant components that are making this feedstock more difficult to degrade than FW and easily biodegradable agricultural substrates.

In Table 5, it is also indicated that some areas remain uncovered by research. In some cases, research will not be applicable such as for instance ensiling for bio-waste. However, other areas were identified as potentially applicable. Among them, distinction was made between the ones in which positive results on the methane yield can be expected and the ones that potentially will provide negative results on the methane yield. They can be used as options for future research and development

Table 5
Biological pretreatments: Effect on biogas and methane yield and *existing full-scale technology* in function of the feedstock.

		Agricultural waste		OFMSW	FW	MSW Landfill	Sludge (WAS)
		Lignocellulose rich	Easily biodegradable				
Enzymes	Protease	--	▨	-/+	-/+	🟩	++
	Lipase	/	▨	-/+	-/+	🟩	-/+
	Carbohydrase	++ *Methaplus® – Optimash®*	+ *Methaplus® – Optimash®*	-/+	-/+	++	++
	Lignin-modifying	++	▨	🟩	▨	++	▨
Anaerobic	Two-Stage	-/+	+ *Bioplex process*	+ *Gicon® - Biomet®*	+ *Gicon® - Biomet®*	/	++ *Monsal™ ADT*
	Enhanced two-stage	+	🟩	🟩	🟩	/	🟩
	Ensiling	+	🟩	/	/	/	/
Aerobic	Simple aeration	++ *Pile composting*	▨	-	--	-/+	++
	Pure culture	+++	▨	+	▨	/	/
	Consortia (solid or liquid)	+++ *Methalyse® - Bacteriometha®*	▨	+	▨	/	🟩

+/++/+++ : Lab or pilot scale positive results -/-- : Lab scale negative results ☐ : Positive results with *existing full-scale technologies*

🟩 : Unexplored field with expected positive results ▨ : Unexplored field with expected negative results / : Not applicable

Table 6
General features of biological pretreatments.

Type of biological pretreatment	Enzyme	Anaerobic	Aerobic
Advantages	Low energy demand Fast process No matter loss Scalability Lignin breakdown Technology readily available Application versatility	Low energy demand No matter loss Limit acidogenesis risk Potential H_2 production (Pathogens removal) Technology readily available	Low energy demand Potentially low-cost Lignin breakdown Scalability
Disadvantages	Current high cost Enzyme lifespan Continuous addition needed Moderate activity/Inhibition	No lignin breakdown Cost for second digester Higher complexity	Matter loss Relatively high exposure time Energy if forced aeration Sterilization can be required Process control Developing technology
Other potential positive effects than methane yield increase	Increase AD rate Use of new/local feedstock Reduce energy need (mixing)	Increase AD rate Limit AD inhibitors	Increase AD rate Use of new/local feedstock Reduce energy need (mixing)
Technological readiness level (from 1 to 9)	7–8	7–8 for two-stage	4–6

projects in this field.

7. General assessment on biological pretreatments

To assess biological pretreatments, the following criteria can be given for a successful pretreatment [139]: (1) low energy input; (2) avoid carbohydrates loss; (3) use minimal and inexpensive chemicals and/or water; (4) avoid expensive pretreatment devices; (5) avoid AD inhibitors formation; (6) avoid the need for waste disposal; (7) be flexible with respect to the feedstock; (8) be environmentally friendly; (9) be cost-effective. These can be confronted with advantages and disadvantages of each biological pretreatment gathered in Table 6. All the biological pretreatments are meeting conditions (1), (3), (6) and (8). Enzymatic pretreatments also meet conditions (2) and (4) but they can generate AD inhibitors especially on lignocellulosic substrates with lignin-modifying enzymes (such as phenols), they have a low flexibility due to the required process optimization and lastly, enzymes high prices are limiting their cost effectiveness. Anaerobic pretreatments with two-stage process are meeting conditions (2), (5) and (7). Nevertheless, they require expensive additional reactor(s) that is impacting negatively cost effectiveness. Finally, aerobic pretreatments can meet conditions (5) and (9). However, the required fine-tuning for a given substrate limits the flexibility of the method. Additionally, carbohydrates loss is difficult to avoid.

Biological pretreatments can also be assessed through the technological readiness level (TRL) scale that goes from 1 (idea) to 9 (full-scale technology widely used). Enzymes and two-stage process are relatively mature technologies, displaying positive results and available at full-scale under the form of several commercialized products. However, their current costs hamper their wide adoption at full-scale. Therefore, their TRL is at 7–8. Aerobic pretreatments, despite existing full-scale technologies, are rather at a development stage. Process optimization is still required for a given substrate to ensure a low mass loss. Besides, in the case of aerobic consortia use, their selection and production are still made at lab scale. Thus, it can be considered that TRL for these pretreatments is comprised between 4 and 6.

From this general assessment, it is clear that biological pretreatments have strong advantages that deserve to work further on the reduction of their current drawbacks. By doing so, cost effectiveness of these technologies may be enhanced and full-scale applications may spread more widely.

8. Conclusions

Biological pretreatments from lab to full-scale were described and evaluated in this review for the following feedstocks: agricultural waste, bio-waste, MSW and sludge. It appears that for a given feedstock, biological pretreatment has to be carefully selected. Here, as for pretreatments in general, there is no standard biological solution for all feedstocks. Therefore, selection guidelines were provided in this review. When appropriate biological pretreatment has been chosen for a given feedstock and its application optimized, subsequent AD can be enhanced through notably its methane yield and AD rate. Besides, their low energy demand feature is another major advantage. If, full-scale applications are not yet widely spread due to mitigate cost effectiveness (enzymes and two-stage) or maturing process (aerobic), biological pretreatments remain a promising field due to aforementioned inherent advantages. Future research and development in this field may permit to develop efficient, cost-competitive and environmentally friendly biological pretreatments.

Acknowledgment

National Research and Technology Association (ANRT) is gratefully acknowledged for the PhD grant allocated to Ulysse Brémond (reference CIFRE No. 2016/0617).

References

[1] ADEME. Avis de l'ADEME Méthanisation; 2016.

[2] Braun R, Weiland P, Wellinger A. Biogas from energy crop digestion. IEA Bioenergy Task; 2008.

[3] Appel F, Ostermeyer-Wiethaup A, Balmann A. Effects of the German Renewable Energy Act on structural change in Agriculture – The case of biogas. Util Policy 2015;41:172–82. http://dx.doi.org/10.1016/j.jup.2016.02.013.

[4] Markard J, Wirth S, Truffer B. Institutional dynamics and technology legitimacy – A framework and a case study on biogas technology. Res Policy 2016;45:330–44. http://dx.doi.org/10.1016/j.respol.2015.10.009.

[5] Lora Grando R, de Souza Antune AM, da Fonseca FV, Sánchez A, Barrena R, Font X. Technology overview of biogas production in anaerobic digestion plants: a European evaluation of research and development. Renew Sustain Energy Rev 2017;80:44–53. http://dx.doi.org/10.1016/j.rser.2017.05.079.

[6] Paudel SR, Banjara SP, Choi OK, Park KY, Kim YM, Lee JW. Pretreatment of agricultural biomass for anaerobic digestion: current state and challenges. Bioresour Technol 2017;245:1194–205. http://dx.doi.org/10.1016/j.biortech.2017.08.182.

[7] Mao C, Feng Y, Wang X, Ren G. Review on research achievements of biogas from anaerobic digestion. Renew Sustain Energy Rev 2015;45:540–55. http://dx.doi.org/10.1016/j.rser.2015.02.032.

[8] Merlin Christy P, Gopinath LR, Divya D. A review on anaerobic decomposition and enhancement of biogas production through enzymes and microorganisms. Renew Sustain Energy Rev 2014;34:167–73. http://dx.doi.org/10.1016/j.rser.2014.03.010.

[9] Fisgativa H, Tremier A, Dabert P. Characterizing the variability of food waste quality: a need for efficient valorisation through anaerobic digestion. Waste Manag 2016;50:264–74. http://dx.doi.org/10.1016/j.wasman.2016.01.041.

[10] Donoso-Bravo A, García G, Pérez-Elvira S, Fdz-Polanco F. Initial rates technique as a procedure to predict the anaerobic digester operation. Biochem Eng J 2011;53:275–80. http://dx.doi.org/10.1016/j.bej.2010.11.007.

[11] Sambusiti C, Ficara E, Malpei F, Steyer JP, Carrère H. Effect of sodium hydroxide pretreatment on physical, chemical characteristics and methane production of five varieties of sorghum. Energy 2013;55:449–56. http://dx.doi.org/10.1016/j.energy.2013.04.025.

[12] Carrere H, Antonopoulou G, Affes R, Passos F, Battimelli A, Lyberatos G, et al. Review of feedstock pretreatment strategies for improved anaerobic digestion: from lab-scale research to full-scale application. Bioresour Technol 2016;199:386–97. http://dx.doi.org/10.1016/j.biortech.2015.09.007.

[13] Kim JS, Lee YY, Kim TH. A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. Bioresour Technol 2016;199:42–8. http://dx.doi.org/10.1016/j.biortech.2015.08.085.

[14] Shrestha S, Fonoll X, Khanal SK, Raskin L. Biological strategies for enhanced hydrolysis of lignocellulosic biomass during anaerobic digestion: current status and future perspectives. Bioresour Technol 2017;245:1245–57. http://dx.doi.org/10.1016/j.biortech.2017.08.089.

[15] Romero-Güiza MS, Vila J, Mata-Alvarez J, Chimenos JM, Astals S. The role of additives on anaerobic digestion: a review. Renew Sustain Energy Rev 2016;58:1486–99. http://dx.doi.org/10.1016/j.rser.2015.12.094.

[16] Wei S. The application of biotechnology on the enhancing of biogas production from lignocellulosic waste. Appl Microbiol Biotechnol 2016;100:9821–36. http://dx.doi.org/10.1007/s00253-016-7926-5.

[17] Divya D, Gopinath LR, Merlin Christy P. A review on current aspects and diverse prospects for enhancing biogas production in sustainable means. Renew Sustain Energy Rev 2015;42:690–9. http://dx.doi.org/10.1016/j.rser.2014.10.055.

[18] Müller L, Kretzschmar J, Pröter J, Liebetrau J, Nelles M, Scholwin F. Does the addition of proteases affect the biogas yield from organic material in anaerobic digestion? Bioresour Technol 2016;203:267–71. http://dx.doi.org/10.1016/j.biortech.2015.12.038.

[19] Wang X, Li Z, Zhou X, Wang Q, Wu Y, Saino M, et al. Study on the bio-methane yield and microbial community structure in enzyme enhanced anaerobic co-digestion of cow manure and corn straw. Bioresour Technol 2016;219:150–7. http://dx.doi.org/10.1016/j.biortech.2016.07.116.

[20] Frigon JC, Mehta P, Guiot SR. Impact of mechanical, chemical and enzymatic pretreatments on the methane yield from the anaerobic digestion of switchgrass. Biomass- Bioenergy 2012;36:1–11. http://dx.doi.org/10.1016/j.biombioe.2011.02.013.

[21] Schroyen M, Vervaeren H, Van Hulle SWH, Raes K. Impact of enzymatic pretreatment on corn stover degradation and biogas production. Bioresour Technol 2014;173:59–66. http://dx.doi.org/10.1016/j.biortech.2014.09.030.

[22] Schroyen M, Vervaeren H, Vandepitte H, Van Hulle SWH, Raes K. Effect of enzymatic pretreatment of various lignocellulosic substrates on production of phenolic compounds and biomethane potential. Bioresour Technol 2015;192:696–702. http://dx.doi.org/10.1016/j.biortech.2015.06.051.

[23] Brijwani K, Rigdon A, Vadlani PV. Fungal laccases: production, function, and applications in food processing. Enzym Res 2010;2010:1–10. http://dx.doi.org/10.4061/2010/149748.

[24] Monlau F, Barakat A, Trably E, Dumas C, Steyer J-P, Carrère H. Lignocellulosic materials into biohydrogen and biomethane: impact of structural features and pretreatment. Crit Rev Environ Sci Technol 2013;43:260–322. http://dx.doi.org/10.1080/10643389.2011.604258.

[25] Romano RT, Zhang R, Teter S, McGarvey JA. The effect of enzyme addition on anaerobic digestion of Jose Tall Wheat Grass. Bioresour Technol 2009;100:4564–71. http://dx.doi.org/10.1016/j.biortech.2008.12.065.

[26] Sutaryo S, Ward AJ, Moller HB. The effect of mixed-enzyme addition in anaerobic digestion on methane yield of dairy cattle manure. Environ Technol 2014;35:2476–82. http://dx.doi.org/10.1080/09593330.2014.911356.

[27] Pérez-Rodríguez N, García-bernet D, Domínguez JM. Extrusion and enzymatic hydrolysis as pretreatments on corn cob for biogas production. Renew Energy 2017;107:597–603. http://dx.doi.org/10.1016/j.renene.2017.02.030.

[28] Ziemiński K, Kowalska-Wentel M. Effect of enzymatic pretreatment on anaerobic co-digestion of sugar beet pulp silage and vinasse. Bioresour Technol 2015;180:274–80. http://dx.doi.org/10.1016/j.biortech.2014.12.035.

[29] Gerhardt M, Pelenc V, Bäuml M. Application of hydrolytic enzymes in the agricultural biogas production: results from practical applications in Germany. Biotechnol J 2007;2:1481–4. http://dx.doi.org/10.1002/biot.200700220.

[30] Sambusiti C, Monlau F, Ficara E, Musatti A, Rollini M, Barakat A, et al. Comparison of various post-treatments for recovering methane from agricultural digestate. Fuel Process Technol 2015;137:359–65. http://dx.doi.org/10.1016/j.fuproc.2015.04.028.

[31] Biofuels DA. Enzyme Products for Biogas Production – Solutions for anaerobic digesters; 2016. ⟨http://www.dupont.com/content/dam/dupont/products-and-services/industrial-biotechnology/documents/DuPont-BiogasEnzymes-brochure-web-EN.pdf⟩ [accessed 1 April 2017].

[32] Demeter H2020 project. 2016. ⟨http://www.demeter-eu-project.eu/⟩.

[33] Schimpf U, Hanreich A, Mähnert P, Unmack T, Junne S, Renpenning J, et al. Improving the efficiency of large-scale biogas processes: pectinolytic enzymes accelerate the lignocellulose degradation. J Sustain Energy Environ 2013;4:53–60.

[34] Parawira W. Enzyme research and applications in biotechnological intensification of biogas production. Crit Rev Biotechnol 2012;32:172–86. http://dx.doi.org/10.3109/07388551.2011.595384.

[35] Capson-Tojo G, Rouez M, Crest M, Steyer J-P, Delgenès J-P, Escudié R. Food waste valorization via anaerobic processes: a review. Rev Environ Sci Biotechnol 2016;15:499–547. http://dx.doi.org/10.1007/s11157-016-9405-y.

[36] Karthikeyan OP, Trably E, Mehariya S, Wong JWC, Carrere H. Pretreatment of food waste for methane and hydrogen recovery: a review. Bioresour Technol 2018;249:1025–39. http://dx.doi.org/10.1016/j.biortech.2017.09.105.

[37] Moon HC, Song IS. Enzymatic hydrolysis of food waste and methane production using UASB bioreactor. Int J Green Energy 2011;8:37–41. http://dx.doi.org/10.

1080/15435075.2011.557845.

[38] Uçkun Kiran E, Trzcinski AP, Liu Y. Enhancing the hydrolysis and methane production potential of mixed food waste by an effective enzymatic pretreatment. Bioresour Technol 2015;183:47–52. http://dx.doi.org/10.1016/j.biortech.2015.02.033.

[39] Ariunbaatar J, Panico A, Esposito G, Pirozzi F, Lens PNL. Pretreatment methods to enhance anaerobic digestion of organic solid waste. Appl Energy 2014;123:143–56. http://dx.doi.org/10.1016/j.apenergy.2014.02.035.

[40] Cesaro A, Belgiorno V. Pretreatment methods to improve anaerobic biodegradability of organic municipal solid waste fractions. Chem Eng J 2014;240:24–37. http://dx.doi.org/10.1016/j.cej.2013.11.055.

[41] Jensen JW, Felby C, Jørgensen H, Rønsch GØ, Nørholm ND. Enzymatic processing of municipal solid waste. Waste Manag 2010;30:2497–503. http://dx.doi.org/10.1016/j.wasman.2010.07.009.

[42] Jensen JW, Ronsch GØ, Antonsen SB. Methods of processing municipal solid waste (MSW) using concurrent enzymatic hydrolysis and microbial fermentation. WO2013185777 A1; 2013.

[43] Soerensen HR, Rosgaard L, Nielsen HB, Baekgaard L, Wawrzynczyk J. Solubilization of MSW with blend enzymes. WO2016030472 A1; 2016.

[44] Ronsch GØ, Jensen JW, Antonsen SB. Methods of processing municipal solid waste (MSW) using microbial hydrolysis and fermentation. WO2014198274 A1; 2014.

[45] Frank RR, Davies S, Wagland ST, Villa R, Trois C, Coulon F. Evaluating leachate recirculation with cellulase addition to enhance waste biostabilisation and landfill gas production. Waste Manag 2016;55:61–70. http://dx.doi.org/10.1016/j.wasman.2016.06.038.

[46] Hettiaratchi JPA, Jayasinghe PA, Bartholameuz EM, Kumar S. Waste degradation and gas production with enzymatic enhancement in anaerobic and aerobic landfill bioreactors. Bioresour Technol 2014;159:433–6. http://dx.doi.org/10.1016/j.biortech.2014.03.026.

[47] Yin Y, Liu YJ, Meng SJ, Kiran EU, Liu Y. Enzymatic pretreatment of activated sludge, food waste and their mixture for enhanced bioenergy recovery and waste volume reduction via anaerobic digestion. Appl Energy 2016;179:1131–7. http://dx.doi.org/10.1016/j.apenergy.2016.07.083.

[48] Yang Q, Luo K, Li X ming, Wang D bo, Zheng W, Zeng G ming, et al. Enhanced efficiency of biological excess sludge hydrolysis under anaerobic digestion by additional enzymes. Bioresour Technol 2010;101:2924–30. http://dx.doi.org/10.1016/j.biortech.2009.11.012.

[49] Yu S, Zhang G, Li J, Zhao Z, Kang X. Effect of endogenous hydrolytic enzymes pretreatment on the anaerobic digestion of sludge. Bioresour Technol 2013;146:758–61. http://dx.doi.org/10.1016/j.biortech.2013.07.087.

[50] Radermacher H, Zobel T, Pascik IKK. Enzyme supported digestion of municipal sludge at the wastewater treatment plant Aachen-Soers. 2nd International Symp. Anaerob. Dig. Solid Waste, Barcelona, 1999, p. 356–360.

[51] Odnell A, Recktenwald M, Stensén K, Jonsson BH, Karlsson M. Activity, lifetime and effect of hydrolytic enzymes for enhanced biogas production from sludge anaerobic digestion. Water Res 2016;103:462–71. http://dx.doi.org/10.1016/j.watres.2016.07.064.

[52] Donoso-Bravo A, Fdz-Polanco M. Anaerobic co-digestion of sewage sludge and grease trap: assessment of enzyme addition. Process Biochem 2013;48:936–40. http://dx.doi.org/10.1016/j.procbio.2013.04.005.

[53] Mansour A, Arnaud T. Method for continuous treatment of water containing organic matter by enzyme treatment. US9249037B2; 2016.

[54] Arun C, Sivashanmugam P. Solubilization of waste activated sludge using a garbage enzyme produced from different pre- consumer organic waste. RSC Adv 2015;5:51421–7. http://dx.doi.org/10.1039/C5RA07959D.

[55] Speda J, Johansson MA, Odnell A, Karlsson M. Enhanced biomethane production rate and yield from lignocellulosic ensiled forage ley by in situ anaerobic digestion treatment with endogenous cellulolytic enzymes. Biotechnol Biofuels 2017;10:1–13. http://dx.doi.org/10.1186/s13068-017-0814-0.

[56] Montgomery LFR, Bochmann G. Pretreatment of feedstock for enhanced biogas production; 2014.

[57] Lindner J, Zielonka S, Oechsner H, Lemmer A. Is the continuous two-stage anaerobic digestion process well suited for all substrates? Bioresour Technol 2016;200:470–6. http://dx.doi.org/10.1016/j.biortech.2015.10.052.

[58] Grimberg SJ, Hilderbrandt D, Kinnunen M, Rogers S. Anaerobic digestion of food waste through the operation of a mesophilic two-phase pilot scale digester – Assessment of variable loadings on system performance. Bioresour Technol 2015;178:226–9. http://dx.doi.org/10.1016/j.biortech.2014.09.001.

[59] Cavinato C, Giuliano A, Bolzonella D, Pavan P, Cecchi F. Bio-hythane production from food waste by dark fermentation coupled with anaerobic digestion process: a long-term pilot scale experience. Int J Hydrog Energy 2012;37:11549–55. http://dx.doi.org/10.1016/j.ijhydene.2012.03.065.

[60] Gioannis G De, Muntoni A, Polettini A, Pomi R, Spiga D. Energy recovery from one- and two-stage anaerobic digestion of food waste. Waste Manag 2017;68:595–602. http://dx.doi.org/10.1016/j.wasman.2017.06.013.

[61] Sen B, Aravind J, Kanmani P, Lay CH. State of the art and future concept of food waste fermentation to bioenergy. Renew Sustain Energy Rev 2016;53:547–57. http://dx.doi.org/10.1016/j.rser.2015.08.065.

[62] Fernández-rodríguez J, Pérez M, Romero LI. Semicontinuous Temperature-phased anaerobic digestion (TPAD) of organic fraction of municipal solid waste (OFMSW). Comparison with single-stage processes. Chem Eng J 2016;285:409–16. http://dx.doi.org/10.1016/j.cej.2015.10.027.

[63] Zhen G, Lu X, Kato H, Zhao Y, Li YY. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: current advances, full-scale application and future perspectives. Renew Sustain Energy Rev 2017;69:559–77. http://dx.doi.org/10.1016/j.rser.2016.11.187.

[64] Leite WRM, Gottardo M, Pavan P, Belli Filho P, Bolzonella D. Performance and energy aspects of single and two phase thermophilic anaerobic digestion of waste activated sludge. Renew Energy 2016;86:1324–31. http://dx.doi.org/10.1016/j.renene.2015.09.069.

[65] Negral L, Carro A, Castrillón L, Marañón E, Fernández S. Inverted phase fermentation as a pretreatment for anaerobic digestion of cattle manure and sewage sludge. J Environ Manag 2017;203:741–4. http://dx.doi.org/10.1016/j.jenvman.2016.08.035.

[66] Hacking R. Achieving energy neutral wastewater treatment with biological hydrolysis. Environ Sci Eng Mag 2016:45–7.

[67] Ding HH, Chang S, Liu Y. Biological hydrolysis pretreatment on secondary sludge: enhancement of anaerobic digestion and mechanism study. Bioresour Technol 2017;244:989–95. http://dx.doi.org/10.1016/j.biortech.2017.08.064.

[68] Sauer M, Marx H, Mattanovich D. From rumen to industry. Microb Cell Fact 2012;11:121. http://dx.doi.org/10.1186/1475-2859-11-121.

[69] Deng Y, Huang Z, Ruan W, Zhao M, Miao H, Ren H. Co-inoculation of cellulolytic rumen bacteria with methanogenic sludge to enhance methanogenesis of rice straw. Int Biodeterior Biodegrad 2017;117:224–35. http://dx.doi.org/10.1016/j.ibiod.2017.01.017.

[70] Yue Z, Li W, Yu H. Application of rumen microorganisms for anaerobic bioconversion of lignocellulosic biomass. Bioresour Technol 2013;128:738–44. http://dx.doi.org/10.1016/j.biortech.2012.11.073.

[71] Zhang H, Zhang P, Ye J, Wu Y, Fang W, Gou X, et al. Improvement of methane production from rice straw with rumen fluid pretreatment: a feasibility study. Int Biodeterior Biodegrad 2016;113:9–16. http://dx.doi.org/10.1016/j.ibiod.2016.03.022.

[72] Li F, Zhang P, Zhang G, Tang X, Wang S. Enhancement of corn stover hydrolysis with rumen fluid pretreatment at different solid contents: effect, structural changes and enzymes participation. Int Biodeterior Biodegrad 2017;119:405–12. http://dx.doi.org/10.1016/j.ibiod.2016.10.038.

[73] Nielsen HB, Mladenovska Z, Ahring BK. Bioaugmentation of a two-stage thermophilic (68°C/55°C) anaerobic digestion concept for improvement of the methane yield from cattle manure. Biotechnol Bioeng 2007;97:1638–43. http://dx.doi.org/10.1002/bit.21342.

[74] Nkemka VN, Gilroyed B, Yanke J, Gruninger R, Vedres D, Mcallister T, et al. Bioaugmentation with an anaerobic fungus in a two-stage process for biohydrogen and biogas production using corn silage and cattail. Bioresour Technol 2015;185:79–88. http://dx.doi.org/10.1016/j.biortech.2015.02.100.

[75] Martin-ryals A, Schideman L, Li P, Wilkinson H, Wagner R. Improving anaerobic digestion of a cellulosic waste via routine bioaugmentation with cellulolytic microorganisms. Bioresour Technol 2015;189:62–70. http://dx.doi.org/10.1016/j.biortech.2015.03.069.

[76] Poszytek K, Ciezkowska M, Sklodowska A, Drewniak L. Microbial consortium with high cellulolytic activity (MCHCA) for enhanced biogas production. Front Microbiol 2016;7:1–11. http://dx.doi.org/10.3389/fmicb.2016.00324.

[77] Nzila A. Anaerobe Mini review: update on bioaugmentation in anaerobic processes for biogas production. Anaerobe 2017;46:3–12. http://dx.doi.org/10.1016/j.anaerobe.2016.11.007.

[78] Wei Y, Li X, Yu L, Zou D, Yuan H. Mesophilic anaerobic co-digestion of cattle manure and corn stover with biological and chemical pretreatment. Bioresour Technol 2015;198:431–6. http://dx.doi.org/10.1016/j.biortech.2015.09.035.

[79] Hu Y, Pang Y, Yuan H, Zou D, Liu Y, Zhu B, et al. Promoting anaerobic biogasification of corn stover through biological pretreatment by liquid fraction of digestate (LFD). Bioresour Technol 2015;175:167–73. http://dx.doi.org/10.1016/j.biortech.2014.10.088.

[80] Rouches E, Herpoël-Gimbert I, Steyer JP, Carrere H. Improvement of anaerobic degradation by white-rot fungi pretreatment of lignocellulosic biomass: a review. Renew Sustain Energy Rev 2016;59:179–98. http://dx.doi.org/10.1016/j.rser.2015.12.317.

[81] Teixeira Franco R, Buffière P, Bayard R. Ensiling for biogas production: critical parameters. A review. Biomass- Bioenergy 2016;94:94–104. http://dx.doi.org/10.1016/j.biombioe.2016.08.014.

[82] Pakarinen A, Maijala P, Jaakkola S, Stoddard FL, Kymäläinen M, Viikari L. Evaluation of preservation methods for improving biogas production and enzymatic conversion yields of annual crops. Biotechnol Biofuels 2011;4:20. http://dx.doi.org/10.1186/1754-6834-4-20.

[83] Liu S, Xu F, Ge X, Li Y. Comparison between ensilage and fungal pretreatment for storage of giant reed and subsequent methane production. Bioresour Technol 2016;209:246–53. http://dx.doi.org/10.1016/j.biortech.2016.02.129.

[84] Zhao X, Liu J, Liu J, Yang F, Zhu W, Yuan X, et al. Effect of ensiling and silage additives on biogas production and microbial community dynamics during anaerobic digestion of switchgrass. Bioresour Technol 2017;241:349–59. http://dx.doi.org/10.1016/j.biortech.2017.03.183.

[85] Herrmann C, Heiermann M, Idler C. Effects of ensiling, silage additives and storage period on methane formation of biogas crops. Bioresour Technol 2011;102:5153–61. http://dx.doi.org/10.1016/j.biortech.2011.01.012.

[86] Kreuger E, Nges IA, Björnsson L. Ensiling of crops for biogas production: effects on methane yield and total solids determination. Biotechnol Biofuels 2011;4:1–8. http://dx.doi.org/10.1186/1754-6834-4-44.

[87] Ravindran R, Jaiswal AK. A comprehensive review on pre-treatment strategy for lignocellulosic food industry waste: challenges and opportunities. Bioresour Technol 2016;199:92–102. http://dx.doi.org/10.1016/j.biortech.2015.07.106.

[88] Girotto F, Peng W, Rafieenia R, Cossu R. Effect of aeration applied during different phases of anaerobic digestion: **9**, 2018, 161-174. Waste Biomass- Valoriz 2018;9:161–74. http://dx.doi.org/10.1007/s12649-016-9785-9.

[89] Tsapekos P, Kougias PG, Vasileiou SA, Lyberatos G, Angelidaki I. Effect of micro-

aeration and inoculum type on the biodegradation of lignocellulosic substrate. Bioresour Technol 2017;225:246–53. http://dx.doi.org/10.1016/j.biortech.2016.11.081.

[90] Tuomela M, Vikman M, Hatakka A, Itävaara M. Biodegradation of lignin in a compost environment: a review. Bioresour Technol 2000;72:169–83. http://dx.doi.org/10.1016/S0960-8524(99)00104-2.

[91] Fu S, Wang F, Yuan X, Yang Z, Luo S. The thermophilic (55 °C) microaerobic pretreatment of corn straw for anaerobic digestion. Bioresour Technol 2015;175:203–8. http://dx.doi.org/10.1016/j.biortech.2014.10.072.

[92] Zhou S, Zhang Y, Dong Y. Pretreatment for biogas production by anaerobic fermentation of mixed corn stover and cow dung. Energy 2012;46:644–8. http://dx.doi.org/10.1016/j.energy.2012.07.017.

[93] Yan Z, Song Z, Li D, Yuan Y, Liu X, Zheng T. The effects of initial substrate concentration, C/N ratio, and temperature on solid-state anaerobic digestion from composting rice straw. Bioresour Technol 2015;177:266–73. http://dx.doi.org/10.1016/j.biortech.2014.11.089.

[94] Rouches E, Zhou S, Steyer JP, Carrere H. White-Rot Fungi pretreatment of lignocellulosic biomass for anaerobic digestion: impact of glucose supplementation. Process Biochem 2015;51:1784–92. http://dx.doi.org/10.1016/j.procbio.2016.02.003.

[95] Theoleyre M-A. La méthanisation des fumiers, le procédé Ducelier-Isman. L'eau, L'industrie, Les Nuisances - Hors Série Méthanisation 2014:106–10.

[96] Brummeler E ten, Koster IW. Enhancement of dry anaerobic batch digestion of the organic fraction of municipal solid waste by an aerobic pretreatment step. Biol Wastes 1990;31:199–210. http://dx.doi.org/10.1016/0269-7483(90)90159-P.

[97] Martínez-Valdez F, Komilis D, Saucedo-Castañeda G, Barrena R, Sanchez A. The effect of a short term aerobic pretreatment step on the anaerobic co-digestion of the organic fraction of municipal solid wastes: liquid extract addition versus solid phase addition. Waste Biomass- Valoriz 2017;8:1793–801. http://dx.doi.org/10.1007/s12649-016-9743-6.

[98] Rafieenia R, Girotto F, Peng W, Cossu R, Pivato A, Raga R, et al. Effect of aerobic pre-treatment on hydrogen and methane production in a two-stage anaerobic digestion process using food waste with different compositions. Waste Manag 2016;59:194–9. http://dx.doi.org/10.1016/j.wasman.2016.10.028.

[99] Ni Z, Liu J, Zhang M. Short-term pre-aeration applied to the dry anaerobic digestion of MSW, with a focus on the spectroscopic characteristics of dissolved organic matter. Chem Eng J 2017;313:1222–32. http://dx.doi.org/10.1016/j.cej.2016.11.020.

[100] Walker L, Cord-ruwisch R, Sciberras S. Performance of a commercial-scale DiCOM ™ demonstration facility treating mixed municipal solid waste in comparison with laboratory-scale data. Bioresour Technol 2012;126:404–11. http://dx.doi.org/10.1016/j.biortech.2011.12.079.

[101] Cossu R, Morello L, Raga R, Cerminara G. Biogas production enhancement using semi-aerobic pre-aeration in a hybrid bioreactor landfill. Waste Manag 2015;55:83–92. http://dx.doi.org/10.1016/j.wasman.2015.10.025.

[102] Xu Q, Tian Y, Kim H, Ko JH. Comparison of biogas recovery from MSW using different aerobic-anaerobic operation modes. Waste Manag 2016;56:190–5. http://dx.doi.org/10.1016/j.wasman.2016.07.005.

[103] Read AD, Hudgins M, Phillips P. Aerobic landfill test cells and their implications for sustainable waste disposal. Geogr J 2001;167:235–47.

[104] Neumann P, Pesante S, Venegas M, Vidal G. Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge. Rev Environ Sci Biotechnol 2016;15:173–211. http://dx.doi.org/10.1007/s11157-016-9396-8.

[105] Carrère H, Dumas C, Battimelli A, Batstone DJ, Delgenès JP, Steyer JP, et al. Pretreatment methods to improve sludge anaerobic degradability: a review. J Hazard Mater 2010;183:1–15. http://dx.doi.org/10.1016/j.jhazmat.2010.06.129.

[106] Montalvo S, Huilinir C, Ojeda F, Castillo A, Lillo L, Guerrero L. Microaerobic pretreatment of sewage sludge: effect of air flow rate, pretreatment time and temperature on the aerobic process and methane generation. Int Biodeterior Biodegrad 2016;110:1–7. http://dx.doi.org/10.1016/j.ibiod.2016.01.010.

[107] Carvajal A, Pena M, Pérez-Elvira S. Autohydrolysis pretreatment of secondary sludge for anaerobic digestion. Biochem Eng J 2013;75:21–31. http://dx.doi.org/10.1016/j.bej.2013.03.002.

[108] Jang HM, Cho UH, Park SK, Ha JH, Park JM. Influence of thermophilic aerobic digestion as a sludge pre-treatment and solids retention time of mesophilic anaerobic digestion on the methane production, sludge digestion and microbial communities in a sequential digestion process. Water Res 2013;48:1–14. http://dx.doi.org/10.1016/j.watres.2013.06.041.

[109] Cheng J, Liu Y, Kong F. Effects of cell lysis in gas yield and sludge stabilization by combined process of thermophilic aerobic and anaerobic digestion. Procedia Environ Sci 2016;31:50–8. http://dx.doi.org/10.1016/j.proenv.2016.02.007.

[110] Dumas C, Perez S, Paul E, Lefebvre X. Combined thermophilic aerobic process and conventional anaerobic digestion: effect on sludge biodegradation and methane production. Bioresour Technol 2010;101:2629–36. http://dx.doi.org/10.1016/j.biortech.2009.10.065.

[111] Rennuit C, Triolo JM, Eriksen S, Jimenez J, Hafner SD, Carrère H, et al. Comparison of pre- and inter-stage aerobic treatment of wastewater sludge: effects on biogas production and COD removal. Bioresour Technol 2018;247:332–9. http://dx.doi.org/10.1016/j.biortech.2017.08.128.

[112] da Silva RR, Pedezzi R, Souto TB. Exploring the bioprospecting and biotechnological potential of white-rot and anaerobic Neocallimastigomycota fungi: peptidases, esterases, and lignocellulolytic enzymes. Appl Microbiol Biotechnol 2017;101:3089–101. http://dx.doi.org/10.1007/s00253-017-8225-5.

[113] Lalak J, Kasprzycka A, Martyniak D, Tys J. Effect of biological pretreatment of Agropyron elongatum "BAMAR" on biogas production by anaerobic digestion. Bioresour Technol 2016;200:194–200. http://dx.doi.org/10.1016/j.biortech.2015.10.022.

[114] Mustafa AM, Poulsen TG, Sheng K. Fungal pretreatment of rice straw with Pleurotus ostreatus and Trichoderma reesei to enhance methane production under solid-state anaerobic digestion. Appl Energy 2016;180:661–71. http://dx.doi.org/10.1016/j.apenergy.2016.07.135.

[115] Liu X, Hiligsmann S, Gourdon R, Bayard R. Anaerobic digestion of lignocellulosic biomasses pretreated with Ceriporiopsis subvermispora. J Environ Manag 2017;193:154–62. http://dx.doi.org/10.1016/j.jenvman.2017.01.075.

[116] Wyman V, Henríquez J, Palma C, Carvajal A. Lignocellulosic waste valorisation strategy through enzyme and biogas production. Bioresour Technol 2018;247:402–11. http://dx.doi.org/10.1016/j.biortech.2017.09.055.

[117] Vasco-correa J, Ge X, Li Y. Fungal pretreatment of non-sterile miscanthus for enhanced enzymatic hydrolysis. Bioresour Technol 2016;203:118–23. http://dx.doi.org/10.1016/j.biortech.2015.12.018.

[118] Wagner AO, Schwarzenauer T, Illmer P. Improvement of methane generation capacity by aerobic pre-treatment of organic waste with a cellulolytic Trichoderma viride culture. J Environ Manag 2013;129:357–60. http://dx.doi.org/10.1016/j.jenvman.2013.07.030.

[119] Fdez.-Güelfo LA, Álvarez-Gallego C, Sales Márquez D, Romero García LI. Biological pretreatment applied to industrial organic fraction of municipal solid wastes (OFMSW): effect on anaerobic digestion. Chem Eng J 2011;172:321–5. http://dx.doi.org/10.1016/j.cej.2011.06.010.

[120] Fu S, Shi X, Dai M, Guo R. Effect of different mixed microflora on the performance of thermophilic microaerobic pretreatment. Energy Fuels 2016;30:6413–8. http://dx.doi.org/10.1021/acs.energyfuels.6b00440.

[121] Sobac. L'amélioration de l'accessibilité de la matière organique et de la production d'énergie sur les installations de méthanisation grâce au Bactériométha® n.d.:1–7. ⟨http://www.bacteriosol-sobac.com/omm/methanisation/methanisation-essai-amelioration-accessibilite-mo.pdf⟩.

[122] Mshandete A, Björnsson L, Kivaisi AK, Rubindamayugi ST, Mattiasson B. Enhancement of anaerobic batch digestion of sisal pulp waste by mesophilic aerobic pre-treatment. Water Res 2005;39:1569–75. http://dx.doi.org/10.1016/j.watres.2004.11.037.

[123] Zhou Y, Li C, Achu I, Liu J. The effects of pre-aeration and inoculation on solid-state anaerobic digestion of rice straw. Bioresour Technol 2017;224:78–86. http://dx.doi.org/10.1016/j.biortech.2016.11.104.

[124] Zhang Q, He J, Tian M, Mao Z, Tang L, Zhang J, et al. Enhancement of methane production from cassava residues by biological pretreatment using a constructed microbial consortium. Bioresour Technol 2011;102:8899–906. http://dx.doi.org/10.1016/j.biortech.2011.06.061.

[125] Hua B, Dai J, Liu B, Zhang H, Yuan X, Wang X, et al. Pretreatment of non-sterile, rotted silage maize straw by the microbial community MC1 increases biogas production. Bioresour Technol 2016;216:699–705. http://dx.doi.org/10.1016/j.biortech.2016.06.001.

[126] Ali SS, Abomohra AE, Sun J. Effective bio-pretreatment of sawdust waste with a novel microbial consortium for enhanced biomethanation. Bioresour Technol 2017;238:425–32. http://dx.doi.org/10.1016/j.biortech.2017.03.187.

[127] Zhong C, Wang C, Wang F, Jia H, Wei P, Zhao Y. Enhanced biogas production from wheat straw with the application of synergistic microbial consortium pretreatment. RSC Adv 2016;6:60187–95. http://dx.doi.org/10.1039/C5RA27393E.

[128] Zheng Y, Zhao J, Xu F, Li Y. Pretreatment of lignocellulosic biomass for enhanced biogas production. Prog Energy Combust Sci 2014;42:35–53. http://dx.doi.org/10.1016/j.pecs.2014.01.001.

[129] Sindhu R, Binod P, Pandey A. Biological pretreatment of lignocellulosic biomass – An overview. Bioresour Technol 2016;199:76–82. http://dx.doi.org/10.1016/j.biortech.2015.08.030.

[130] Thomsen ST, Londoño JEG, Ambye-Jensen M, Heiske S, Kádár Z, Meyer AS. Combination of ensiling and fungal delignification as effective wheat straw pretreatment. Biotechnol Biofuels 2016;9:16. http://dx.doi.org/10.1186/s13068-016-0437-x.

[131] Arreola-Vargas J, Flores-Larios A, González-Álvarez V, Corona-González RI, Méndez-Acosta HO. Single and two-stage anaerobic digestion for hydrogen and methane production from acid and enzymatic hydrolysates of Agave tequilana bagasse. Int J Hydrog Energy 2016;41:897–904. http://dx.doi.org/10.1016/j.ijhydene.2015.11.016.

[132] Gallegos D, Wedwitschka H, Moeller L, Zehnsdorf A, Stinner W. Effect of particle size reduction and ensiling fermentation on biogas formation and silage quality of wheat straw. Bioresour Technol 2017;242:216–24. http://dx.doi.org/10.1016/j.biortech.2017.08.137.

[133] Mustafa AM, Poulsen TG, Xia Y, Sheng K. Combinations of fungal and milling pretreatments for enhancing rice straw biogas production during solid-state anaerobic digestion. Bioresour Technol 2017;224:174–82. http://dx.doi.org/10.1016/j.biortech.2016.11.028.

[134] Alexandropoulou M, Antonopoulou G, Fragkou E, Ntaikou I, Lyberatos G. Fungal pretreatment of willow sawdust and its combination with alkaline treatment for enhancing biogas production. J Environ Manag 2017;203:704–13. http://dx.doi.org/10.1016/j.jenvman.2016.04.006.

[135] Michalska K, Bizukojć M, Ledakowicz S. Pretreatment of energy crops with sodium hydroxide and cellulolytic enzymes to increase biogas production. Biomass-Bioenergy 2015;80:213–21. http://dx.doi.org/10.1016/j.biombioe.2015.05.022.

[136] Baêta BEL, Lima D, Filho J, Adarme O, Gurgel L, Aquino SF De. Evaluation of hydrogen and methane production from sugarcane bagasse hemicellulose hydrolysates by two-stage anaerobic digestion process. Bioresour Technol 2016;218:436–46. http://dx.doi.org/10.1016/j.biortech.2016.06.113.

[137] Li W, Guo J, Cheng H, Wang W, Dong R. Two-phase anaerobic digestion of municipal solid wastes enhanced by hydrothermal pretreatment: viability,

performance and microbial community evaluation. Appl Energy 2017;189:613–22. http://dx.doi.org/10.1016/j.apenergy.2016.12.101.

[138] Schroyen M, Hulle SWH Van, Holemans S, Vervaeren H, Raes K. Laccase enzyme detoxifies hydrolysates and improves biogas production from hemp straw and miscanthus. Bioresour Technol 2017;244:597–604. http://dx.doi.org/10.1016/j.biortech.2017.07.137.

[139] Budzianowski WM. A review of potential innovations for production, conditioning and utilization of biogas with multiple-criteria assessment. Renew Sustain Energy Rev 2016;54:1148–71. http://dx.doi.org/10.1016/j.rser.2015.10.054.