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Pre-treatments to enhance biogas yield and quality from anaerobic digestion of whiskey distillery and brewery wastes: A review

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ABSTRACT

In order to encourage industrial growth based on sustainability, the replacement of fossil fuels with renewable sources has gained global importance. Anaerobic digestion (AD) fulfils the requirements for a sustainable alternative fuel, and is also an environmentally friendly waste treatment method. It requires less energy than other methods such as gasification or pyrolysis due to its low operating temperature. Whiskey distillery and brewery waste streams are classed as high strength organic wastes due to their high BOD/COD content, thus rendering them a suitable feedstock for anaerobic digestion. Due to large global alcohol production, millions of tonnes of solid and liquid waste is discharged annually, so the potential for waste-to-energy conversion can make anaerobic digestion an attractive treatment option for the waste streams of distilleries and breweries rather than diversion to landfill or incineration. However, these waste streams are lignocellulosic, containing high fractions of lignin and crystalline cellulose, meaning pre-treatments prior to anaerobic digestion can significantly enhance the biogas yield and organic matter degradation. Acid pre-treatment and enzymatic pre-treatment are particularly promising, with improvement in quality up to 74% CH_4 for AD of spent grain, with 16% increase in biogas yield, and up to 87% reduction in COD. However, industrial application of pre-treatments prior to anaerobic digestion remains limited. This review collates the literature to date on pre-treatments applied prior to anaerobic digestion of whiskey distillery/brewery wastes as well as current industrial practices and different reactor configurations. A particular focus is placed on the impact of pre-treatments on biogas yield in order to highlight potential enhancements in biogas yields for industrial implications.

1. Introduction

Widespread usage of non-renewable fuels (in particular fossil fuels) for energy production has been implicated as the cause of many ecological and environmental concerns which impact on human migration and climate conditions. This is due primarily to the continuous emission of greenhouse gases such as CO_2 [1] from such usage. In order to address this problem, The European Union aims to reduce the total greenhouse gas emissions in developed countries to 80%–95% of 1990 levels by 2050 [2]. Exploration of alternative energy sources has arisen as a result of increasing energy demand as well as economic and environmental reasons. Biogas (a methane rich gas produced by biological means) is considered to be one of the most environmental friendly fuels owing to its non-toxic characteristics and potential for ease of use as an alternative to traditional fossil fuels [3].

Whiskey and beer manufacturing processes generate large amounts of high strength co-products which contain high levels of chemical oxygen demand (COD), biological oxygen demand (BOD), phosphorus, ammonia, metal ions like copper and iron, as well as complex organic materials such as lignin, yeast cells, protein [4]. Due to the characteristics of these waste streams, the alcoholic beverage industry is a highly polluting industry [5]. Approximately 3.4 million tonnes of solid wastes, including spent yeast and spent grain, is produced per year in the EU, which is directed to animal feed ingredients. In addition, approximately 8–15 L aqueous waste generated per litre of malt whiskey and 3–10 L/L of beer [4–8]. Disposal of brewery and distillery wastes has been legislated for in most countries for more than 20 years [9]. In countries such as Ireland and the UK there has been a massive increase in the occurrence of small “craft” breweries and distilleries. These small or micro-breweries/distilleries, defined as such based on volume of production which is less than 1760 m^3 annually, would in particular benefit from potential methods for reducing costs associated with waste

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Nomenclature

ABR	Anaerobic Baffled Reactor
AD	Anaerobic Digestion
AcoD	Anaerobic Co-Digestion
AF	Anaerobic Filter Reactor
AnMBR	Anaerobic Membrane Bioreactor
ASBR	Anaerobic Sequential Batch Reactor
BMP	Biomethane Potential
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CHP	Combined Heat and Power
CSTR	Continuously Stirred Tank Reactor
C:N	Carbon Nitrogen Ratio
EGSB	Expanded Granular Sludge Blanket
GBR	Granular Bed Reactor
GRABBR	Granular Bed Anaerobic Baffled Reactor
HRT	Hydraulic Retention Time
OLR	Organic Loading Rate
SRT	Solid Retention Time
SS-AD	Solid State Anaerobic Digestion
UASB	Upflow Anaerobic Sludge Blanket
VFA	Volatile Fatty Acid

treatment [10]. Fig. 1 for example provides the number of micro scale breweries in Ireland since 2012, with data referring to the number of breweries in production at approximately mid-year [11,12].

Furthermore according to Irish Whiskey Association data, the number of whiskey distilleries in operation increased from 4 to 18 between 2013 to August 2017, with 16 further planned [13].

AD is becoming more widely accepted as an efficient method to convert organic matter, in particular highly recalcitrant waste streams of distilleries/breweries, into biogas, which can significantly improve the energy balance and economics of the industry [14,15]. Anaerobic Digestion has proven to be more efficient than conventional methods as the existing waste management method for distilleries and breweries is mainly landfill applications and animal nutrition [16,17]. The establishment of anaerobic digestion plants for the treatment of high organic content wastes has undergone a major development amongst wastewater treatment facilities in Europe [15] and the application of AD in the treatment of distillery/brewery wastes is increasing.

Spent grain and yeast are the solid phase co-products of mashing and fermenting processes, which are initial and essential operations in distilleries and breweries [6], while pot ale is the main liquid phase by-product of the distillation process in whiskey production [18]. These waste streams are highly lignocellulosic, making them resistant to degradation by biological means [19]. Distillery/brewery wastes have a complex heterogeneous structure. Primarily due to the high lignin content, implementation of pre-treatments is necessary in order to obtain a higher biogas yield from AD [20]. Pre-treatments play a significant role in modifying the structure of the substrates to make them more easily degradable. Different types of pre-treatments are discussed in detail in Section 5.

The whiskey manufacturing process, outlined in Table 1 and Fig. 2, can be divided into six main steps: milling, malting, mashing, fermentation, distillation and maturation [18,21].

The manufacture of craft beer has many similarities with the initial stages of the whiskey production process. It also starts with malting and mashing steps of barley or other grains. Hops are also added to give the characteristic bitterness flavour of beer and avoid bacterial spoilage. The product of the fermentation step is then subjected to filtration and stabilization, maturated, and bottled/kegged [22].

Due to the similarities of these two processes, solid waste fractions, spent barley and spent yeast, are not much different; however, distilleries also generate massive amounts of pot ale (8.5–11.5 L per litre of malt whiskey) as a co-product of the distillation steps. Spent wash from the fermenter is also a significant liquid waste (e.g. 16–21 L per litre of grain whiskey [23]).

In a typical whiskey distillery, liquid residues left in the wash and spirit still after the distillation steps comprise the majority of the waste stream, known as pot ale and spent lees, respectively. In terms of solid waste, spent grain (also called draff) arise from the mash tun and fermenter of both distilleries and breweries [18].

Pot ale is a highly turbid, concentrated, caramelised and cumbersome liquid effluent [21]; with large discharge volumes [24]. As such, disposing of this liquid waste is a major concern for distilleries; the characteristics of which are summarized in Table 2. Pot ale has high COD and BOD contents, and contains significant levels of phosphorus and ammonia [9,18,23,24]. As copper stills are typically used in the distillation step, copper, which is toxic to micro and macroorganisms, is commonly seen in pot ale due to mass transfer between refluxing liquid and hot stills [4,21]. Pot ale is harmful especially for aquatic life because of the high level of COD/BOD leading to decreases in the level of solubilised oxygen and eutrophication [25], and due to its dark coloured nature it can block the penetration of sunlight into the receiving water, reducing the level of dissolved oxygen by restricting photosynthesis [26]. Spent lees have lower COD/BOD and contain volatile organic acids such as formic, acetic, propionic, butyric and pentanoic, which are also the intermediate products of AD [18,27].

The polluting strength of these liquid waste streams is significantly high, due to the large amounts of biodegradable organic material (sugars, lignins, hemicelluloses, dextrins, resins and organic acids) and fertilizers such as potassium, phosphorus and nitrogen [9,23,28]. The by-products/waste streams produce undesirable odours as a result of the presence of skatole, indole and other sulphur compounds [9]. Furthermore, uncontrolled land discharge of distillery and brewery waste water causes high levels of acidification. It has been shown that land discharge of distillery liquid wastes can impair seed germination [29]; potentially due to a decline in soil pH, leading to inhibition of agricultural crops. It also potentially causes leaching of protein and carbohydrates from the seeds along with a decrease in the activity level of crucial enzymes for crops growth such as alkaline phosphatase and ATPase [30].

Due to the potential hazards of the land spreading applications, environmental regulations are forcing distilleries to enhance existing treatment technologies as well as adopt new and more efficient methods for waste management. Thus, recovery of organic waste streams has become a major focus of waste management policies, with

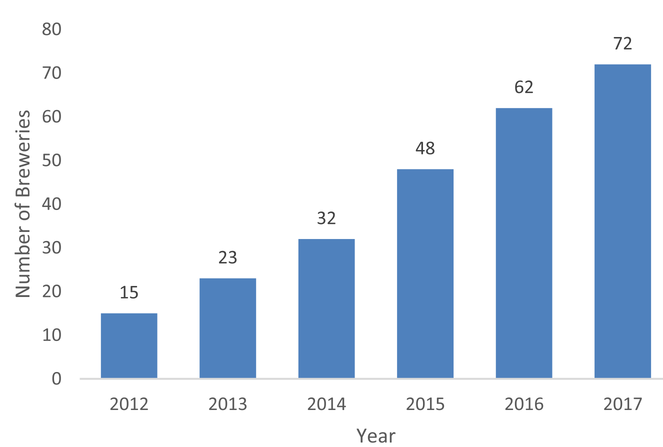

Fig. 1. Number of Irish microbreweries in production.

Table 1
Whiskey production steps.

Process Step	Purpose
Malting	The grain is steeped in water and dried to give characteristic malt flavour to the grain
Milling	Reduction of barley grain size; removal of husks
Mashing	Long chain starch molecules broken down to soluble sugars by enzymatic action at high temperature; Wort
Fermentation	Wort is fermented using yeast to obtain 6–7% ethanol by v/v
Distillation	Alcohol is separated in batch (still) distillation as a top product with 20% ethanol concentration; Pot Ale produced as bottoms
Maturation; Bottling	Flavour establishment typically in wooden casks for 10–25 years

biological processes, predominantly anaerobic digestion, being seen as the main solution for high organic content wastes [15].

Major solid waste streams of distilleries and breweries consist of spent yeast and spent grain, typically termed draff when combined. Yeast cells are covered by a thick cell wall, which is formed of a complex matrix of phosphomannans, glucans, chitin and protein, and as such are not readily biodegradable [23]. Spent grain, draff, such as spent barley, spent yeast and spent hops, in breweries only, is generated in relatively large amounts [6,33]. Spent grain basically consists of kernel husk, pericarp and seed coat, which have high levels of cellulose (16.8–25.4%), hemicellulose (mostly arabinoxylans) (21.8–28.4%), lignin (11.9–27.8%), proteins and fibres. Hence, it is considered a lignocellulosic material [34,35].

In the first step of AD (hydrolysis), cellulose and hemicellulose are broken down to their monomers, however lignin limits the degradation of lignocellulosic material due to its high level of recalcitrance [36]. Spent grain is often used for animal feed (mainly for cattle) due to its both highly nutritious content and low/no cost. It is used either in wet form or as dried conventionally [37]. However, when pot ale and spent grain mixture are used, this might lead to a high level of toxicity depending upon copper level (from the distillation in copper stills) as some animals (particularly sheep) cannot metabolise copper [21]. Although cattle are tolerant of high level of copper, digesting pot ale syrup is not suitable for their diet. Pot ale can only be used as a blending material to mix with hay, straw or molasses without exceeding 10% of the total amount, thus limiting the usage of pot ale in comparison to the discharge amount [38]. As such, treatment technologies focusing on treatment of pot ale are of high importance.

Table 2
Characteristics of distillery liquid residues.

Parameter	Pot ale	Spent lees	Reference
Total solids	23	17	[23]
Total suspended solids	9.6	4.5–7	[31]
Volatile suspended solids	9.4	8.1	[23]
Total nitrogen	37	5–7	[7,23]
COD	30–50	85–110	[18,31]
BOD	25–35	25–35	[24,32]
pH	3.5–4.5	4.0–4.2	[23]

*Units are in g/L except pH.

This review paper presents a comprehensive investigation of whiskey and beer manufacturing processes, anaerobic digestion technology including the thermodynamics of the biochemical reactions, as well as presenting the details of the pre-treatment strategies applied to whiskey distillery and brewery wastes. The challenges to full-scale implementation of pre-treatments prior to AD as a more efficient waste management method are discussed. Research gaps and areas for future research are highlighted. Future prospects are also outlined to highlight the importance of pre-treatments in an anaerobic digestion context. This review is timely due to the proliferation in small-scale breweries and distilleries at European level currently, who could benefit greatly from improvement in facility energy management from the application of appropriate pre-treatment prior to anaerobic digestion of their wastes. The anaerobic digestion of distillery and brewery wastes has not been dealt with comprehensively in the literature to date.

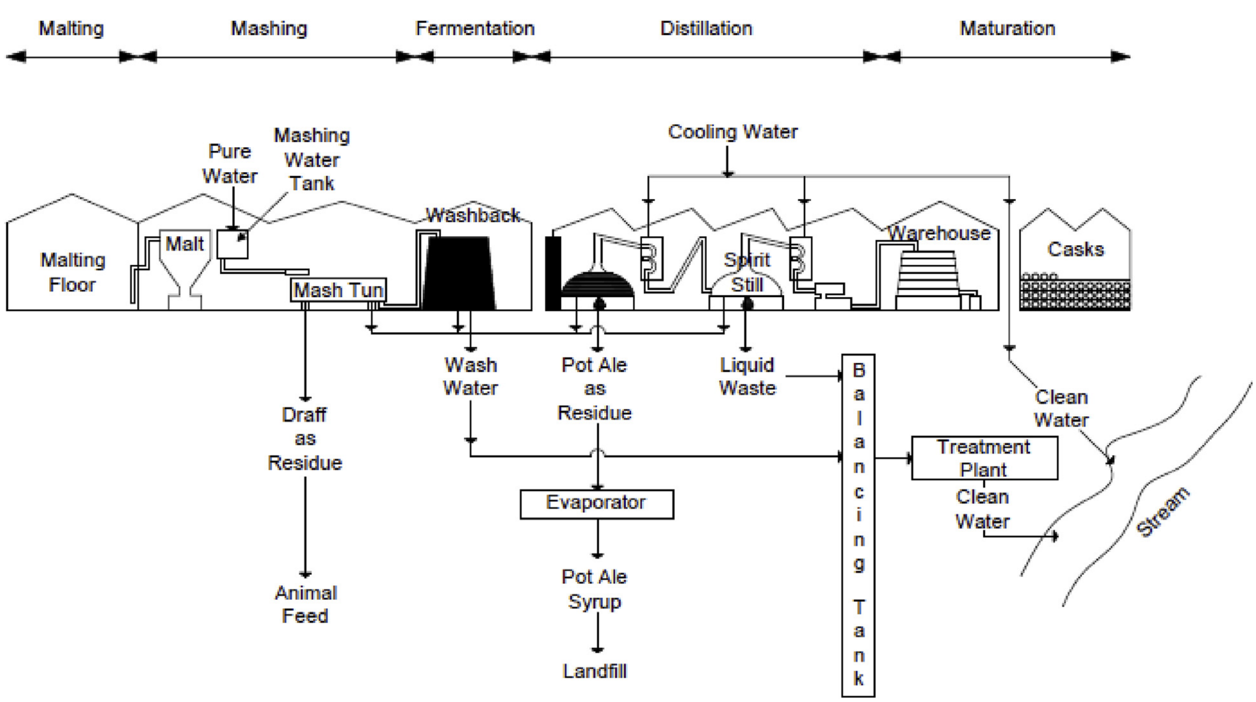

Fig. 2. Main steps of whiskey distillery process (adapted from Ref. [21]).

2. General process description of anaerobic digestion

AD is considered as a widely accepted and well-studied technology for the treatment of organic wastes [39], appropriate for stabilizing high organic content wastes with limited environmental impact and high energy recovery potential [40,41]. It can be possible to convert a significant amount of COD (> 50%) to biogas which might be used as an in-plant fuel (self-energy efficient distilleries/breweries) depending on the further purification due to the existence of impurities such as hydrogen sulphide, nitrogen and most importantly carbon dioxide [23,42]. Digestate is a co-product of AD process which contains undigested materials as well as produced microbial biomass. The digestate is typically high in nitrogen, phosphorus and potassium, it therefore has potential for use as both an organic fertiliser and soil amendment [27] (Fig. 3).

AD has some advantages over conventional aerobic wastewater treatment technologies, for instance less sludge production, low energy consumption, destruction of the pathogens in the sludge, limitation of odour problem arising from existence of putrescible matter as well as higher ability to cope with the recalcitrant distillery and brewery wastes [43,44].

2.1. Biochemical reactions in anaerobic digestion

The kinetics of the rate limiting step (generally considered the initial step of hydrolysis) affect the overall performance of AD. Hydrolytic enzymatic activity shows variability with environmental factors such as pH and temperature as well as the chemical composition of the substrate, i.e. biodegradability, availability of enzymatic attack [45]. AD is a complex and sequential process, which provides the degradation of organic materials by microorganisms' activity in the oxygen depleted environment (oxidation reduction potential (ORP) < -200 mV), resulting in production of biogas rich in methane [46,47]. The type of bacteria involved in the sequential steps are known as acidogenic (or fermentative) bacteria, acetogenic (or syntrophic) bacteria, and methanogenic archaea [48]. Presence of sulphate, sulfite, or thiosulfate in the reaction mixture results in reduction of oxidized sulphur matter to different forms of dissolved sulphide (HS^-, S^{-2}, H_2S) in the digestate and to hydrogen sulphide (H_2S) in the generated biogas [49]. Fig. 4 illustrates the process of AD of complex organic materials with the group of bacterial activity in each step.

Complex organic materials like carbohydrates, lipids and proteins are first decomposed to their component monomers as a result of the hydrolytic enzymatic attack. Degradation of complex molecules into their monomers has a significant importance prior to the acidogenesis step, as acidogens cannot absorb complex organic compounds directly into their cells [41]. Acidogenic fermentative bacteria convert the end product of the hydrolysis stage (soluble monomers of complex feedstock) into simple organic compounds, predominantly short-chain volatile organic acids such as formic, acetic, propionic, butyric, pentanoic acids; alcohols, for example methanol, ethanol; and aldehydes, carbon dioxide and hydrogen. Acetate is the most important organic acid as it can be directly used as substrate for methanogenic bacteria [50]. Acetogenesis reactions are thermodynamically unfavourable; nevertheless, they occur naturally during AD as a result of interaction of the activity of methanogenetic and acetogenetic bacteria [48], while all other reactions are thermodynamically favourable (Table 3). On the other hand, the sulfidogenesis stage also limits AD of distillery/brewery wastes due to favourable bacterial competition to sulphate reducing bacteria based upon the thermodynamics of the reactions [51]. To prevent thermodynamic impediments, H_2 produced by acetogenic bacteria should be continuously purged to ensure production of acetate is not blocked as it is the key intermediate product. Such biological reactions are favourable under low hydrogen partial pressure [49,52–54].

Macronutrients, for instance carbon (C), nitrogen (N), phosphorous (P), and sulphur (S), are essential for the growth of anaerobic microorganisms. An imbalance in the nutrients available is considered a critical limiting factor on AD [56]. The C:N ratio is generally subcategorised within AD nutrients as the relative amount of carbon and nitrogen that has a direct effect on the methane production due to its direct relation to potential inhibitions [57]. The known optimum C:N ratio is between 20:1–30:1 for any type anaerobic digester to supply adequate amount of N for bacterial growth as well as prevent excess [58]. A high C:N (> 35:1) ratio [59] is not suitable for bacterial growth, in particular methane forming bacteria, because of the inadequate level of nitrogen. It can thus result in lower methane production; as can substrates with low C:N ratio (15:1 or lower) [60]. On the other hand, the same process can lead to ammonia accumulation by means of methanogenic activity, resulting in pH increase up to 8 which is toxic for acidogens [61,62].

Temperature is one of the major parameters of the process of AD [63]. Anaerobic digesters can be operated over three different nominal temperature ranges; 10–20 °C (psychrophilic); 30–40 °C (mesophilic) or 50–60 °C (thermophilic) [64]. Optimum temperatures are defined according to different methane-forming bacterial strains [65]. It has traditionally been thought that higher methane yield is achieved under thermophilic conditions, however, it has recently been shown that

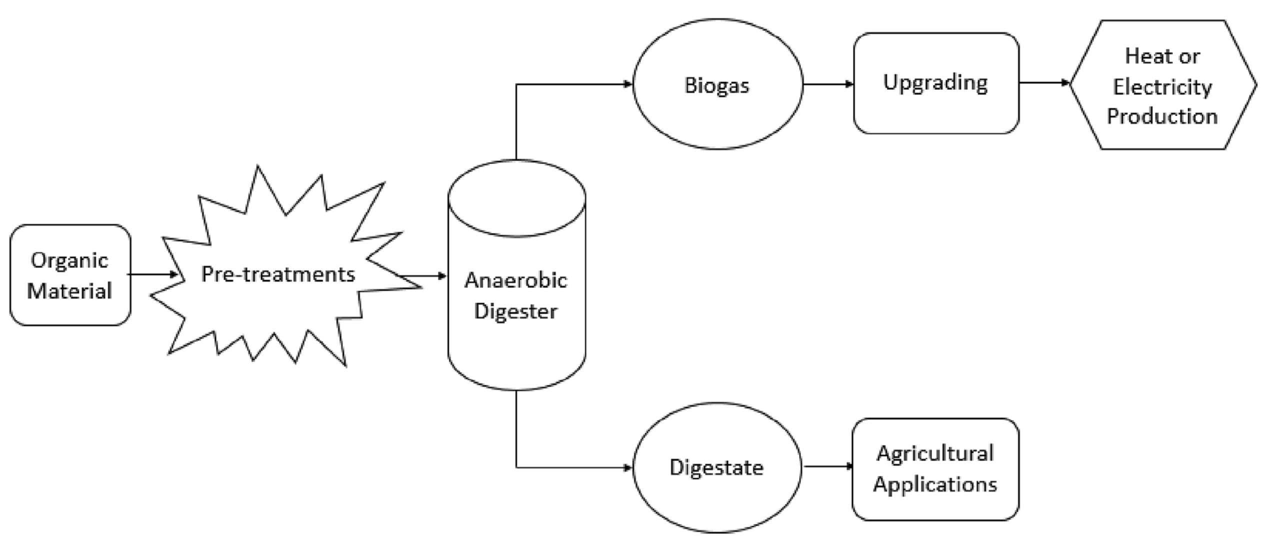

Fig. 3. The overview of AD and the potential usage of the final products (adapted from Ref. [27]).

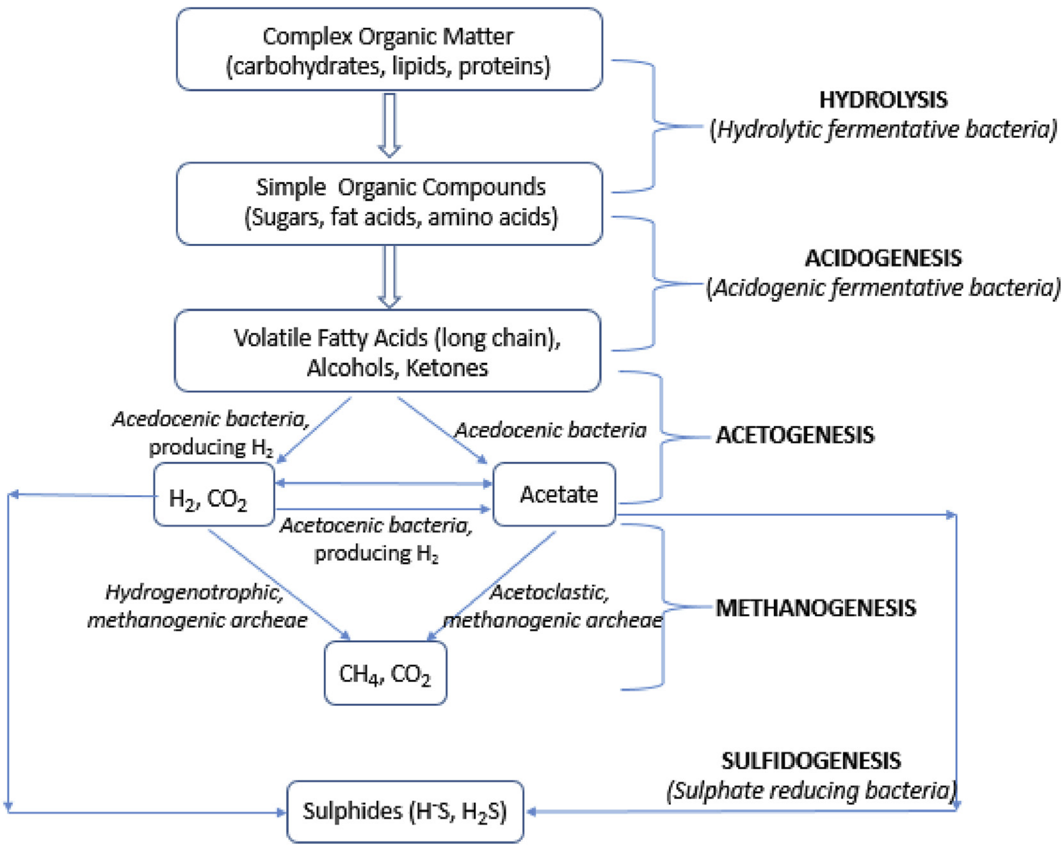

Fig. 4. Stages of anaerobic digestion process with the involved bacteria (adapted from Ref. [48]).

Table 3
Common reactions in an anaerobic digestion with Gibbs free energy in standard conditions [48,51,55].

Reaction Type		ΔG° (kJ/reaction)
Acidogenesis	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COO^- + 2CO_2 + 2H^+ 4H_2$	−206
	$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COO^- + 2H_2O + 2H^+$	−358
	$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COO^- + 2CO_2 + H^+ + 2H_2$	−255
Acetogenesis	$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$	+76
	$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+48.1
	$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2$	+9.6
Methanogenesis	$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- + 2H_2$	−31.0
	$H_2 + 1/4\ HCO_3^- + 1/4\ H^+ \rightarrow 1/4\ CH_4 + 4/3H_2O$	−33.9
	$HCOO^- + 1/4H_2O + 1/4\ H^+ \rightarrow 1/4\ CH_4 + 3/4\ HCO_3$	−32.6
Sulfidogenesis	$CH_3CH_2COO^- + 3/4\ SO_4^{2-} \rightarrow HS^- + 4H_2O$	−37.7
	$CH_3CH_2COO^- + 1/2\ SO_4^{2-} \rightarrow 2CH_3COO^- + 1/2\ HS^- + 1/2\ H^+$	−27.8
	$CH_3CH_2OH + 1/2\ SO_4^{2-} \rightarrow CH_3COO^- + 1/2\ HS^- + 1/2\ H^+ + H_2O$	−66.4

psychrophilic conditions increase the energy output of bioreactor per unit volume [66]. Moreover, psychrophilic and mesophilic digesters have some advantages in comparison to thermophilic digesters such as less energy demand for heating, and ease of control, as cold adapted bacteria are not as sensitive to unexpected temperature fluctuations as mesophilic and thermophilic bacteria [27]. A small temperature change (± 1 °C) has a negative impact on biogas production under thermophilic conditions while mesophilic bacteria can tolerate fluctuations up to ± 3 °C without a significant reduction of biogas generation [67]. Thus, reactors under psychrophilic and mesophilic conditions have higher process stability [68]. Furthermore, thermophilic conditions show a suppressive effect on methanogens which results in a lower biogas yield due to the formation of volatile gases such as ammonia [69].

AD performance is strongly dependent on pH as the group of bacteria involved at each stage requires specific pH; for hydrolysis and acidogenesis these are 5.5 and 6.5 [70] respectively, while methanogenesis (which is the most sensitive to pH) has an optimum range of 7.0 ± 0.2 [48]. Key intermediate products such as volatile fatty acids and acetate are produced by acidogens, potentially leading to a significant pH drop (to 5) in the reactor which can be fatal for methanogens. Alkalinity is also increased in AD as a result of degradation of proteins due to the ammonia release [62]. In order to balance the fluctuation in pH, it has been suggested that the initial pH for the AD process should be adjusted to 7 [71]. Where this has been done there has been a corresponding higher biogas yield in AD of pot ale [23].

Besides principle knowledge of AD, processing parameters such as the organic loading rate (OLR) and the hydraulic residence time (HRT) are considered the most important operational parameters of AD since they both affect biogas yields and plant efficiency for both batch and continuous operations [72].

In theory, maximal methane yield is achieved when reactor is operated at low OLR and long HRT because higher OLR causes inhibition

Table 4
Studies of anaerobic digestion for whiskey distillery/brewery wastes.

Substrate	Temperature	Reactor Configuration, operation volume	Pre-treatment	[a]COD feedstock) (mg L^{-1})	HRT (d)	[b]OLR	[c] ηCH_4	[d] εCOD (%)	References
Pot ale	Mesophilic 35 °C	UASB two stages, 113 ml	$NaHCO_3$ addition	37 060–50 700	29	30	0.019	55	[90]
Pot ale	Mesophilic 35 °C	UASB, 1050 ml	Alkaline ($NaHCO_3$ addition)	21 050	2.1	10.2	N/A	93	[18]
Pot ale	Mesophilic 37 °C	Batch, 1000 ml	Enzymatic	61 500	10	N/A	N/A	87	[23]
Spent wash	Mesophilic 37 °C	Batch, 1000 ml	Enzymatic	46 300	10	N/A	N/A	45	[23]
Spent wash	Mesophilic 37 °C	Full scale UASB, 143 000 L	–	25 000–33 000	N/A	6–11	0.25	90	[103]
Spent grain	Mesophilic 35 °C	EGSB, 3800 ml	Enzymatic	800–4000	45	1–10	[e]0.7	90	[114]
Spent grain	Mesophilic 37 °C	UASB, 8180 ml	–	16 500–22 520	3.4–0.4	33.3	0.318	80–97.3	[105]
Spent grain	Mesophilic 37 °C	Batch, 250 ml	Glucose addition	7614	28–30	N/A	0.516	90	[115]
Spent grain	Thermophilic 55 °C	Batch, 250 ml	Glucose addition	7299	28–30	N/A	0.373	44	[115]
Spent grain	Psychrophilic 20 °C	SS-AD, 3000 ml	Acid	N/A	1	N/A	[f]74	N/A	[34]
Spent Grain	Mesophilic 37 °C	CSTR, 30 000 ml	High shear homogeniser	107 200	33.7	2.51	N/A	69.6	[35]
Spent grain	Mesophilic 37 °C	CSTR, 30 000 ml	Alkali	101 400	39.5	2.07	N/A	73.1	[35]
Spent grain	Mesophilic 37 °C	CSTR, 30 000 ml	Thermo- chemical	101 000	35.1	1.85	N/A	70.4	[35]
Excess yeast (2.8%) + spent wash	Mesophilic 32–35 °C	UASB, 12 000 ml	Alkali addition for pH (6.5) adjustment	2240	N/A	12.6 ± 3.48 0.290	N/A	85.7–95.8	[102]
Excess yeast (0.7%) + spent wash	Mesophilic 32–35 °C	EGSB, 4 000 000 ml Full scale	Alkali addition for pH (6.5) adjustment	3522	0.6	5.15 ± 2.18	N/A	82.1 ± 3.9	[102]
Spent yeast	Mesophilic 37 °C	Batch, 180 ml	NH_4Cl addition	3800	45	N/A	0.0422	24.2	[116]
Distillery wastewater	Mesophilic 37 °C	GRABBR, lab scale	Alkali, NaOH	16 600–58 000	4	4.75	N/A	80–92	[111]
Mix of distillery waste	Mesophilic 36 °C	Two-Stages AF+ UASB, 1500 ml	–	49 000–53 000	[g]10–19 [h]20–39	[g]2.5–5.1 [h]0.6–2.5	N/A	[14]54 [15]93	[95]
Brewery wastewater	Mesophilic 35 °C	AnMBR, 15 000 ml	–	10 200	1.8	3.5–11.5	0.53 ± 0.015	98	[8]
Brewery wastewater	Mesophilic 35 °C	Two-Stage UASB, 3000 ml	Acidic	1910	0.1–1.9	25	0.27–0.30	80	[101]
Brewery wastewater	Mesophilic, 34-39 °C	AF, 5 843 000 ml	–	2832	0.4	8	0.15	96	[96]
Pot ale	Mesophilic 37 °C	[i]UAFP, 780 ml	Enzymatic	Given as TOC: 15 380	18	[j]0.0108	N/A	N/A	[24]
Pot ale	Mesophilic 37 °C	Batch, 165 ml	–	57 100	40	N/A	N/A	N/A	[117]

[a] Influent chemical oxygen demand.
[b] Organic loading rate in kg COD/m^3day.
[c] Methane yield coefficient in m^3 CH4/kg COD $_{removal}$.
[d] COD removal efficiency.
[e] Unit in $gCOD_{CH4}$/g COD $_{fed}$ (The amount of methanised COD relative to the amount of COD fed to the reactor).
[f] % of biomethane potential.
[g] In the 1st stage.
[h] In the 2nd stage.
[i] Upflow anaerobic filter process.
[j] Unit in kg TOC/L day.

due to accumulated volatile fatty acids. However, it results in low treatment efficiency per unit time. Therefore operation at high ORL requires larger reactor size in order to achieve a complete digestion which might make the process unfeasible at industrial scale [73,74]. In order to address this problem hydrogenotrophic methanogens can be mainly selected for methanogenesis step, which is the most sensitive to variations in pH [75], as they are capable of tolerating lower pH (< 6) in comparison with acetoclastic methanogens.

3. Reactor configurations applied to distillery/brewery waste streams

A variety of reactor configurations have been used for anaerobic digestion of whiskey distillery/brewery wastes at industrial scale (Table 4). Reactors can be categorized based on the design (vertical, horizontal, inclined), feedstock (single, co-digestion), mode of operation (batch, continuous, semi-continuous) and operating temperature (psychrophilic, mesophilic, thermophilic). Batch reactors provide better process control than continuous mode reactors [46,76]. Reactors for AD can also be run as single, two stage or multi stage, which can be advantageous due to the different pH requirements of microbes involved in the different stages of the process [77–79]. In single stage systems all biochemical reactions occurs simultaneously in one reactor whereas in a two/multi stage AD system the hydrolytic-acidogenic stage is separated from the methanogenic stage; in this way acidogenic microbes could be stimulated to produce more enzymes, so resulting in more expanded degradation [40,80]. Both single and multi-stage reactors have advantages and drawbacks. For example, single stage digesters are required to operate under the same system conditions despite different microbial growth rates and optimal pH for each step of AD. This results in sudden pH changes within the reactor and consequently inhibits methanogenic activity. In order to overcome this problem in multi stage digesters, first reactor parameters are designed to maximise breaking down biopolymers and releasing fatty acids (hydrolysis/acidogenesis). Methanogenesis then occurs in the second reaction stage with the product of the first reactor; however a decline in biogas potential is sometimes observed due to the loss of solid particles from the feedstock to the further stage(s) where distinct reactor vessels are employed rather than sequencing batch reactors [46].

3.1. Conventional anaerobic reactor configurations for whiskey distillery/brewery waste treatment

3.1.1. Anaerobic batch reactor

Batch reactors are loaded with fresh feedstock with inoculum and sealed for the retention time. This ensures completion of biochemical reactions within the reactor which can be established by monitoring biogas production rate. Once a batch reactor is opened, the residual is removed. Batch reactors are generally considered as accelerated landfill boxes even though they show much higher biogas production rate than typical landfill areas [46]. Integration of a recirculating liquid phase (leachate), which requires little investment and maintenance, into traditional batch reactors enhances the AD yield; this process is termed a leaching batch reactor [81]. Leachate has a key role on the biogas production rate as it is not only provides a better dispersion of microorganisms and feedstock, but also guarantees better mixing conditions [81]. Therefore, leaching batch reactors, (also known as leaching bed reactors) do not require complicated mixing or agitation equipment, or expensive high pressure vessels, which correspondingly reduces the capital costs [46]. Advantages and drawbacks of batch reactors with and without leachate recirculation has been reviewed comprehensively in previous publications [81,82].

Typically, fundamental knowledge of new generation anaerobic digesters comes from batch operation. Usage examples of the batch reactors for all whiskey distillery/brewery waste streams from lab to full scale are given in Table 4.

3.1.2. Solid state anaerobic reactor (SS-AD)

The SS-AD has been gaining popularity with a sharp increase in Europe since the early 1990s for treatment of lignocellulosic biomass [83,84]. The SS-AD is capable of digesting high solid content feedstock, typically operating at 15–40% total solid content. Single stage SS-AD as well as the combination of SS-AD and granular bed reactor (GBR) for the treatment of brewery spent yeast has been employed previously [34]. The working principle of GBR is very similar to the upflow anaerobic sludge blanket (UASB) [76], which is discussed in detail in Section 3.2.3.

The main advantages of SS-AD over liquid anaerobic digesters include; an ability to treat more material in the same size, lower energy demand for heating and process operation and less effluent production. Furthermore, it has 2–7 times greater methane production capacity than liquid digestion [85]. It is therefore considered as a more suitable configuration for lignocellulosic matter like whiskey distillery/brewery wastes [34,63]. Potential operational problems such as longer retention time requirement, relatively slower mass transfer rate in comparison with liquid digesters [57] and the potential inhibitions arising from those problems along with potential solutions have also been reported [57,63,83]. SS-AD has received scant attention in the literature for AD of whiskey distillery/brewery wastes, although bench scale application on spent grain resulted in 74% methane yield under psychrophilic conditions [34].

3.1.3. Anaerobic sequential batch reactor (ASBR)

Although it was first conceived over 90 years ago, the ASBR has received increased attention in the literature recently due to operational simplicity, efficient quality control of the effluent, flexibility of use as well as better process control advantage [76,86,87]. ASBR works under a fill-and-draw treatment cycle which includes feed, reaction, settling and discharge stages. Once the tank is filled, it operates as a batch reactor for a certain period of time, and after reaching the desired level of treatment, it is allowed to settle, and the clarified supernatant is taken out of the reactor. There is a requirement for good mixing as the biomass settling determines the system performance. This mixing can be performed by an agitator or a recycling stream, to ensure sufficient mass transfer is seen during the reaction time [59,76,88,89]. Usage of inert supports such as polyurethane foam has been recommended to ensure high organic compound removal efficiency and high solids retention [88]. ASBR has received scant attention in the literature to date for whiskey distillery/brewery wastes; however a high quality gas with 77 ± 5% of biomethane has been achieved for AD of malt whiskey pot ale using ASBR [90].

3.1.4. Continuously stirred batch reactor (CSTR)

The 1950s saw the introduction of intense mechanical mixing within anaerobic reactors. This is considered as a first-generation high rate anaerobic digestion. A suspended growth bacteria system is evidenced within the CSTR with intermittent or continuous agitation, facilitated by good contact between bacteria and substrate. However, slight mass transfer resistance is also seen. CSTRs have been shown to be suitable for treating high levels of suspended solids, with 2-3-fold improvement in performance over low rate digesters; unstirred or intermittently stirred reactors. Along with effluents, the microbial population is washed out of the reactor in low-rate digesters. Prevention of microbial washout is thought to lead to microorganisms having a greater concentration in the reactor, therefore improving the efficiency of the digester [59,76,91]. Rapid acidification takes place due to mixing and continuous stirring as a result of large VFA production. To overcome this problem, the feedstock is diluted with recirculated digestate. The CSTR can be operated as either single and two stage as well as in plug flow or semi continuous mode [59,92], and has been shown to be effective at 30 L scale for AD of whiskey distillery/brewery waste with spent grain and different applied pre-treatments [35].

3.2. Second generation anaerobic reactor configurations for whiskey distillery/brewery waste treatment

The concept of second generation anaerobic digesters is based on the ability of retaining high viable biomass via a method of bacterial sludge immobilisation.

3.2.1. Anaerobic filter reactor (AFR)

An AFR has a packed bed biofilm configuration, which offers intimate interaction between substrate and bacterial mass by attached support media. As a characteristic of this configuration, a supporting biofilm is generated on the packing media that supports the biomass separation from the effluent [76,93].

AF can be run either though an upflow or downflow pathway. Recycling and upflow operation is more common for treating highly recalcitrant wastes because it leads to the formation of a high concentration of suspended biomass in the structure of the fixed bed [59,93,94]. On the other hand, the possibility of clogging of filter media during the treatment of high suspended solids containing waste can lead to the potential risk of failure of the system [59]. Nonetheless, the success of AF reactors creates the fundamentals of novel high-rate anaerobic digesters [76,95]. The Single AF reactor has been used for AD of pot ale [24] and brewery wastewater [96] as well as in combination with UASB for anaerobic digestion of mix distillery waste [95]. The AD of brewery wastewater showed the highest methane yield with the value of 0.15 m^3 CH_4/kg COD removal along with 96% CH_4 (Table 4).

3.2.2. Anaerobic membrane bioreactor (AnMBR)

The AnMBR combines membrane filtration with an AD reactor, allowing removal of treated effluent with the retention of sludge, thus offering high biomass operations [97,98]. Better retention of microorganisms eventually leads to a greater hydrolysis and decomposition as only a small amount of particulate matter is expelled from the system. Thus, AnMBR reactors are expected to be operated efficiently with short HRT and high solids retention time (SRT) at low temperatures, as nearly absolute biomass retention is obtained within the reactor in comparison to conventional digesters [99,100]. The AnMBR can be subcategorised based on the location of the membrane as external cross-flow, internal submerged, or external submerged. Fouling of the membrane, mainly as a result of organic matter adsorption, inorganic matter precipitation and microbial cells adhesion to the membrane surface, is considered as the common challenge for all configurations. Reactor subcategories, effects of HRT and SRT as well as fouling control has been thoroughly reviewed [98]. Although the AnMBR is capable of both high and low strength waste treatment, high strength wastes have received scant attention in the literature, with little application to whiskey distillery/brewery waste. It has however been shown that 0.53 m^3 CH_4/kg COD removal biogas yield is achievable under mesophilic conditions for AnMBR AD of brewery wastewater [8].

3.2.3. Upflow anaerobic sludge blanket reactor

UASB reactors, which are considered high rate anaerobic digesters, were invented in the 1970s by observing development of sludge into granules which causes self-separation of active sludge from feedstock [76]. As a result, a sludge bed and overlying granules, called a 'sludge blanket' is developed within the reactor, which can support active biofilms, while feed enters through the bottom of the reactor and flows upward. A gas–liquid–solid separator is necessary to ensure that solid granular sludge is retained in the system while gas and liquid effluent are removed [101,102].

UASBs are one of the most popular high rate anaerobic digester configurations with many examples of full scale and lab scale operation for treatment of highly recalcitrant brewery and whiskey distillery pot ale [8,23,103–105]. The efficiency of the reactor mainly relies on existence of settleable active granules which consist of aggregated self-immobilised anaerobic bacteria into compact form. Satisfactory level of methanogen retention in the system provides high digestion potential in terms of COD removal and methane yield as well as a better quality of effluent [23,30,76,105]. OLR is another major parameter which impairs microbial ecology within the UASB and, correspondingly, the performance of the reactor. Accumulation of VFAs and insufficient (too short) HRT for giving enough time to the microbes to degrade the substrate are considered the main reasons of this limitation [74]. For instance, UASB has been operated at varied OLRs (HRT was fixed to 2.1) for 250 days by Ref. [18].

Proximity of the syntrophic microorganisms, for instance hydrogen producing microorganisms (acidogens and acetogens) and hydrogen utilization (methanogens) has a significant role on both overall reactor performance and degree of granulation [94,95,106]. The Investigation of the AD process has been separated into two stages; first where hydrolysis, acidification, and liquefaction takes place and next, where acetate, hydrogen, and carbon dioxide are converted into methane [74,95,101]. The main advantages of UASB are good removal efficiency at low temperatures, low energy consumption, low sludge production, ability of long term preservation of inoculum, good mixing. In terms of disadvantages strict temperature control is required, partial remove of pathogens, and working with relatively low OLR [107].

3.2.4. Expanded granular sludge blanket (EGSB)

The UASB reactor was upgraded in terms of hydrodynamics by increasing (i) capacity of accommodating high organic and hydraulic loadings, (ii) treating wastewaters containing lipids and toxic/inhibitory compounds and (iii) feasibility of acidifying wastewaters under psychrophilic conditions [76]. This new variation of UASB, called expanded granular sludge blanket (EGSB), provides more advantages over a conventional UASB via special use of granular sludge, greater mixing and slight bed expansion due to the higher up-flow velocities and improved mass transfer between substrate and sludge aggregates due to increased stability of granular biofilms [59,108].

A relatively higher upflow superficial velocity (4–10 m/h versus 0.6–1.79 m/h) is a distinctive feature for EGSB. This is obtained by a height/diameter ratio of the reactor or/and by the recycling of the effluent, thus preventing the failure of the reactor because of accumulation of inhibitory compounds at the influent portion of the reactor [76,109]. Operation at high upflow velocity provides a better hydraulic mixing than the levels that can be achieved by UASB, it also minimises the blind areas within the reactor. Therefore it enhances the diffusion of substrate from the bulk to the granule biofilms and results in improved biodegradation of substrate [110]. Application of EGSB is commonly seen on large scale (bench and full scales) treatments of wide range of strength (low strength as well as medium and high) feedstock [59,76,102,110]. However, the removal of suspended solids may not be performed very well [59]. Operation of full scale EGSB at 5.15 ± 2.18 kg COD/m^3day OLR for AD of brewery waste water and spent yeast mix resulted in a biogas generation rate of 2.59 ± 1.12 m^3/m^3 day and 82.1 ± 3.9% methane conversion [102]. However, EGSB has received a scant attention in the literature to the date.

3.3. Anaerobic reactors with phase separation

3.3.1. Granular bed anaerobic baffled reactor (GRABBR)

The GRABBR is a hybrid reactor, which combines the advantages of anaerobic baffled reactor (ABR) and the UASB by using anaerobic phase separation and granular biomass characteristics. It is therefore considered an upgraded version of UASB empowered with the ability of phase separation of ABR due to the existence of compartmentalization [16,30]. The GRABBR has shown a superior process stability compared to the UASB at high OLR in a comparative studies [111]. The UASB has already been discussed, but the ABR has not been applied for whiskey distillery/brewery wastes so there is no section for it specifically. However [112], summarized it from different aspects.

In the structure of GRABBR wastewater is forced up through the sludge blanket and this flow characteristic results in a horizontal movement (gentle rising and settling with a slower rate) of the bacteria within the reactor. This movement enhances the phase separation within the GRABBR and allows bacteria to develop under the most favourable conditions by separating acidogenesis and methanogenesis longitudinally down the reactor [59,76,113]. The division of different microbial communities is also seen by Ref. [16] where front compartments are occupied by acidogens, whereas methanogens are dominant in the rear compartments. In the poor settling of GRABBR, acidogenic sludge occurs upstream of the granular methanogenic sludge zone, eventually, preventing the wash out of the former with the influent from the reactor and so enhances process stability [76]. Accordingly, GRABBR is considered as a solution to two stage anaerobic reactor expenses [113]. It has been operated for AD of high strength distillery wastewater (with a COD range of 16 600–58000 mg/L) and 80–92% CH_4 conversion was achieved, with an OLR rate of kg 4.75 COD/m^{3}day [111]. Despite the advantages of GRABBR over conventional high rate digesters, it has again received scant attention to the date for AD of whiskey distillery/brewery wastes.

4. Current application of AD technology at industrial scale for distillery wastes

Although anaerobic digestion technology is commonplace e.g. for municipal wastewater, industrial scale implementation for whiskey distilleries or breweries has not been widely utilised. Scotland is the most progressive, with several companies applying anaerobic digestion as a waste and energy management method. The Scottish Whiskey Association targets to deliver 20% of the primary energy requirements from sustainable energy sources by 2020, with a further aim of 80% by 2050 [118].

Diageo is the largest UK whiskey distiller with 28 malt distilleries and 1 grain distillery in Scotland. Diageo's Dailuaine Distillery uses pot ale to generate biogas then used in a Combined Heat & Power (CHP) to produce electricity and steam for use in their on-site distillery dark grains plant since 2010. The AD plant produces 0.5 MW of biogas, providing 40% of electrical demand for the site as well as reducing CO_2 emissions by 250 tonnes. The solid fraction of the digestate is used as bio fertiliser whereas the liquid part can be discharged to river, meeting the regulatory requirements for discharge [119]. Diageo's Roseisle Distillery also recovers 8.6 mW of energy, which is equivalent to about 84% of its total steam load requirement, by a combination of biomass combustion and anaerobic digestion as well as reducing the potential CO_2 emission by approximately 13 000 tonnes [120,121]. Meanwhile Cameronbridge Distillery in Fife is estimated to produce 30 MW of energy recovers 95% of site electricity and 98% of the total steam demand through an anaerobic digestion and a combined heat and power plant [121,122]. Glendullan Distillery at Duffton treats approximately 1000 m^3 malt whiskey by-products per day with the capacity of producing 8000 MWh of thermal energy for the distillery, which allows about 1 million m^3 biogas generation annually [122,123]. William Grant & Sons Distillery has a capacity of producing renewable energy in the form of 25 MWh of heat and 60 MWh of electricity on a daily basis by burning the produced biogas in the turbines. A reduction in the level of COD in the plant effluent was achieved as a result of the implementation of anaerobic digestion [120]. The North British Distillery also aims to generate up to 1 MW of renewable electrical energy and reduce CO emissions by 9000 tonnes per year which is equivalent of removing 3000 cars from street. Glenmorangie Tain distillery performed onsite feasibility studies to construct a membrane based AD plant in 2016 [124]. Since then, 95% COD was removed from the aqueous waste stream. Over a 10 year period, it is predicted that 12 million tonnes of water will be treated to remove 45 000 tonnes of COD from the discharge. Utilising the generated biogas will reduce the CO_2 emissions by 2.7 million kg CO_2 annually [124]. Slane Distillery, established in 2017, is the only distillery in Ireland utilising AD (an EGSB reactor) for biogas generation and sludge biofertilizer production [125]. Introducing a pre-treatment step prior to AD could provide a further enhancement in both biogas and waste treatment yields based on significantly higher biogas production and organic matter removal levels in previously published studies.

5. Co-digestion strategy and pre-treatmens for AD of distillery/brewery waste

Co-digestion (simultaneous digestion of two or more organic matters simultaneously) has some advantages over mono digestion such as mitigation of the inhibitory effects by dilution, enhancement of the C:N ratio and the balance of nutrients and improvement of methane production kinetics, operating at a higher OLR [126]. It has been recently reported that the brewery wastes, in particular, are considered as an attractive feedstock for anaerobic co-digestion [127]. Composition and properties of the substrates are the critical factors directly affecting anaerobic co-digestion (AcoD). Readily degradable materials can be selected as co-substrate as well as the materials which have slower biodegradation [126].

AcoD not only results in a greater CH_4 yield per unit COD input than the mono-digestion due to the synergetic effect of the different substrates, but it can also enhance the biogas generation kinetics by changing final biodegradability as a result of weakening the effect of intermediate inhibitory compounds [128,129]. Consequently, scientific and commercial interest in AcoD has risen significantly. Available co-substrates, digester capacity, process parameters and performance in full scale AcoD studies have recently been reviewed by Ref. [127].

Research into AD pre-treatments over the past 30 years has focused on chemical, biological, mechanical and thermal processes; with the aim of enhancing organic compound solubilisation and biodegradability of the feed stream, in order to obtain a higher methane yield and improve the rate of hydrolysis. Those pre-treatments offer a deep modification, weakening the molecular bonds between lignin and carbohydrates by reducing the degree of polymerisation. Thus, an increased surface area is obtained for bacterial attack [15,45,46,130,131].

To investigate the influence of pre-treatments, the biomethane potential test (BMP test), which is a standard method developed based upon DIN 2006; ISO 1995, is commonly used. This method provides information about the cumulative amount of biogas generated as well as rate of its production [132,133]. It can be seen from Fig. 5 that a pre-treatment method can increase the rate of anaerobic digestion (case b) or can increase the methane yield (case c) in comparison to the non-treated substrate (case a).

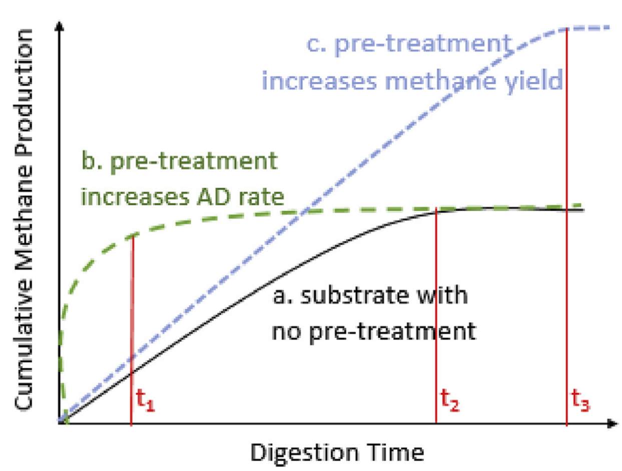

Fig. 5. *Effects of pre-treatments on rate of anaerobic digestion and total methane production (Adopted from* Ref. [134]*).*

As has been seen in previous sections whiskey distillery and brewery waste streams are mainly composed of cellulose, hemicelluloses and lignin. Three different phenylpropanoid units are seen in the amorphous structure of lignin due to the fact that cellulose and hemicellulose are physically protected from degradation which render lignin resistant to hydrolysis stage of AD process. Furthermore, the crystalline complex structure of cellulose is highly recalcitrant. Pre-treatments are therefore needed to modify or remove structural obstacles prior to hydrolysis stage [6,19,135–138]. Fig. 6 illustrates the structure of the lignocellulosic materials before and after pre-treatment.

Cellulose is inaccessible to enzymes in the structure of lignocellulosic materials, such as spent grain of whiskey distillery/brewery wastes. This results in the decrease of the rate of hydrolysis step of AD as has already discussed. During the pre-treatment of the feedstock, reduction in the crystalline structure of cellulose molecules and degree of polymerisation is achieved in addition to removal of lignin and hemicellulose [139].

5.1. Chemical pre-treatment

Chemical pre-treatment, which is considered a cost effective method for maximising biodegradation of complex materials, is used to degrade organic compounds by means of strong acids, alkalis, bicarbonates or peroxide [27,140]. Based upon the kinetics of the reactions, the acidogenesis step takes place at higher rate than acetogenesis and methanogenesis. Therefore, the accumulation of excess production of volatile fatty acids, especially acetate, potentially impairs the balance of reactors [95,141]. This occurs as a result of the lack of capability of methanogens of removing hydrogen and volatile organic acids rapidly enough [142]. In order to overcome the sharp drop of pH, the alkalinity of sodium/potassium bicarbonates or carbonate salts (sodium, potassium) are commonly used as those chemicals are capable to release bicarbonate directly or produced hydrogen can be bound to carbonates, respectively [46,47,95]. Furthermore an increase of over two fold in the removal percentages of total solids (from 31 to 37%) and VS (from 40 to 84%) of AD of barley was achieved due to the implementation of NaOH pre-treatment as well as reaching full methanation potential [143]. The necessity of adding alkali supplements, such as $NaHCO_3$ and NH_4Cl, is seen in the literature of anaerobic digestion of whiskey distillery/brewery wastes in order to overcome unbalanced operational pH as well as to modify the acidic nature of pot ale. Alkali pre-treatment appears to be the most commonly applied pre-treatment method for whiskey distillery/brewery waste streams since it provides a rapid increase in saccharification even at ambient temperature. Moreover, it is a more effective method in breaking the ester bonds between lignin and cellulose along with preventing hemicellulose fragmentation than acid pre-treatment and usage of oxidative reagents [144].

Acid pre-treatments of lignocellulosic materials, on the other hand, is generally achieved by using H_2SO_4, HCl, HNO_3, providing high hemicellulose and cellulose solubilisation; however acid pre-treatment is typically not seen to be effective in dissolving lignin except in the cases of high concentrations (30–70%) [145]. Moreover it enhances hydrolysis of cellulose and hemicellulose into monosaccharides, while the lignin condenses and precipitates [34,40]. Around 20% and 70% protein and fibre respectively are seen in the structure of brewery spent grain [146] and lignin hinders the hydrolysis of fibre. Acids may also be effective at preventing potential ammonia inhibition as a result of digestion of protein content. Acid pre-treatment is therefore considered a suitable method for brewery spent grain [15,34,147]. However not many examples of acid pre-treatment have been seen for whiskey distillery by-products in particular. It can be associated with the high risks of corrosion problems in industrial applications as well as formation of several types of inhibitors such as carboxylic acids, furans and phenolic compounds which inhibit the microbial growth and fermentation [147].

5.2. Mechanical pre-treatment

Mechanical pre-treatments are generally achieved by special devices such as grinder, mill, high shear homogeniser or screw press, and result in increasing the surface area of the lignocellulosic matter. By increasing the surface area, this allows better interaction between the anaerobic bacteria and the substrate which enhances the hydrolysis yield by 5–25% for lignocellulosic materials [40], and subsequently the overall anaerobic digestion yield [148]. Mechanical pre-treatment methods are preferred as they are promising for maximising degradation of total suspended solids by up to 90% [40]. The high shear homogeniser is the only mechanical pre-treatment applied on brewery spent grain in the literature. This fragmented the substrate by recirculating it through high shear field, resulting in particle size smaller than 0.5 mm. Mechanically pre-treated brewery spent grain achieved 69.6% average COD removal with an average biogas production rate of 1.10 m^3/m^3 day, although it was inhibited with the phenolic compounds mainly p-cresol [35].

Moreover, as no odour is generated, it has an easy application and typically leads to greater dewaterability of the final anaerobic residue [149]. However, It has been shown that excessively small particle size, which occurs as a result of mechanical pre-treatments, might accelerate production of volatile fatty acids which might possibly cause process imbalance [150].

5.3. Biological pre-treatment

Biological pre-treatment methods include both aerobic and anaerobic methods, besides the addition of specific enzymes such as peptidase, carbohydrolase, lipase or a certain type of bacteria such as hydrolytic bacteria to the AD system [40]. Among known biological pre-treatments methods, addition of enzyme is the only one that has been applied in the literature to whiskey distillery/brewery waste streams. Enzymatic hydrolysis as a biological pre-treatment technique can accelerate the degradation of complex organic matter. Commercial enzymes such as lyticase, alpha amylase, cellulase, beta-glucosidase, beta-glucanase, lipase, protease, enzyme complex and papain have been used for AD of pot ale in order to support microorganisms. This results in higher yields of monosaccharides, and correspondingly better yields of biochemical reactions in subsequent steps of AD [23,48,82]. Moreover, a significant (> 87%) COD reduction has been achieved by implementation of enzymatic pre-treatment prior to AD [23].

Enzymatic pre-treatment is considered an efficient method for

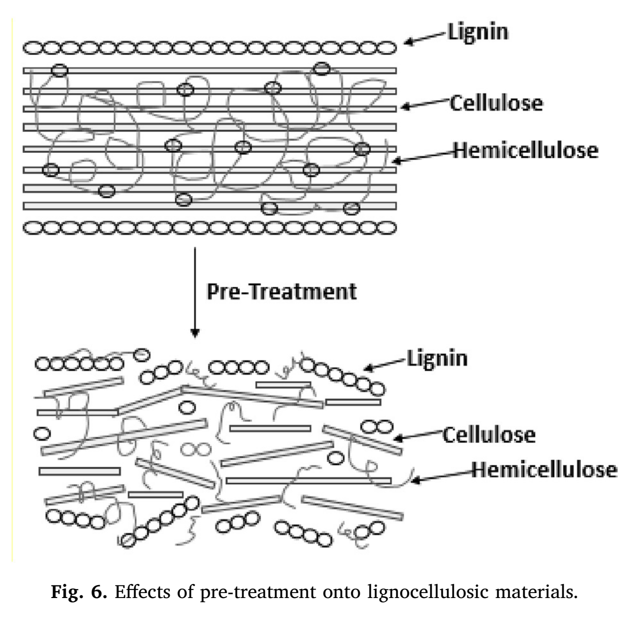

Fig. 6. Effects of pre-treatment onto lignocellulosic materials.

breaking the lignocellulosic materials into their component monomers in an environmental friendly way [151]. In addition, it provides solubilisation of phenolic compounds so avoiding their potential inhibitory effect on biogas yield [152]. Therefore, enzymatic pre-treatment overcomes the drawbacks of chemical pre-treatments such as side product formation (furfurals, levulinic acid or formic acid) [147]. On the other hand, it requires a much longer treatment time and a higher operation cost for maintaining constant temperature during the treatment [153].

5.4. Thermal pre-treatment

Thermal pre-treatment is one of the most studied pre-treatment methods, and has been successfully applied as a conditioning process for the sludge at industrial scale as it improves the pathogen elimination, the dewaterability of the wastes and reduces the viscosity of the digestate [15,40]. The main effect of thermal pre-treatment is dispersion of cell membranes, therefore resulting in solubilisation of organic compounds. COD solubilisation and temperature have a direct correlation; higher solubilisation can be obtained at lower temperatures, but longer treatment time is necessary [68,78]. Coupling thermal and chemical pre-treatments might result in higher AD yield [45,149]. However, production of inhibitory matters, mainly in form of phenolic compounds originating from lignin content, should also be controlled [35]. Another potential inhibition due to the high temperature thermal pre-treatment (> 110 °C) or long interaction time at low temperature thermal pre-treatment is usually associated with the Maillard reactions between amino acids and carbohydrates. This results in the generation of complex substrates, melanoidins, which are difficult to degrade [154]. An average of 70.4% COD removal was achieved although the reactor was inhibited in the early stage of AD which indicates increased rate of hydrolysis [35].

Advantages and disadvantages of pre-treatments used for whiskey distillery/brewery wastes are summarized in Table 5.

6. Research gaps, future prospects and practical implications

Although anaerobic digestion is a promising sustainable technology for whiskey distillery and brewery waste management, there are several obstacles that challenge scaling up to industrial level. The major challenge is considered to be the predominance of empirical methodologies in the fundamental studies of AD of whiskey distillery wastes. Moreover, the pre-treatment aspect of the process has received a very scant attention in literature to the date. The link between applicability of the pre-treatment at micro and macro scale is non-existent with respect to its impacts on the whole system. Although commonly used batch tests establish the methane production under specific pre-treatment and digestion conditions, it may fail to give accurate predictions for full scale AD performance due its dependency on inoculum type, the ratio of inoculum to substrate used, and the different reactor configurations [45]. For the full-scale application, it can be challenging to maintain long term operation with microbiological stability during biogas production as well as during subsequent re-use of inoculum [92], whereas it is replaced with a fresh supply for lab/bench scale applications. In order to increase the accuracy of the prediction for scaling up purposes, enhanced experimental methodologies should be followed evaluating mass transfer fluxes, actual kinetics involved in microbial growth and organic material conversion, the hydrodynamic behaviour of the selected reactor configuration as well as a deep investigation into the biochemistry and microbiology of the AD process [48]. A progressive scale-up of the process could be achieved with the aid of computer simulation tools. A well-established simulation process can enable the investigation of various scenarios in a short period of time. The state of art model for AD is considered to be the ADM1 model which takes into account carbon, nitrogen balance of the substrate, reaction kinetic for bacterial decay and organic matter degradation, reactor hydrodynamic as well as several potential inhibition factors such as volatile fatty acids, dissolved hydrogen and ammonia [159]. The technology-integrated experimental approach could increase the accuracy of biogas yield predictions for full scale applications to obtain a more reliable design. It is therefore advised as the next step to take for the industrial modelling of various types of pre-treatments prior to anaerobic digestion.

7. Conclusions

As outlined in this review, whiskey and beer manufacturing processes generate large amounts of organic waste. AD appears to be a sustainable treatment alternative method over conventional aerobic wastewater treatment processes and land spreading by means of converting the organic matter into methane. This can further be converted to an energy source and eventually be utilised in alcohol production. Different reactor configurations from lab scale to full scale which have been utilised for AD of whiskey distillery/brewery wastes are critically reviewed in order to define the required operation parameters to

Table 5
Advantages and disadvantages of applied pre-treatment method onto distillery/brewery waste.

Pre-treatment	Method	Advantages	Disadvantages	Reference
Chemical	Alkali	Reduction in degree of polymerisation crystallinity of cellulose	Long interaction time required	[155]
		Partial hydrolysis and solubilisation of hemicellulose and lignin	Formation of irrecoverable salts	[138]
	Acid	High hemicellulose solubilisation, condensation and precipitation lignin	Might cause production of inhibitory by-	[148,156]
		Increases surface area	products, such as furfural,	
		Low capital cost	hydroxymethylfurfural	
			High operation expense for large scale	[157]
			Corrosion problems	[147]
Mechanical	High shear homogeniser	Increases accessible surface area	High start-up cost	[15,40,138]
		No requirement for organic solvent	Demand on electricity	
		Provides implementation on large scale	No significant pathogen removal	
		No odour problem		
		Better dewaterability of final anaerobic residue		
Biological	Enzymatic	No harsh chemicals required	Slow processing	[147]
		Low electricity/heat consumption	High cost of enzymes	[138]
		No restriction of specific digester	Continuous addition demand	[23]
		Environmentally friendly		[82]
Thermal	High temperature (> 110)	Gel structure degradation and cell wall lysis	Generating inhibitory intermediates through Maillard reaction	[47,148,158]
		Most likely ensure process stability		[15]
		Increase specific surface area	High energy demand	

achieve a balanced digestion of these lignocellulosic streams. The major focus of all pre-treatments is to render lignocellulosic structures accessible to enzymatic attack by means of reducing the cellulose crystallinity, the lignin protection and increasing its surface area in order to achieve sufficient hydrolysis. Examples of successful industrial applications of anaerobic digestion particularly for treatment of whiskey distillery waste streams are seen in Scotland which provides a significant reduction in CO_2 emission as well as sustainable waste management for distilleries. Despite the structural difficulties of AD, the literature analysis indicates that there is a great potential for the use of whiskey distillery/brewery wastes as feedstock for anaerobic digestion in respect of both environmental and energy recovery considerations. The recalcitrant nature of lignocellulosic structure can be addressed by application of appropriate pre-treatment methods prior to anaerobic digestion as well as adopting ideal operation parameters for the reactor. The current research stage of AD technology as a sustainable waste/energy management method for whiskey distilleries and breweries including different reactor configurations and most importantly the effects of applied pre-treatment on substrate structure were discussed, however there is a significant lack of research in this area which needs to be addressed. Despite promising results at bench scale, no examples of pre-treatment technologies at industrial scale were seen. Techno-economic and logistics assessments for scale-up are vital for implementation, however the lack of scaleable data from published studies remains a barrier to widespread adoption of this potentially energy-efficient waste management approach.

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References

[1] Bundhoo MAZ, Mohee R, Hassan MA. Effects of pre-treatment technologies on dark fermentative biohydrogen production: a review. J Environ Manag 2015;157:20–48. https://doi.org/10.1016/j.jenvman.2015.04.006.
[2] Bryngelsson D, Wirsenius S, Hedenus F, Sonesson U. How can the EU climate targets be met? A combined analysis of technological and demand-side changes in food and agriculture. Food Policy 2016;59:152–64. https://doi.org/10.1016/j.foodpol.2015.12.012.
[3] Ghanavati H, Nahvi I, Karimi K. Organic fraction of municipal solid waste as a suitable feedstock for the production of lipid by oleaginous yeast cryptococcus aerius. Waste Manag 2015;38:141–8. https://doi.org/10.1016/j.wasman.2014.12.007.
[4] Dionisi D, Bruce SS, Barraclough MJ. Effect of pH adjustment, solid–liquid separation and chitosan adsorption on pollutants' removal from pot ale wastewaters. J Environ Chem Eng 2014. https://doi.org/10.1016/j.jece.2014.08.013.
[5] Saha NK, Balakrishnan M, Batra VS. Improving industrial water use: case study for an Indian distillery. Resour Conserv Recycl 2005;43:163–74. https://doi.org/10.1016/j.resconrec.2004.04.016.
[6] Aliyu S, Bala M. Brewer's spent grain: a review of its potentials and applications. Afr J Biotechnol 2013;10:324–31. https://doi.org/10.4314/ajb.v10i3.
[7] Acharya BK, Mohana S, Madamwar D. Anaerobic treatment of distillery spent wash - a study on upflow anaerobic fixed film bioreactor. Bioresour Technol 2008;99:4621–6. https://doi.org/10.1016/j.biortech.2007.06.060.
[8] Chen H, Chang S, Guo Q, Hong Y, Wu P. Brewery wastewater treatment using an anaerobic membrane bioreactor. Biochem Eng J 2016;105:321–31. https://doi.org/10.1016/j.bej.2015.10.006.
[9] Pant D, Adholeya A. Biological approaches for treatment of distillery wastewater: a review. Bioresour Technol 2007;98:2321–34. https://doi.org/10.1016/j.biortech.2006.09.027.
[10] Brewers Association. Craft beer industry market segments. 2018https://www.brewersassociation.org/statistics/market-segments/.
[11] Feeney B. Craft beer and microbreweries in Ireland , 2016 a report for the independent craft brewers of Ireland and bord bia final report , August 2016 number of production microbreweries by year bernard feeney , economic consultant. 2016.
[12] Brendan F. Craft beer and microbreweries in Ireland in 2017" a report for bord bia and the independent craft brewers of Ireland. A rep bord bia indep Cr brew Ireland 2017 accessed http://www.bordbia.info/Craft-Beer-2017/#p = 4, Accessed date: 1 July 2018.
[13] ABFI. Whiskey industry in Ireland. 2018 accessed http://www.abfi.ie/Sectors/ABFI/ABFI.nsf/vPagesWhiskey/Industry_in_Ireland ~ whiskey-industry-in-ireland!OpenDocument, Accessed date: 1 July 2018.
[14] Liao X, Li H, Zhang Y, Liu C, Chen Q. Accelerated high-solids anaerobic digestion of sewage sludge using low-temperature thermal pretreatment. Int Biodeterior Biodegrad 2016. https://doi.org/10.1016/j.ibiod.2015.10.023.
[15] Cesaro A, Belgiorno V. Pretreatment methods to improve anaerobic biodegradability of organic municipal solid waste fractions. Chem Eng J 2014;240:24–37. https://doi.org/10.1016/j.cej.2013.11.055.
[16] Akunna JC, Clark M. Performance of a granular-bed anaerobic baffled reactor (GRABBR) treating whisky distillery wastewater. Bioresour Technol 2000;74:257–61.
[17] Handous N, Gannoun H, Hamdi M, Bouallagui H. Two-stage anaerobic digestion of meat processing solid wastes: methane potential improvement with wastewater addition and solid substrate fermentation. Waste Biomass Valoriz 2017;0:1–12. https://doi.org/10.1007/s12649-017-0055-2.
[18] Goodwin JAS, Finlayson JM, Low EW. A further study of the anaerobic biotreatment of malt whisky distillery pot ale using an UASB system. Bioresour Technol 2001;78:155–60.
[19] Raud M, Tutt M, Olt J, Kikas T. Dependence of the hydrolysis efficiency on the lignin content in lignocellulosic material. Int J Hydrogen Energy 2015;41:16338–43. https://doi.org/10.1016/j.ijhydene.2016.03.190.
[20] Weiß S, Tauber M, Somitsch W, Meincke R, Müller H, Berg G, et al. Enhancement of biogas production by addition of hemicellulolytic bacteria immobilised on activated zeolite. Water Res 2010;44:1970–80. https://doi.org/10.1016/j.watres.2009.11.048.
[21] Graham J, Peter B, Walker G. Characterisation of the pot ale profile from a malt whisky distillery. Distill Spirits Sci Sustain 2012;43:1–7.
[22] Ferreira IMPLVO, Pinho O, Vieira E, Tavarela JG. Brewer's Saccharomyces yeast biomass: characteristics and potential applications. Trends Food Sci Technol 2010;21:77–84. https://doi.org/10.1016/j.tifs.2009.10.008.
[23] Mallick P, Akunna JC, Walker GM. Anaerobic digestion of distillery spent wash: influence of enzymatic pre-treatment of intact yeast cells. Bioresour Technol 2009;101:1681–5. https://doi.org/10.1016/j.biortech.2009.09.089.
[24] Tokuda M, Ohta N, Morimura S, Kidaz K. Methane fermentation of pot ale from a whisky distillery after enzymatic or microbial treatment. J Ferment Bioeng 1998;85:495–501.
[25] Ansa-Asare OD, Marr IL, Cresser MS. Evaluation of modelled and measured patterns of dissolved oxygen in a freshwater lake as an indicator of the presence of biodegradable organic pollution. Water Res 2000;34:1079–88. https://doi.org/10.1016/S0043-1354(99)00239-0.
[26] Ravikumar R, Vasanthi N S, Saravanan K. Single factorial experimental design for decolorizing anaerobically treated distillery spent wash using Cladosporium cladosporioides. Int J Environ Sci Technol 2010;8:97–106. https://doi.org/10.1007/BF03326199.
[27] Aboerheeba AKM. Novel approach to pre-treatment of agricultural products and food waste to improve biogas production. 2013.
[28] Sangave PC, Pandit AB. Ultrasound pre-treatment for enhanced biodegradability of the distillery wastewater. Ultrason Sonochem 2004;11:197–203. https://doi.org/10.1016/j.ultsonch.2004.01.026.
[29] Ramana S, Biswas AK, Singh AB. Effect of distillery effluents on some physiological aspects in maize vol. 84. 2002. https://doi.org/10.1016/S0960-8524(02)00053-6.
[30] Mohana S, Acharya BK, Madamwar D. Distillery spent wash: treatment technologies and potential applications. J Hazard Mater 2009;163:12–25. https://doi.org/10.1016/j.jhazmat.2008.06.079.
[31] Sankaran K, Premalatha M, Vijayasekaran M, Somasundaram VT. DEPHY project: distillery wastewater treatment through anaerobic digestion and phycoremediation - a green industrial approach. Renew Sustain Energy Rev 2014;37:634–43. https://doi.org/10.1016/j.rser.2014.05.062.
[32] Goodwin JAS, Stuart JB. Anaerobic digestion of malt whisky distillery pot ale using upflow anaerobic sludge blanket reactors. Bioresour Technol 1994;49:75–81. https://doi.org/10.1016/0960-8524(94)90175-9.
[33] Mussatto SI, Dragone G, Roberto IC. Brewers' spent grain: generation, characteristics and potential applications. J Cereal Sci 2006;43:1–14. https://doi.org/10.1016/j.jcs.2005.06.001.
[34] Panji M, Drago G, Zeli B. Anaerobic biodegradation of raw and pre-treated brewery spent grain utilizing solid state anaerobic digestion. 2015. p. 818–27. https://doi.org/10.17344/acsi.2015.1534.
[35] Sežun M, Zupančič GD, Logar RM, Grilc V. Anaerobic digestion of brewery spent Grain : inhibition by phenolic degradation products. 2000. p. 158–66.
[36] Neves L, Oliveira R, Alves MM. Anaerobic co-digestion of coffee waste and sewage sludge. Waste Manag 2006;26:176–81. https://doi.org/10.1016/j.wasman.2004.12.022.
[37] Öztürk S, Ö Özboy, Ox D, Köksel H, Brew JI. Effects of brewer's spent grain on the quality and dietary fibre content of cookies. J Inst Brew Brew 2002;108:23–7.
[38] Hamill A. National waste prevention programme 2014-2018 final report for green enterprise programme (GEP) phase 2 improved treatment of distillery wastes vols. 1–58. 2015.
[39] Kamalinasab M, Vakili A, Mesgaran MD, Valizadeh R, Nabavi SR. Modelling Anaerobic Digestion of Cow Manure to predict Methane Flow Rate: discovery Service para Timbó. Iran J Appl Anim Sci 2016;6:525–33.
[40] 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. https://doi.org/10.1016/j.apenergy.2014.02.035.
[41] Boe K. Online monitoring and control of the biogas process. 2006. doi:nei-dk-4757.pdf.
[42] Petersson A. Wellinger a. Biogas upgrading technologies–developments and innovations. IEA Bioenergy 2009:20.
[43] Jáuregui-Jáuregui JA, Méndez-Acosta HO, González-Álvarez V, Snell-Castro R, Alcaraz-González V, Godon JJ. Anaerobic treatment of tequila vinasses under

seasonal operating conditions: start-up, normal operation and restart-up after a long stop and starvation period. Bioresour Technol 2014;168:33–40. https://doi.org/10.1016/j.biortech.2014.04.006.
[44] Li H, Li C, Liu W, Zou S. Optimized alkaline pretreatment of sludge before anaerobic digestion. Bioresour Technol 2012;123:189–94. https://doi.org/10.1016/j.biortech.2012.08.017.
[45] Carlsson M, Lagerkvist A, Morgan-Sagastume F. The effects of substrate pre-treatment on anaerobic digestion systems: a review. Waste Manag 2012;32:1634–50. https://doi.org/10.1016/j.wasman.2012.04.016.
[46] Nayono SE. Anaerobic digestion of organic solid waste for energy production. 2009.
[47] Appels L, Baeyens J, Degrève J, Dewil R. Principles and potential of the anaerobic digestion of waste-activated sludge. Prog Energy Combust Sci 2008;34:755–81. https://doi.org/10.1016/j.pecs.2008.06.002.
[48] Moraes BS, Zaiat M, Bonomi A. Anaerobic digestion of vinasse from sugarcane ethanol production in Brazil: challenges and perspectives. Renew Sustain Energy Rev 2015;44:888–903. https://doi.org/10.1016/j.rser.2015.01.023.
[49] O'Flaherty V, Collins G, Mahony T. The microbiology and biochemistry of anaerobic bioreactors with relevance to domestic sewage treatment. Rev Environ Sci Biotechnol 2006;5:39–55. https://doi.org/10.1007/s11157-005-5478-8.
[50] Ziemiński K, Frąc M. Methane fermentation process as anaerobic digestion of biomass: transformations, stages and microorganisms. Afr J Biotechnol 2014;11:4127–39. https://doi.org/10.5897/AJBX11.054.
[51] Collins G, Woods A, McHugh S, Carton MW, O'Flaherty V. Microbial community structure and methanogenic activity during start-up of psychrophilic anaerobic digesters treating synthetic industrial wastewaters. FEMS Microbiol Ecol 2003;46:159–70. https://doi.org/10.1016/S0168-6496(03)00217-4.
[52] Madsen M, Holm-Nielsen JB, Esbensen KH. Monitoring of anaerobic digestion processes: a review perspective. Renew Sustain Energy Rev 2011;15:3141–55. https://doi.org/10.1016/j.rser.2011.04.026.
[53] Wirth R, Kovács E, Maróti G, Bagi Z, Rákhely G, Kovács KL. Characterization of a biogas-producing microbial community by short-read next generation DNA sequencing. Biotechnol Biofuels 2012;5:41. https://doi.org/10.1186/1754-6834-5-41.
[54] Leitão RC, Van Haandel AC, Zeeman G, Lettinga G. The effects of operational and environmental variations on anaerobic wastewater treatment systems: a review. Bioresour Technol 2006;97:1105–18. https://doi.org/10.1016/j.biortech.2004.12.007.
[55] Science W, Wijhe BK, Hgw B, Soiltech H. Metabolic interactions in methanogenic and sulfate-reducing bioreactors 2005.
[56] Fricke K, Santen H, Wallmann R, Hu A, Dichtl N, Dinitrous NO. Operating problems in anaerobic digestion plants resulting from nitrogen in MSW vol. 27. 2007. p. 30–43. https://doi.org/10.1016/j.wasman.2006.03.003.
[57] Li Y, Park SY, Zhu J. Solid-state anaerobic digestion for methane production from organic waste. Renew Sustain Energy Rev 2011;15:821–6. https://doi.org/10.1016/j.rser.2010.07.042.
[58] Wang K, Yin J, Shen D, Li N. Anaerobic digestion of food waste for volatile fatty acids (VFAs) production with different types of inoculum: effect of pH. Bioresour Technol 2014;161:395–401. https://doi.org/10.1016/j.biortech.2014.03.088.
[59] 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. https://doi.org/10.1016/j.rser.2015.02.032.
[60] Wu X, Yao W, Zhu J, Miller C. Biogas and CH4productivity by co-digesting swine manure with three crop residues as an external carbon source. Bioresour Technol 2010;101:4042–7. https://doi.org/10.1016/j.biortech.2010.01.052.
[61] Fatma A. Alfarjani. Design and optimization of process parameters in bio-gas production systems BY fatma a . alfarjani , B . Sc a thesis submitted for the degree of master of engineering (MEng) supervisor dr. Abdul Ghani Olabi School of Mechanical and Manufacturing Engine; 2012.
[62] Ostrem K. Greening waste: anaerobic digestion for treating the organic fraction of municipal solid waste. Dep Earth Environ Eng Fu Found Sch Eng Appl Sci Columbia Univ; 2004. p. 1–59.
[63] Yang L, Xu F, Ge X, Li Y. Challenges and strategies for solid-state anaerobic digestion of lignocellulosic biomass. Renew Sustain Energy Rev 2015;44:824–34. https://doi.org/10.1016/j.rser.2015.01.002.
[64] Caye M, Phu N, Terry H. Biofuel Eng Process Technol 2008:3–351.
[65] Ogejo J, Wen Z, Ignosh J, Bendfeldt E, Collins Jr. E. Biomethane technology. Virginia Coop Ext 2009;1–11.
[66] Saady NMC, Massé DI. Psychrophilic anaerobic digestion of lignocellulosic biomass: a characterization study. Bioresour Technol 2013;142:663–71. https://doi.org/10.1016/j.biortech.2013.05.089.
[67] Kim Y, Park JM. Potentials of macroalgae as feedstocks for biorefinery. Bioresour Technol 2014;135:182–90. https://doi.org/10.1016/j.biortech.2012.10.025.
[68] Ferrer I, Ponsá S, Vázquez F, Font X. Increasing biogas production by thermal (70°C) sludge pre-treatment prior to thermophilic anaerobic digestion. Biochem Eng J 2008;42:186–92. https://doi.org/10.1016/j.bej.2008.06.020.
[69] Trent JD, Tozzi S, Trent J, Wiley P, Tozzi S, Mckuin B, et al. Research Spotlight : the future of biofuels : is it in the bag ? The future of biofuels : is it in the bag ? 2012. https://doi.org/10.4155/bfs.12.53.
[70] Khalid A, Arshad M, Anjum M, Mahmood T, Dawson L. The anaerobic digestion of solid organic waste. Waste Manag 2011;31:1737–44. https://doi.org/10.1016/j.wasman.2011.03.021.
[71] Zhou J, Zhang R, Liu F, Yong X, Wu X, Zheng T, et al. Biogas production and microbial community shift through neutral pH control during the anaerobic digestion of pig manure. Bioresour Technol 2016;217:44–9. https://doi.org/10.1016/j.biortech.2016.02.077.
[72] Montingelli M. Development and application of a mechanical pretreatment to increase the biogas produced from Irish macroalgal biomass. 2015.
[73] Kwietniewska E, Tys J. Process characteristics, inhibition factors and methane yields of anaerobic digestion process, with particular focus on microalgal biomass fermentation. Renew Sustain Energy Rev 2014;34:491–500. https://doi.org/10.1016/j.rser.2014.03.041.
[74] Aslanzadeh S, Rajendran K, Taherzadeh MJ. A comparative study between single- and two-stage anaerobic digestion processes: effects of organic loading rate and hydraulic retention time. Int Biodeterior Biodegrad 2014;95:181–8. https://doi.org/10.1016/j.ibiod.2014.06.008.
[75] Weedermann M, Seo G, Wolkowicz G. Mathematical model of anaerobic digestion in a chemostat: effects of syntrophy and inhibition. J Biol Dyn 2013;7:59–85. https://doi.org/10.1080/17513758.2012.755573.
[76] Tauseef SM, Abbasi T, Abbasi SA. Energy recovery from wastewaters with high-rate anaerobic digesters. Renew Sustain Energy Rev 2013;19:704–41. https://doi.org/10.1016/j.rser.2012.11.056.
[77] Massé D, Gilbert Y, Topp E. Pathogen removal in farm-scale psychrophilic anaerobic digesters processing swine manure. Bioresour Technol 2011;102:641–6. https://doi.org/10.1016/j.biortech.2010.08.020.
[78] Mottet A, Steyer JP, Déléris S, Vedrenne F, Chauzy J, Carrère H. Kinetics of thermophilic batch anaerobic digestion of thermal hydrolysed waste activated sludge. Biochem Eng J 2009;46:169–75. https://doi.org/10.1016/j.bej.2009.05.003.
[79] Jang HM, Cho HU, 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 2014;48:1–14. https://doi.org/10.1016/j.watres.2013.06.041.
[80] Parawira W, Murto M, Read JS, Mattiasson B. Profile of hydrolases and biogas production during two-stage mesophilic anaerobic digestion of solid potato waste. Process Biochem 2005;40:2945–52. https://doi.org/10.1016/j.procbio.2005.01.010.
[81] Degueurce A, Tremier A, Peu P. Dynamic effect of leachate recirculation on batch mode solid state anaerobic digestion: influence of recirculated volume, leachate to substrate ratio and recirculation periodicity. Bioresour Technol 2016;216:553–61. https://doi.org/10.1016/j.biortech.2016.05.113.
[82] Quiñones TS, Plöchl M, Budde J, Heiermann M. Results of batch anaerobic digestion test - effect of enzyme addition. Agric Eng Int CIGR J 2012;14:38–50.
[83] Ge X, Xu F, Li Y. Solid-state anaerobic digestion of lignocellulosic biomass: recent progress and perspectives. Bioresour Technol 2016;205:239–49. https://doi.org/10.1016/j.biortech.2016.01.050.
[84] Brown D, Li Y. Solid state anaerobic co-digestion of yard waste and food waste for biogas production. Bioresour Technol 2013;127:275–80. https://doi.org/10.1016/j.biortech.2012.09.081.
[85] Wantanasak S, Kongjan P, Imai T, O-Thong S. Biogas production from solid waste residues of palm oil mill industry by solid-state anaerobic digestion. (((Abstracts of)))The 11th Young. Sci Semin Int Res Netw Trop Bioresour Their Util 2015;95:43. https://doi.org/10.1016/j.indcrop.2016.11.002.
[86] Singh M, Srivastava RK. Sequencing batch reactor technology for biological wastewater treatment: a review. Asia Pac J Chem Eng 2011;6:3–13. https://doi.org/10.1002/apj.490.
[87] Massé DI, Masse L, Croteau F. The effect of temperature fluctuations on psychrophilic anaerobic sequencing batch reactors treating swine manure. Bioresour Technol 2003;89:57–62. https://doi.org/10.1016/S0960-8524(03)00009-9.
[88] Camargo EFM, Ratusznei SM, Rodrigues JAD, Zaiat M, Borzani W. Treatment of low-strength wastewater using immobilized biomass in a sequencing batch external loop reactor: influence of the medium superficial velocity on the stability and performance. Braz J Chem Eng 2002;19:267–75. https://doi.org/10.1590/S0104-66322002000300001.
[89] Rajagopal R, Massé DI, Singh G. A critical review on inhibition of anaerobic digestion process by excess ammonia. Bioresour Technol 2013;143:632–41. https://doi.org/10.1016/j.biortech.2013.06.030.
[90] Uzal N, Gökcay CF, Demirer GN. Sequential (anaerobic/aerobic) biological treatment of malt whisky wastewater. Process Biochem 2003;39:279–86. https://doi.org/10.1016/S0032-9592(03)00071-2.
[91] Hu J. Anaerobic digestion of sludge from brackish RAS: CSTR performance, analysis of methane potential and phosphatase. 2013. struvite crystallization.
[92] Tiwary A, Williams ID, Pant DC, Kishore VVN. Emerging perspectives on environmental burden minimisation initiatives from anaerobic digestion technologies for community scale biomass valorisation. Renew Sustain Energy Rev 2015;42:883–901. https://doi.org/10.1016/j.rser.2014.10.052.
[93] Young JC, McCarty PL. The anaerobic filter for waste treatment. J Water Pollut Control Fed 1969;41(Suppl):R160+. https://doi.org/10.2307/25036652.
[94] Saravanan V, Sreekrishnan TR. Modelling anaerobic biofilm reactors-A review. J Environ Manag 2006;81:1–18. https://doi.org/10.1016/j.jenvman.2005.10.002.
[95] Blonskaja V, Menert A, Vilu R. Use of two-stage anaerobic treatment for distillery waste. Advabces Environ Res 2003;7:671–8.
[96] Leal K, Chacin E, Behling E, Gutierez E, Fernandez N, Forster CF. A mesophilic digestion of brewery wastewater in an unheated anaerobic filter. Bioresour Technol 1998;65:51–5. https://doi.org/10.1016/S0960-8524(98)00025-X.
[97] Padmasiri SI, Zhang J, Fitch M, Norddahl B, Morgenroth E, Raskin L. Methanogenic population dynamics and performance of an anaerobic membrane bioreactor (AnMBR) treating swine manure under high shear conditions. Water Res 2007;41:134–44. https://doi.org/10.1016/j.watres.2006.09.021.
[98] Smith AL, Stadler LB, Love NG, Skerlos SJ, Raskin L. Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: a critical review.

Bioresour Technol 2012;122:149–59. https://doi.org/10.1016/j.biortech.2012.04.055.
[99] Smith AL, Skerlos SJ, Raskin L. Psychrophilic anaerobic membrane bioreactor treatment of domestic wastewater. Water Res 2013;47:1655–65. https://doi.org/10.1016/j.watres.2012.12.028.
[100] Lew B, Tarre S, Beliavski M, Dosoretz C, Green M. Anaerobic membrane bioreactor (AnMBR) for domestic wastewater treatment. Desalination 2009;243:251–7. https://doi.org/10.1016/j.desal.2008.04.027.
[101] Ahn YH, Min KS, Speece RE. Pre-acidification in anaerobic sludge bed process treating brewery wastewater. Water Res 2001;35:4267–76. https://doi.org/10.1016/S0043-1354(01)00171-3.
[102] Zupančič GD, Škrjanec I, Marinšek Logar R. Anaerobic co-digestion of excess brewery yeast in a granular biomass reactor to enhance the production of biomethane. Bioresour Technol 2012;124:328–37. https://doi.org/10.1016/j.biortech.2012.08.064.
[103] Akarsubasi AT, Ince O, Oz NA, Kirdar B, Ince BK. Evaluation of performance, acetoclastic methanogenic activity and archaeal composition of full-scale UASB reactors treating alcohol distillery wastewaters. Process Biochem 2006;41:28–35. https://doi.org/10.1016/j.procbio.2005.01.029.
[104] Harada H, Uemura S, Chen A-C, Jayadevan J. Anaerobic treatment of a recalcitrant distillery wastewater by a thermophilic UASB reactor. Bioresour Technol 1996;55:215–21. https://doi.org/10.1016/0960-8524(96)00003-X.
[105] Gao M, She Z, Jin C. Performance evaluation of a mesophilic (37 @BULLET C) upflow anaerobic sludge blanket reactor in treating distiller's grains wastewater. J Hazard Mater 2007;141:808–13. https://doi.org/10.1016/j.jhazmat.2006.07.047.
[106] McCarty PL, Smith DP. Anaerobic wastewater treatment. Environ Sci Technol 1986;20:1200–6. https://doi.org/10.1021/es00154a002.
[107] Latif MA, Ghufran R, Wahid ZA, Ahmad A. Integrated application of upflow anaerobic sludge blanket reactor for the treatment of wastewaters. Water Res 2011;45:4683–99. https://doi.org/10.1016/j.watres.2011.05.049.
[108] Lettinga G. The route of anaerobic waste (water) treatment. Environ Anaerob Technol Appl New Dev 1987:1–15. https://doi.org/10.1142/9781848165434_0001.
[109] Xing BS, Guo Q, Zhang ZZ, Zhang J, Wang HZ, Jin RC. Optimization of process performance in a granule-based anaerobic ammonium oxidation (anammox) upflow anaerobic sludge blanket (UASB) reactor. Bioresour Technol 2014;170:404–12. https://doi.org/10.1016/j.biortech.2014.08.026.
[110] Chou HH, Huang JS, Jheng JH, Ohara R. Influencing effect of intra-granule mass transfer in expanded granular sludge-bed reactors treating an inhibitory substrate. Bioresour Technol 2008;99:3403–10. https://doi.org/10.1016/j.biortech.2007.08.011.
[111] Shanmugam AS, Akunna JC. Modelling head losses in granular bed anaerobic baffled reactors at high flows during start-up. Water Res 2010;44:5474–80. https://doi.org/10.1016/j.watres.2010.06.062.
[112] Barber WP, Stuckey DC. The use of the anaerobic baffled reactor (ABR) for wastewater treatment: a review. Water Res 1999;33:1559–78. https://doi.org/10.1016/S0043-1354(98)00371-6.
[113] Baloch MI, Akunna JC. Granular bed baffled reactor (grabbr): solution to a two-phase Anaerobic digestion system. J Environ Eng 2003;129:1015–21. https://doi.org/10.1061/(ASCE)0733-9372. 2003)129:11(1015).
[114] Wang H, Tao Y, Temudo M, Bijl H, Kloek J, Ren N, et al. Biomethanation from enzymatically hydrolyzed brewer's spent grain: impact of rapid increase in loadings. Bioresour Technol 2015;190:167–74. https://doi.org/10.1016/j.biortech.2015.04.073.
[115] Gonçalves IC, Fonseca A, Morão AM, Pinheiro HM, Duarte AP, Ferra MIA. Evaluation of anaerobic co-digestion of spent brewery grains and an azo dye. Renew Energy 2015;74:489–96. https://doi.org/10.1016/j.renene.2014.08.053.
[116] Sosa-Hernandez O, Parameswaran P, Alem??n-Nava GS, Torres CI, Parra-Saldivar R. Evaluating biochemical methane production from brewer's spent yeast. J Ind Microbiol Biotechnol 2016;43:1195–204. https://doi.org/10.1007/s10295-016-1792-0.
[117] Barrena R, Traub JE, Gil CR, Goodwin JAS, Harper AJ, Willoughby NA, et al. Batch anaerobic digestion of deproteinated malt whisky pot ale using different source inocula. Waste Manag 2018;71:675–82. https://doi.org/10.1016/j.wasman.2017.06.025.
[118] Grant G, House I, Group TE. Case study - reducing reliance on fossil fuel. 2013.
[119] Scotch SWA. Whisky industry environmental strategy report 2012 SWA 2nd report to stakeholders scotch whisky and our environmental performance. 2012.
[120] Brinkerhoff WP. Future energy opportunities: a guide for distillers. 2012.
[121] Andrews J, Hancock J, Ludford-Brooks J, Murfin I, Houldsworth L, Phillips M. 125th anniversary review: some recent engineering advances in brewing and distilling. J Inst Brew 2011;117:23–32. https://doi.org/10.1002/j.2050-0416.2011.tb00439.x.
[122] Duguid L, Strachan P. Sustainable energy using anaerobic digestion of by-products: islay whisky industry case study. 2016.
[123] Clearfleau. Whiskey power: bio-energy transforms distillery sector. 2015 accessed http://clearfleau.com/diageo-whisky-power-bio-energy-transforms-distillery-sector/, Accessed date: 23 July 2018.
[124] The glenmorangie company hydro nation. Scotish environ bus award. 2017 accessed http://www.vibes.org.uk/winners-stories/2017/the-glenmorangie-company-ltd/, Accessed date: 15 August 2018.
[125] Slane WEW. Castle whiskey. 2018 accessed http://www.weweng.ie/slane.html, Accessed date: 24 August 2018.
[126] Xie S, Hai FI, Zhan X, Guo W, Ngo HH, Price WE, et al. Anaerobic co-digestion: a critical review of mathematical modelling for performance optimization. Bioresour Technol 2016;222:498–512. https://doi.org/10.1016/j.biortech.2016.10.015.
[127] Shen Y, Linville JL, Urgun-Demirtas M, Mintz MM, Snyder SW. An overview of biogas production and utilization at full-scale wastewater treatment plants (WWTPs) in the United States: challenges and opportunities towards energy-neutral WWTPs. Renew Sustain Energy Rev 2015;50:346–62. https://doi.org/10.1016/j.rser.2015.04.129.
[128] Mata-Alvarez J, Dosta J, Macé S, Astals S. Codigestion of solid wastes: a review of its uses and perspectives including modeling. Crit Rev Biotechnol 2011;31:99–111. https://doi.org/10.3109/07388551.2010.525496.
[129] Astals S, Batstone DJ, Mata-Alvarez J, Jensen PD. Identification of synergistic impacts during anaerobic co-digestion of organic wastes. Bioresour Technol 2014;169:421–7. https://doi.org/10.1016/j.biortech.2014.07.024.
[130] Lafitte-Trouqué S, Forster C. The use of ultrasound and γ-irradiation as pre-treatments for the anaerobic digestion of waste activated sludge at mesophilic and thermophilic temperatures. Bioresour Technol 2002;84:113–8. https://doi.org/10.1016/S0960-8524(02)00038-X.
[131] Fdez-Güelfo LA, Álvarez-Gallego C, Sales D, Romero LI. The use of thermo-chemical and biological pretreatments to enhance organic matter hydrolysis and solubilization from organic fraction of municipal solid waste (OFMSW). Chem Eng J 2011;168:249–54. https://doi.org/10.1016/j.cej.2010.12.074.
[132] Montgomery DC. Time series analysis and forecasting. 2016. https://doi.org/10.1007/978-3-319-28725-6.
[133] Sosa-Hern??ndez O, Parameswaran P. Alem??n-Nava GS, Torres CI, Parra-Sald??var R. Evaluating biochemical methane production from brewer???s spent yeast. J Ind Microbiol Biotechnol 2016;43:1195–204. https://doi.org/10.1007/s10295-016-1792-0.
[134] Montgomery Lucy FR, Bochmann G. Pretreatment of feedstock for enhanced biogas production. IEA; 2014.
[135] Gao J, Chen L, Yuan K, Huang H, Yan Z. Ionic liquid pretreatment to enhance the anaerobic digestion of lignocellulosic biomass. Bioresour Technol 2013;150:352–8. https://doi.org/10.1016/j.biortech.2013.10.026.
[136] Kim J-Y, Shin E-J, Eom I-Y, Won K, Kim YH, Choi D, et al. Structural features of lignin macromolecules extracted with ionic liquid from poplar wood. Bioresour Technol 2011;102:9020–5. https://doi.org/10.1016/j.biortech.2011.07.081.
[137] Ahring BK, Biswas R, Ahamed A, Teller PJ, Uellendahl H. Making lignin accessible for anaerobic digestion by wet-explosion pretreatment. Bioresour Technol 2014;175C:182–8. https://doi.org/10.1016/j.biortech.2014.10.082.
[138] Hendriks ATWM, Zeeman G. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour Technol 2009;100:10–8. https://doi.org/10.1016/j.biortech.2008.05.027.
[139] Sun Y, Cheng J. Hydrolysis of lignocellulosic materials for ethanol production : a review. Bioresour Technol 2002;83:1–11. https://doi.org/10.1016/S0960-8524(01)00212-7.
[140] Of C. Chemical TWO, of P, for S, production B, anaerobic BY. Comparison of Two Chemical Pretreatments of Rice. 7. 2012. p. 3223–36.
[141] Shanmugam P, Horan NJ. Optimising the biogas production from leather fleshing waste by co-digestion with MSW. Bioresour Technol 2009;100:4117–20. https://doi.org/10.1016/j.biortech.2009.03.052.
[142] Siegert I, Banks C. The effect of volatile fatty acid additions on the anaerobic digestion of cellulose and glucose in batch reactors. Process Biochem 2005;40:3412–8. https://doi.org/10.1016/j.procbio.2005.01.025.
[143] Neves L, Ribeiro R, Oliveira R, Alves MMÃ. Enhancement of methane production from barley waste vol. 30. 2006. p. 599–603. https://doi.org/10.1016/j.biombioe.2005.12.003.
[144] Gáspár M, Kálmán G, Réczey K. Corn fiber as a raw material for hemicellulose and ethanol production. Process Biochem 2007;42:1135–9. https://doi.org/10.1016/j.procbio.2007.04.003.
[145] Taherzadeh MJ, Karimi K. Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review. BioResources 2007;2:472–99. https://doi.org/10.15376/biores.2.3.472-499.
[146] Mussatto SI, Dragone G, Roberto IC. Brewers' spent grain: generation, characteristics and potential applications. J Cereal Sci 2006;43:1–14. https://doi.org/10.1016/j.jcs.2005.06.001.
[147] Taherzadeh MJ, Karimi K. Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review vol. 9. 2008. https://doi.org/10.3390/ijms9091621.
[148] 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. https://doi.org/10.1016/j.jhazmat.2010.06.129.
[149] Toreci I, Kennedy KJ, Droste RL. Evaluation of continuous mesophilic anaerobic sludge digestion after high temperature microwave pretreatment. Water Res 2009;43:1273–84. https://doi.org/10.1016/j.watres.2008.12.022.
[150] Izumi K, Okishio Y, Nagao N, Niwa C, Yamamoto S, Toda T. Effects of particle size on anaerobic digestion of food waste. Int Biodeterior Biodegrad 2010;64:601–8. https://doi.org/10.1016/j.ibiod.2010.06.013.
[151] Pérez-Rodríguez N, García-Bernet D, Domínguez JM. Effects of enzymatic hydrolysis and ultrasounds pretreatments on corn cob and vine trimming shoots for biogas production. Bioresour Technol 2016;221:130–8. https://doi.org/10.1016/j.biortech.2016.09.013.
[152] 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. https://doi.org/10.1016/j.biortech.2014.09.030.
[153] Kratky L, Jirout T. Biomass size reduction machines for enhancing biogas production. Chem Eng Technol 2011;34:391–9. https://doi.org/10.1002/ceat.201000357.
[154] Appels L, Degrève J, Van der Bruggen B, Van Impe J, Dewil R. Influence of low

temperature thermal pre-treatment on sludge solubilisation, heavy metal release and anaerobic digestion. Bioresour Technol 2010;101:5743–8. https://doi.org/10.1016/j.biortech.2010.02.068.
[155] Modenbach AA, Nokes SE. The use of high-solids loadings in biomass pretreatment-a review. Biotechnol Bioeng 2012;109:1430–42. https://doi.org/10.1002/bit.24464.
[156] Moreira MM, Morais S, Barros AA, Delerue-Matos C, Guido LF. A novel application of microwave-assisted extraction of polyphenols from brewer's spent grain with HPLC-DAD-MS analysis. Anal Bioanal Chem 2012;403:1019–29. https://doi.org/10.1007/s00216-011-5703-y.
[157] Harris PW, McCabe BK. Review of pre-treatments used in anaerobic digestion and their potential application in high-fat cattle slaughterhouse wastewater. Appl Energy 2015;155:560–75. https://doi.org/10.1016/j.apenergy.2015.06.026.
[158] Zhang D, Li X, Jia S, Dai L, Zhao J, Chen Y, et al. A review: factors affecting excess sludge anaerobic digestion for volatile fatty acids production. Water Sci Technol 2015;72:678. https://doi.org/10.2166/wst.2015.280.
[159] Zhang Y, Piccard S, Zhou W. Improved ADM1 model for anaerobic digestion process considering physico-chemical reactions. Bioresour Technol 2015;196:279–89. https://doi.org/10.1016/j.biortech.2015.07.065.