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Review

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Emerging Technologies for the Pretreatment of Lignocellulosic Biomass

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Abstract

Pretreatment of lignocellulosic biomass to overcome its intrinsic recalcitrant nature prior to the production of valuable chemicals has been studied for nearly 200 years. Research has targeted eco-friendly, economical and time-effective solutions, together with a simplified large-scale operational approach. Commonly used pretreatment methods, such as chemical, physico-chemical and biological techniques are still insufficient to meet optimal industrial production requirements in a sustainable way. Recently, advances in applied chemistry approaches conducted under extreme and non-classical conditions has led to possible commercial solutions in the marketplace (e.g. High hydrostatic pressure, High pressure homogenizer, Microwave, Ultrasound technologies). These new industrial technologies are promising candidates as sustainable green pretreatment solutions for lignocellulosic biomass utilization in a large scale biorefinery. This article reviews the application of selected emerging technologies such as ionizing and non-ionizing radiation, pulsed electrical field, ultrasound and high pressure as promising technologies in the valorization of lignocellulosic biomass.

Keywords: Lignocellulose; pretreatment; green technology; emerging technology; advanced biorefinery.

Abbreviations: LC, lignocellulose; MW, microwaves; US, ultrasound; HHP, high hydrostatic pressure; HPH, high pressure homogenization; UHPH, ultra-high pressure homogenization; PEF, pulsed-electric field; EB, electron beam.

1 Introduction

Since the industrial revolution 250 years ago, the world has pursued a linear economic model of “take, make & dispose” that was built on the presumption of plentiful and inexpensive natural resources. Contrasting with this approach, the new “Bioeconomy” economic model of the 21st century encourages the reuse and recovery of resources, instead of the mere use of natural non-renewable resources, in order to achieve economic prosperity and ecological survival. In this context, the biorefinery is the economic engine propelling society to achieve a sustainable economy by conversion of the abundantly available, renewable and non-edible lignocellulosic biomass, such as agricultural residue and food industry waste, into usable energy, fuels and chemicals.

However, due to the complex hierarchical structure and recalcitrant nature of lignocellulosic biomass, pretreatment steps present the most critical challenge to biomass utilization prior to conversion. The principal treatment regimes available for lignocellulosic biomass pretreatment may be categorized as biological, chemical, physical or physicochemical approaches (Kumar and Sharma, 2017). Generally, currently used pretreatment approaches suffer significant disadvantages in the goal to achieve cost effective, industrial scale, eco-friendly production.

The harsh chemicals and high conventional heating methods used for biomass pretreatment require extensive amounts of energy and are not environmentally friendly. Furthermore, these pretreatment strategies lead to the formation of numerous undesirable compounds, such as aliphatic acids, vanillic acid, uronic acid, 4-hydroxybenzoic acid, phenol, furaldehydes, cinnamaldehyde, and formaldehyde, which may all interfere with the growth of the fermentative microorganisms during fermentation (Ravindran and Jaiswal, 2016). This encouraged the movement from non-sustainable conventional pretreatments (e.g. chemical

and physiochemical pretreatments) to sustainable green pretreatments (e.g. biological pretreatments). However, long treatment times, low yields and loss of carbohydrate during pretreatment are considered to be the major challenges in biological pretreatment by microorganisms (Saha et al., 2016). Furthermore, pretreatment processes can cost more than 40% of the total processing cost, and represent the most energy intensive aspects in biomass conversion to value added products (Sindhu et al., 2016). Thus, the challenge of low efficiency production associated with green pretreatments encouraged the investigation of using large scale technologies that are now available on the market as scalable green pretreatments to achieve sustainable and efficient pretreatment process of lignocellulosic biomass.

In recent years, advances in applied research within the field of chemistry, and featuring extreme and non-classical conditions, has led to the development of novel food processing technologies that are now available on a commercial scale. Interestingly, some of these technologies hold promise as green approaches for the pretreatment of lignocellulosic biomass, with possible advantages of lower cost and higher productivity within the context of a commercial-scale biorefinery. Numerous articles have reviewed common biomass pretreatment methods (Chen et al., 2017; Kumar and Sharma, 2017), green technologies (Capolupo and Faraco, 2016), and emerging technologies (Singh et al., 2016). However, a review of all emerging pretreatment technologies is missing in the current literature. This article reviews the application of selected emerging technologies for pretreatment of lignocellulosic biomass, including non-ionizing radiation (microwaves), ionizing radiation (gamma ray, electron beam), pulsed-electric field, high pressure (high hydrostatic pressure, high pressure homogenization) and ultrasound.

2 Lignocellulosic biomass

Lignocellulosic biomass refers to plant biomass that can be divided into four categories: hardwood, softwood, agricultural wastes and grasses. Interestingly, agricultural residues are being produced in very large amounts (billions of tons) each year around the world, but the majority of these residues are either discarded or burned. Food waste is defined as any discarded food (including inedible parts), removed from the food supply chain and which may be either recovered for alternative use or disposed (including composted, crops ploughed in/not harvested, anaerobic digestion, bio-energy production, co-generation, incineration, disposal to sewer, landfill or discarded to sea) (Östergren et al., 2014). In the EU-28 countries, it is estimated that an average of 9 to 10 kg of waste is generated for every tonne of food in the primary production sector, while an average of 22 kg of food waste is generated for every tonne in the food processing sector (Stenmarck et al., 2016). The latter EU figures do not include by-products destined for animal feed and bio-based products. Lignocellulosic wastes generated from agriculture and food processing can be utilized as feedstock for the second generation of sustainable biorefineries.

Plant biomass is composed mainly of polysaccharides (cellulose, hemicellulose) and lignin. Polysaccharides are polymers of sugars and therefore a potential source of fermentable sugars, while lignin can be used for the production of chemicals. Generally, cereal residues (e.g. rice straw, wheat straw, corn stover, and sugarcane bagasse) contain a large fraction of lignocellulose substances and represent the favourite feedstock for biorefineries, while grasses, fruit and vegetable wastes have less lignocellulosic content.

The ECN Phyllis2 database (www.phyllis.nl) is an open literature facility which is readily available to users and documents the composition of biomass and waste. Furthermore, table 1 shows the chemical composition of different lignocellulosic feedstocks based on recent

literatures published in 2016, 2017 and 2018. Biomass on a dry weight basis generally contains cellulose (50%), hemicellulose (10–30% in woods, or 20–40% in herbaceous biomass) and lignin (20–40% in woods or 10–40% in herbaceous biomass) (Sharma et al., 2015). However, these ratios between cellulose, hemicellulose and lignin within a single plant will vary with different factors like age, harvesting season and culture conditions.

Pretreatment of lignocellulosic biomass is a necessary step to convert biomass into fermentable sugars and to enable enzymatic hydrolysis to break the lignin and hemicellulose structures and to free the buried cellulose (Sun et al., 2016). Pretreatment steps should be simple, eco-friendly, cost-effective and economically feasible (Ravindran et al., 2018). In addition, the pretreatment process should not give rise to inhibitory compounds or loss in the fraction of interest (polysaccharide or lignin). Moreover, to date, there is no harmonised pretreatment strategy to suit all types of lignocellulosic biomass, and the pretreatment process depends mostly on the type of lignocellulosic biomass and the desired products. However, the use of a combination of two or more pretreatment strategies can significantly increase the efficiency of the process, and represents an emerging approach in this field of study.

3 Conventional approaches for pretreatment of lignocellulosic biomass

Generally, each of the common pretreatment approaches that fall under the four categories of physical, chemical, physio-chemical and biological methods work differently to break the complex structure of the lignocellulosic material. As a result, different products and yields can be obtained from each pretreatment approach, and each method has its advantages and disadvantages that are summarized in Table 2. While some of the methods listed have successfully made the transition from research platform to the industrial stage, significant challenges remain, including in some cases the generation of environmentally hazardous

wastes and/or high energy inputs; there is a pressing need for green technology solutions to this challenge (Capolupo and Faraco, 2016).

4 Green approaches for pretreatment of lignocellulosic biomass

In recent years, the concept of “Green Chemistry” has gained increasing interest as a possible approach to the challenge of developing a viable biorefinery concept. Central to achieving this goal is the development of technology that uses raw materials more efficiently, eliminates waste and avoids the use of toxic and hazardous materials. Selected green methods currently being pursued for pretreatment of lignocellulosic biomass are summarised in Table 3. Although these green methods are environmentally friendly, problems exist regarding high production costs and poor efficiency, as well as lack of availability of commercial equipment suited to industrial scale processing. However, the more widespread adoption of such technology by the food industry, with anticipated decreases in initial capital cost and increased scale of operation, may encourage uptake for pretreatment of lignocellulosic biomass.

5 Emerging technologies for pretreatment of Lignocellulosic biomass

Chemical approaches conducted under extreme or non-classical conditions are currently a dynamically developing area in minimal food processing. Microwaves, ultrasound, gamma ray, electron beam, pulsed-electric field, high hydrostatic pressure, and high pressure homogenization are non-thermal food processing technologies that also being investigated for pretreatment of lignocellulosic biomass.

5.1 Microwave Irradiation

Microwaves are an electromagnetic radiation with wavelengths ranging from 1 mm to 1 m. They are located between 300 and 300,000 MHz on the electromagnetic spectrum and are a nonionizing radiation that transfers energy selectively to different substances (Huang et al., 2016a). Microwaves have attracted renewed interest since the 1980s, when Gedye et al. (1986) reported the increase of hydrolysis, oxidation, alkylation and esterification processes by energy efficient microwave heating. Researchers have reported good lignocellulosic pretreatment performance using microwave radiation over the past 30 years, and have gradually moved from laboratory to pilot scale (Li et al., 2016a). Currently, microwave-assisted pretreatment technologies of lignocellulosic biomass can be classified into two main groups: (a) Microwave-assisted solvolysis under mild temperatures ($<200\text{ }^{\circ}\text{C}$) that depolymerises the biomass to produce value-added chemicals, and (b) Microwave-assisted pyrolysis of lignin without oxygen, under high temperatures ($>400\text{ }^{\circ}\text{C}$) to convert biomass to bio-oil or bio-gases. Each of the two groups of technologies might be accomplished with catalysts. However, microwave-assisted pyrolysis is discussed largely due to energy shortage and sustainability plans of most of the Countries.

Compared with conventional heating, microwave radiation has significant advantages such as: (a) fast heat transfer, short reaction time, (b) selectivity and uniform volumetric heating performance (c) easy operation and energy efficient and (d) low degradation or formation of side products. In addition, microwave hydrothermal pretreatment removes more acetyl groups in hemicellulose, which may be raised from the hot spot effect of microwave irradiation (Dai et al., 2017).

In the case of conventional heating, energy is transferred from the outside surface of the material inwards to the core of the material by conduction. Thus, overheating can occur on

the outside surface whilst still maintaining a cooler inner region. Contrasting with this, microwaves induce heat at the molecular level by direct conversion of the electromagnetic energy into heat. Energy is therefore uniformly dissipated throughout the material.

Materials can be grouped into three categories according to their response to microwaves: insulators, absorbers, and conductors. Insulators are materials which are transparent to microwaves (e.g., glass and ceramics), conductors are materials which show high conductivity and thus reflect microwaves from the surface (e.g., metals), while absorbers or dielectrics are materials that can absorb microwaves and convert microwave energy into heat (Huang et al., 2016b). Most biomass is generally considered as low lossy materials, and they need to be supported with materials that achieve rapid heating, such as graphite, charcoal, activated carbons and pyrites.

Interestingly, Salema et al. (2017) studied the dielectric properties of different biomass from agriculture and wood-based industries (including oil palm shell, empty fruit bunch, coconut shell, rice husk, and sawdust) and reported that all were low loss dielectric materials. Such materials do not absorb microwaves well during microwave-assisted pyrolysis until the char is formed, and the microwave absorption will then be significantly higher.

5.1.1 Microwave-assisted solvolysis (pretreatment of lignocellulosic biomass)

In conventional heating methods, the lignocellulosic biomass is ground into small particles to prevent large temperature gradients and then heated by indirect heat conduction or high pressure steam injection up to 160–250 °C. Therefore, fermentable sugar recovery and conversion might be affected by degradation of the hemicellulose into furfural or humic acids (Li et al., 2016a). Alternatively, microwave heating is reported to enhance enzymatic

saccharification through fibre swelling and fragmentation (Diaz et al., 2015) as a result of the internal uniform and rapid heating of large biomass particles. Almost no effect is observed in plant fibre material when treated with microwaves under temperatures that are equal to or below 100 °C (Chen et al., 2017).

The performance of microwaves depends on the dielectric properties of biomass which represent the ability of the material to store electromagnetic energy and to convert this energy into heat. Although, biomass usually is a low microwave absorber, the presence of relatively high moisture and inorganic substances can improve the absorption capacity of biomass (Li et al., 2016b). The increasing commercial availability of flow-through microwave systems may be of particular relevance to lignocellulosic pretreatment.

Choudhary et al. (2012) evaluated the pretreatment of sweet sorghum bagasse (SSB) biomass through microwave radiation, and reported that about 65% of maximal total sugars were recovered when 1 g of SSB in 10 ml water was subjected to 1000 W for 4 minutes. Scanning electron microscope analysis of microwave-assisted pretreatment of corn straw and rice husk in alkaline glycerol showed clear disruption of the plant cell structure (Diaz et al., 2015). Recently, Ravindran et al. (2018) reported that microwave-assisted alkali pretreatment was the best pretreatment method for brewers' spent grain (1g of BSG in 10 ml 0.5% NaOH was pretreated using 400 W for 60 seconds), as compared with dilute acid hydrolysis, steam explosion, ammonia fiber explosion, organosolv and ferric chloride pretreatment. The authors found that BSG after microwave-assisted alkali pretreatment yielded 228.25 mg of reducing sugar/g of BSG which was 2.86-fold higher compared to untreated BSG (79.67 mg/g of BSG). Others have also found that microwave radiation for lignocellulosic pretreatment

possesses the advantage of low capital cost, easy operation and significant energy efficiency (Kostas et al., 2017).

5.1.2 Microwave-assisted pyrolysis of lignocellulosic biomass

In this technique, microwave irradiation is used as a pretreatment method followed by biological conversion of biomass into biofuel, as well as a thermo-chemical pyrolysis of biomass. Pyrolysis is the conversion of biomass to liquid (bio-oil), solid (bio-char) and gaseous (syn-gas) fractions, by heating the biomass in the absence of air to high temperatures. Pyrolysis can convert the lignocellulosic biomass into biofuels or chemicals more completely and more quickly (Huang et al., 2016b). Microwave-assisted pyrolysis can convert fifty percent of lignocellulosic biomass processed into bioenergy gas products (Huang et al., 2015). Oil obtained from the fast pyrolysis of lignocellulosic materials contains a complex mixture of phenolic compounds derived primarily from lignin (Bu et al., 2011). Huang et al. (2016a) compared the heating rate of both microwave and conventional pyrolysis methods using the same input power level. They reported that the heating rate of microwave pyrolysis was higher by up to 42 % when compared with the heating rate of conventional processes; this means that microwave pyrolysis requires less time to reach the target temperature, indicating superior performance over conventional heating.

When converting agricultural biomass to higher value products using pyrolysis, the process may be tailored to meet either qualitative or quantitative objectives, such as maximizing the yield of solids, liquids or gases, as well as improving the energy density of chars or producing good quality syngas for the synthesis of bio-based chemicals. Calculations of the Energy Return On Investment (EROI) for microwave pyrolysis by Lo et al. (2017) provided evidence for the energetic efficiency and economic feasibility of microwave pyrolysis of

lignocellulosic biomass. The authors reported that when microwave pyrolysis is conducted on biomass feedstock (rice straw, rice husk, corn stover, sugarcane bagasse, bamboo leaves, sugarcane peel, or waste coffee grounds) with a heating value of 16 MJ/kg using microwave power of 500 W for 30 min, the EROI was be approximately 3.56. This finding may support the feasibility of the process, considering that minimum EROI for sustainable society is 3.0 (Hall et al., 2009). EROI is the ratio of the energy supplied to society and the energy invested to capture and deliver that energy (Hall et al., 2013).

5.2 Ultrasound

Over 90 years ago, Wood and Loomis (1927) reported the effects of the ultrasonic treatment on cellular biomass, such as floc fragmentation, cell rupture and destruction. Ultrasound in the range of 20 kHz to 1 MHz is used in chemical processing, while higher frequencies are used in medical and diagnostic applications. Ultrasound pretreatment of biomass results in alteration of the surface structure and production of oxidizing radicals that chemically attack the lignocellulosic matrix (Luo et al., 2013). Additionally, ultrasound can disrupt α -O-4 and β -O-4 linkages in lignin (Shirkavand et al., 2016) which results in the splitting of structural polysaccharides and lignin fractions by formation of small cavitation bubbles (Kumar and Sharma, 2017). The bubbles formed grow to a certain critical size and then become unstable, collapsing violently, and achieving pressures up to 1,800 atmospheres and temperatures of 2,000–5,000 K (Kunaver et al., 2012). Hence, ultrasonic disruption may represent an effective green technology for the pretreatment of lignocellulosic biomass.

Kunaver et al. (2012) studied the utilization of forest wood wastes to produce valuable chemicals using high energy ultrasound at a power of 400 W and amplitudes ranging from 20% to 100%, and reported shorter reaction times (by a factor of up to nine). Sun et al.,

(2004) reported that ultrasound irradiated sugarcane bagasse achieved 90% hemicellulose and lignin removal at an ultrasound power of 100 W and sonication time for 2 hours in distilled water at 55° C. The ultrasound was found to attack the integrity of cell walls, cleaving the ether linkages between lignin and hemicelluloses, and increasing the accessibility and extractability of the hemicelluloses. This is in agreement with another study for ultrasound-assisted alkaline pretreatment of sugarcane bagasse using 400 W microwave power for 47.42 minutes in 2.89% NaOH and 70.15° C, where the theoretical reducing sugar yield recovered was about 92% (Velmurugan, 2012).

Ultrasound-assisted, alkali pretreatment can enhance lignin degradation and enzymatic saccharification rates by breaking hydrogen bonds between molecules of lignocellulosics and lowering its crystallinity. However, the ultrasonic vibration energy is too low to change the surface conformation of the raw material biomass particles (Zhang et al., 2008). Subhedar et al. (2017) recently investigated the ultrasound-assisted delignification and enzymatic hydrolysis of three biomass types (groundnut shells, pistachio shell and coconut coir) and reported an approximate 80–100% increase in delignification over conventional alkali treatments, where biomass loading was 0.5%, ultrasound power was 100 W and duty cycle was 80% for 70 minutes. Additionally, reducing sugar yields in the case of ultrasound-assisted enzymatic hydrolysis under optimised conditions of enzyme loading at 0.08% w/v, substrate loading at 3.0% w/v, ultrasound power of 60 W and duty cycle of 70% for 6.5h, were 21.3, 18.4 and 23.9 g/L for groundnut shells, pistachio shells and coconut coir respectively, significantly more than that found for alkali hydrolysis (10.2, 8.1 and 12.1 g/L). It was also reported that reducing sugar yield was increased by a factor of approximately 2.4 by the application of ultrasound at a power of 60 W and duty cycle of 70 % for pretreatment of lignocellulosic waste paper at substrate loading of 3.0% (w/v) and cellulase loading of

0.8% (w/v) for 6.5 hours (Subhedar et al., 2015). Moreover, acoustic cavitation was found to successfully decrease the crystallinity of the microcrystalline cellulose, enabling enhanced enzymatic digestibility (Madison et al., 2017).

Combining ultrasound with ammonia pre-treatment of sugarcane bagasse (sonication time of 45 minutes in 400 w power, 100% amplitude and 24 kHz frequency, biomass loading of 1 g per 10 ml of 10% ammonia and temperature of 80° C) resulted in a cellulose recovery of 95.78%, with 58.14% delignification (Ramadoss and Muthukumar, 2014). Additionally, the synergistic effect of combining ammonia with ultrasound reduced by-product formation, enabled the treatment to be conducted at moderate temperature and reduced cellulose crystallinity. This is with an agreement with recent work carried out on ultrasound-assisted dilute aqueous ammonia (2.0% w/v aqueous ammonia) pretreatment of corn cob, corn stover and sorghum stalk using ultrasound at 90 W power and 50 kHz frequency (Xu et al., 2017); the highest enzymatic hydrolysis sugar yield was approximately 81% in corn cob (70° C, 4h), 66% in corn stover (60° C, 2 h) and 57% in sorghum stalk (50° C, 4 h). Similarly, pretreatment of spent coffee waste by ultrasound assisted potassium permanganate (biomass loading of 1.0 g at 10 ml of 4% KMnO_4 for 20 minutes, ultrasonic frequency of 47 kHz and power of 310 W) resulted in 98% cellulose recovery and 46% lignin removal (Ravindran et al., 2017).

5.2.1 Combination of Microwave and Ultrasound

Both microwaves and ultrasound are energy that may be applied to biomass to reduce the size, increase the exposed surface area and increase availability of cellulose, hemicellulose and oligosaccharides present in the biomass, facilitating further processing to produce target chemicals (Dunson *et al.*, 2006). Ultrasonication and microwave pretreatments were found to accelerate hydrolysis and biodegradability of agriculture wastes (grape pomace and olive

pomace) and wastewater sludges used to produce biogas. The author concluded also that ultrasonication was found to be more effective pretreatment method than microwaves alone (Alagöz et al., 2016). The applicability of the combination of microwaves with ultrasound for pretreatment of biomass has been considered in a number of patents (Olsen, 2011; Augustin et al., 2012; Gjermansen, 2014). Such a hybrid approach was found to selectively degrade waxes and lignin, and microwaves were reported to remove the waxy layer from the surface of biomass to increase the surface area available for enzymic action.

In hemicellulose degradation, the combination of ultrasound and microwave energy was found to provide a supplemental method of heating the biomass internally, which rapidly hydrolyzed the hemicellulose (North, 2016). Hydrothermal pretreatment of corncobs was also achieved using ultrasound (20 and 60 kHz for 10 and 20 minutes respectively), and microwaves (400 w and 600 w for 1 and 130 minutes respectively) to produce a high yield of xylose maize hydrolyzate core (Junli et al., 2016).

Most recently, patent inventors reported on the superimposed dual-energy of an ultrasound and microwave-assisted ionic liquid. A microwave power of 15~1000W (frequency of 1500~3000 MHz) combined with ultrasound (200 ~ 1000W and 15 ~ 30KHz) effectively removed lignin, could enhance the efficiency of enzyme hydrolysis of cellulose, and significantly increased fermentable sugar (glucose and xylose) yield (Xing et al., 2017).

5.3 Gamma ray

Gamma ray radiation is obtained from radioisotopes (Cobalt-60 or Cesium-137) and has also been tested as a lignocellulosic pretreatment. Ionizing radiation can easily penetrate the

lignocellulosic structure, causing modification of the lignin and a breakdown of cellulose crystal regions. The latter effect is facilitated by the formation of free radicals which decay quickly from the amorphous regions after the termination of radiation, while decay at a certain period from the crystalline regions also causes further degradation of the biomass (Hyun Hong et al., 2014).

Liu et al. (2015) studied the effect of γ -irradiation on the bioconversion efficiency of microcrystalline cellulose (MCC), as compared with other pretreatment methods (ionic liquids - ILs, acidic aqueous ionic liquids, 1% HCL, and 1% H₂SO₄). They reported that the most effective irradiation dose (891 kGy) possessed almost the same efficiency of MCC bioconversion as ILs pretreatment, and higher than that of other tested pretreatment methods. As a promising pretreatment technology, numerous articles have demonstrated that γ -irradiation pretreatment can enhance enzymatic hydrolysis of lignocellulosic biomass (Li et al., 2016c; Liu et al., 2016; Zhou et al., 2016; Liu et al., 2017). Gamma irradiation of rapeseed straw at 1200 kGy was found to induce a series of changes in the physical and chemical properties of the material. The latter included alteration of the linkage between the carbohydrates and lignin in the plant biomass, decreases in particle size, narrowing of the distribution range, increases in the specific surface area, and decreases in the thermal stability of the treated biomass (Zhang et al., 2016a).

5.4 Electron beam (EB) irradiation

EB ionising radiation is obtained from a linear accelerator. This pretreatment uses accelerated beams of electrons to irradiate lignocellulosic biomass in order to disrupt the structure of cell wall polymers (lignin, cellulose, hemicellulose) by such processes as production of free

radicals, inducing cross-link formation or chain scission, decrystallization, and/or decreasing the degree of polymerization (Grabowski, 2015).

EB irradiation of sugar maple (at dosages up to 1000 kGy) was found to depolymerize cellulose and hemicellulose structures to varying degrees, and increased the yield of phenolics (Mante et al., 2014). Yang et al. (2015) reported that the optimal EB irradiation was 500 kGy to treat Korean *Miscanthus sinensis* prior to enzymatic hydrolysis for fermentable sugar production. EB is mainly effective on depolymerizing cellulose, and so therefore there is a requirement for use in combination with other pretreatments, such as steam explosion or alkali, for hydrolyses of hemicellulose and lignin (Leskinen et al., 2017; Xiang et al., 2017).

5.5 Pulsed-electric field

Pulsed-electric field (PEF) processing uses a simple device without moving parts that treats plant biomass or bio-suspensions between two electrodes to voltage pulses, with an electrical field strength of 0.1–80kV/cm for a very short time (10^{-4} and 10^{-2} s). Under the effect of PEF, the biological membrane is disrupted and local structural changes occur which result in a loss of semi-permeability, allowing the passage of intracellular compounds to the surrounding solution (Barba et al., 2015). This also facilitates the entry of hydrolytic enzymes through the pores of the treated plant cell membrane (Kumar and Sharma, 2017). Kumar et al. (2011) found that pretreatment of lignocellulosic materials (wood chip and switchgrass) with 2000 pulses at field strength of 10 kV/cm could improve the cellulose hydrolysis for conversion to fuel and chemicals.

PEF may contribute to delignification of lignocellulosic biomass (Janositz et al., 2011), and depending on the PEF parameters, cell wall structure may be variably affected (Cholet et al., 2014). Future work is needed to explain the effects of pulsed electric fields on lignocellulosic structures (Golberg et al., 2016).

5.6 High hydrostatic pressure (HHP)

High hydrostatic pressure (HHP) has been used for decades as a tool in the food industry for “non-thermal” Pasteurization that involves subjecting products to a high hydrostatic pressure (100–600 MPa) without a deterioration in product quality or compromising safety. The industrial application of HHP is currently successful in the United States, Europe and Japan for Pasteurization of food products. Initial capital and operating costs have been reduced due to innovative concepts introduced by different equipment manufacturers. HPP tolling is another option for manufacturers who otherwise would never have access to the technology because of equipment costs which are still relatively high.

HPP treatment is based on two fundamental principles: (a) pressure is distributed proportionally in all parts of a biomass, irrespective of its shape and size; and (b) pressure favours all structural reactions and changes that involve a decrease in volume. Although researchers do not often have to take changes in pressure into account, like temperature it is a thermodynamic parameter of any enzyme-catalyzed reaction. Pressure treatment has the advantage over thermal treatment in not being time/mass-dependent. Additionally, pressure also only affects hydrogen bonds, leaving covalent bonds untouched and thus reducing the processing time. In addition, pressure affects the activity of some enzymes by direct changes in enzyme structure, changes in the reaction mechanism and modifications to the physical properties of substrate (Eisenmenger and Reyes-De-Corcuera, 2009).

Oliveira et al. (2012) reported that high hydrostatic pressure is a promising tool for the engineering of enzymatic reactions within lignocellulosic biomass to obtain products with tailored properties, as changing the pressure and the exposure time of high hydrostatic pressure during the pretreatment step can control the rate and the extent of enzymatic hydrolysis. The authors investigated the effect of hydrostatic pressures of 300–400 MPa for 15–45 min on *Eucalyptus globulus* kraft pulp, and found a 5–10-fold increase in the initial hydrolysis rate of xylan by xylanase after this pretreatment. In 2013, Castañón-Rodríguez et al. used increasing HPP up to 400–800 MPa to pre-treat sugarcane bagasse, in combination with different concentrations of chemical compounds, and reported significant increases in the susceptibility of biomass to enzymatic hydrolysis and a rise in glucose concentrations. Results showed few cracks, tiny holes and some fragments flaked off from the compacted lignocellulosic structure by the HPP treatments at an optimally efficient pressure of 250 MPa.

It is reported also that hydrolytic performance of fungal cellulases on coconut husk biomass increased by a factor of 2 under pressurised conditions (Albuquerque et al., 2016). Results showed porous areas and rupturing on coconut fibres treated by pressure values of 300 MPa for 30 minutes. HPP is a promising choice, not only for biomass pretreatment, but also for inducing hydrolytic enzymes stability and activation (Murao et al., 1992).

5.7 High-pressure homogenization (HPH)

HPH is a well-known mechanical method for cell disruption and recovery of intracellular bio-products. The homogenizer is geared towards producing a homogenous size distribution of particles suspended in a liquid, by using a pressure pump to force the liquid through a specific valve to achieve homogenization. Depending on the operating pressure, the process

is called high-pressure homogenization (HPH, up to 150-200 MPa), or ultra-high pressure homogenization (UHPH, up to 350-400 MPa).

Jin et al. (2015a) pre-treated four different lignocellulosic materials (corn straw, grass clipping, pine sawdust, and catalpa sawdust) with HPH under 10 MPa working pressure. The authors reported a decrease of biomass particle size and an increase in the accessible surface area for enzyme hydrolysis, which led to high reducing sugars yield. Compared with alkaline-heat pretreatment of grass clippings, HPH pretreatment is a promising eco-friendly method for biogas production from lignocellulosic biomass, which can destroy the microstructure of lignocellulosic biomass to an “empty-inside” structure, accessible for enzyme attack without loss in hemicellulose (Jin et al., 2015b). Chen et al. (2010) found that sugarcane bagasse treated with HPH (100 MPa) resulted in a significant decrease in particle size and a disturbance in the microstructure of the biomass that increased accessible surface area by 3-fold. This highly efficient, yet simple and green, mechanical homogenization has been used recently to isolate nano-fibrillated cellulose from lignocellulosic biomass (Saelee et al., 2016).

6 Techno-economic feasibility

Equipment based on emerging technologies are available in the market, and are used mainly in food processing industry. Example of these equipment includes: continuous flow microwaves (Advanced Microwave Technologies, United Kingdom), ultrasonic processors (Industrial Sonomechanics, United States), pulsed electric field systems (Pulsemaster, Netherlands), electron beam system (Pro-beam, Germany), and high pressure systems (Multivac, France).

Microwave use in chemical processing has been shown to be a technically and economically feasible alternative to conventional heating. Hasna (2011) evaluated the cost-benefit of using

microwave drying in corrugated paperboard manufacturing as an alternative to conventional steam platens. It was concluded that the microwave capital cost (\$7000 per kW) could be offset against utilities and power savings (from \$128.00 to \$38.00 per hour), compared with conventional steam platens. Such savings were achievable in less than one year with an assumption that operation hours are 6000 per year. The author also reported additional benefits from using microwave drying in corrugated paperboard manufacturing, such as improved quality, reduced wastage, and minimum starch consumption. In a recent feasibility study on ginger processing to oleoresin, an ultrasound pretreatment step was introduced as a novel method to enhance extraction of chemical constituents from plant materials (*Romis Consultants Ltd*, 2017); however, the study did not focus on economics related to ultrasound specifically. A feasibility study in Egypt on using gamma rays for food preservation indicated that the cost of irradiation for one ton of frozen poultry was US \$130.4, smoked fish US \$78.2, spices \$ 260.1 and dried vegetable \$ 26. Economic analysis evaluation indicated that the average rate-of-return would be about 16.9% annually, with a payback period of about 6 years (Eldin et al., 2002). The feasibility and the economic impact of electron beam processing in chestnut fruits was evaluated by Lopes (2014), who reported a strong dependence on processed quantity per unit time and product costing. Puértolas et al. (2010) calculated the economic cost of the treatment of grape mass to improve the phenolic extraction for red wine fermentation using PEF, and reported that cost could be around 0.01 and 0.2 €/ton. However, the author reported that inactivation of wine spoilage microorganisms by PEF is not feasible and can increase production costs by 4.2-8.4 €/ton due to energy inputs needed. The cost of high pressure processing (HPP) in comparison with thermal pasteurization was estimated to be 10.7 ¢/l for processing 16,500,000 l/year (3,000 l/h), which corresponds to 7-fold higher than thermal pasteurization (Sampedro et al., 2014). Generally, the economic feasibility of emerging technologies is limited by the high cost of

capital investment for new equipment. For commercial application of the emerging technologies in pretreatment of lignocellulosic biomass further feasibility studies will be needed considering the complexities of biorefining process, inter-dependence of pretreatment processes and the economics related to the market of the finished product.

7 Conclusion

To date, sustainability, energy saving, capital cost minimization and downstream process efficiency are still challenges toward commercial scale pretreatment of lignocellulosic biomass. The tendency is thus to use energy efficient green technologies. Interestingly, green commercial innovations from food technology present promising opportunities. Different emerging technologies have been investigated for pretreatment of lignocellulosic biomass; however, capital cost is generally high, and comparative efficiency of these techniques on different lignocellulosic biomass is not available. Hence, further studies are needed to identify the most efficient emerging technology, as well as feasibility studies to evaluate the viability of using these technologies in a commercial biorefinery.

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Table 1. Chemical composition of different lignocellulosic feedstocks (% dry basis)

Source	Cellulose	Hemicellulose	Lignin	References
Hardwood				
Eucalyptus	44.9	28.9	26.2	(Muranaka et al., 2017)
Oak	43.2	21.9	35.4	(Yu , 2017)
Rubber wood	39.56	28.42	27.58	(Khan et al., 2018)
Softwood				
Spruce	47.1	22.3	29.2	(Yu , 2017)
Pine	45.6	24.0	26.8	(Yu , 2017)
Japanese cedar	52.7	13.8	33.5	(Muranaka et al., 2017)
Grasses				
Bamboo	46.5	18.8	25.7	(Chen et al., 2017)
Amur silver-grass	42.00	30.15	7.00	(Raud et al., 2016)
Natural hay	44.9	31.4	12.0	(De Caprariis et al., 2017)
Hemp	53.86	10.60	8.76	(Raud et al., 2016)
Rye	42.83	27.86	6.51	(Raud et al., 2016)
Reed	49.40	31.50	8.74	(Raud et al., 2016)
Sunflower	34.06	5.18	7.72	(Raud et al., 2016)
Silage	39.27	25.96	9.02	(Raud et al., 2016)
Szarvasi-1	37.85	27.33	9.65	(Raud et al., 2016)
Agroindustrial waste				
Walnut shell	23.3	20.4	53.5	(De Caprariis et al., 2017)
Groundnut shell	37	18.7	28	(Subhedar et al, 2017)
Pistachio shell	15.2	38.2	29.4	(Subhedar et al, 2017)
Almond shell	27	30	36	(Álvarez et al., 2018)
Pine nut shell	31	25	38.0	(Álvarez et al., 2018)
Hazelnut shell	30	23	38.0	(Álvarez et al., 2018)
Coconut coir	44.2	22.1	32.8	(Subhedar et al, 2017)
Cotton stalk	67	16	13	(Kim et al., 2016)
Hemp stalk	52	25	17	(Kim et al., 2016)
Acacia pruning	49	13	32	(Kim et al., 2016)
Sugarcane peel	41.11	26.40	24.31	(Huang et al., 2016b)
Rice husk	40	16	26	(Daza Serna et al., 2016)
Rice straw	38.14	31.12	26.35	(Huang et al., 2016b)
Barley straw	35.4	28.7	13.1	(Liu et al., 2017)
Coffee grounds	33.10	30.03	24.52	(Huang et al., 2016b)
Extracted olive pomace	19	22	40.0	(Álvarez et al., 2018)
Palm oil frond	37.32	31.89	26.05	(Khan et al., 2018)
Corn stover	43.97	28.94	21.82	(Huang et al., 2016b)
Bamboo leaves	34.14	25.55	35.03	(Huang et al., 2016b)
Hazel branches	30.8	15.9	19.9	(Liu et al., 2017)

Table 2. Major advantages and disadvantages of each of the common pretreatment methods

Pretreatment Method	Effects	Advantage	Disadvantage	References
Mechanical Milling	Reduce the particle size and crystallinity of lignocellulosic materials	Control of final particle size, Make handling of material easy	High energy consumption	(Devendra et al., 2015)
Extrusion	Shortening of fiber and defibrillation	operate at high solids loadings, low production of inhibitory compounds, short time	High energy consumption, effect is limited when no chemical agents are used, mostly effective on herbaceous type biomass	(Duque et al., 2017)
Acid	Hemicellulose and lignin fractionation	Enzymatic hydrolysis is sometimes not required as the acid itself may hydrolyses the biomass to yield fermentable sugars	High cost of the reactors, chemicals are corrosive and toxic, and formation of inhibitory by-products	(Jönsson and Martín, 2016)
Alkaline	Lignin and hemicelluloses removal	Cause less sugar degradation than acid pretreatment	Generation of inhibitors	(Zhang et al., 2016c)
Organosolv	Lignin removal and hemicellulose fractionation	Produce low residual lignin substrates that reduce unwanted adsorption of enzymes and allows their recycling and reuse.	High capital investment, Handling of harsh organic solvents, formation of inhibitors	(Nitsos and Rova, 2017)
Oxidation	Removal of lignin and hemicelluloses	Lower production of by products	Cellulose is partly degraded, High cost	(Chandel and da Silva, 2013)
Ionic liquid	Cellulose crystallinity reduction and partial hemicellulose and lignin removal	low vapor pressure designer solvent, working under mild reaction conditions	Costly, complexity of synthesis and purification, toxicity, poor biodegradability and inhibitory effects on enzyme activity	(Yoo et al., 2017)
Liquid Hot Water	Removal of soluble lignin and Hemicellulose	The residual lignin put a negative effect on the subsequent enzymatic hydrolysis	High water consumption and energy input	(Zhuang et al., 2016)
AFEX	Lignin removal	High efficiency and selectivity for reaction with lignin	It is much less effective for softwood, Cost of ammonia and its environmental concerns	(Bajpai, 2016)
SPORL	Lignin removal	Effective against hardwood and softwood, and energy efficient	Pretreatment is preceded by biomass size-reduction	(Noparat et al., 2017)

Table 3. Major advantages and disadvantages of selected green chemistry pretreatment methods.

Pretreatment Methods	Effects	Advantage	Disadvantage	References
Deep eutectic solvents	lignin removal and hemicellulose fractionation	Green solvent, biodegradable and biocompatible	Poor Stability under higher pretreatment temperatures,	(Zhang et al., 2016b)
Steam Explosion	lignin softening, particle size reduction	low capital investment, moderate energy requirements and low environmental impacts	It is much less effective for softwood	(Pielhop et al., 2016)
Supercritical fluids	Cellulose crystallinity reduction and lignin removal	Green solvent is used, it does not cause degradation of sugars, method is suitable for mobile biomass processor	Total utilities costs are high	(Daza Serna et al., 2016)
Microbes	Lignin and hemicellulose degradation	Environment friendly, selective degradation of lignin and hemicelluloses	Very long pretreatment time (several weeks) due to slow yield	(Sun et al., 2016)

Highlights

- Conventional pretreatment methods of lignocellulose suffer significant disadvantages.
- Non-thermal food processing technologies investigated as emerging pretreatments.
- Emerging technologies are promising candidates as sustainable green pretreatments.
- Comparative and feasibility studies are required for the emerging pretreatments.