Cellulose (2016) 23:2761–2789
DOI 10.1007/s10570-016-1023-x

REVIEW PAPER

Role of energy irradiation in aiding pretreatment of lignocellulosic biomass for improving reducing sugar recovery

Yu-Loong Loow · Ta Yeong Wu · Ge Hoa Yang · Jamaliah Md. Jahim · Wen Hui Teoh · Abdul Wahab Mohammad

Received: 11 January 2016 / Accepted: 29 July 2016 / Published online: 18 August 2016

Abstract With the depletion of crude oil reserves, the ever-increasing global energy consumption encourages the efforts to find alternative renewable sources for production of biofuels and value-added chemicals. The conversions of lignocellulosic biomass into biofuels and commodity chemicals via the biotechnological pathway have been the recent trend. Specifically, these products can be obtained through fermentation of reducing sugars, which are the main but basic derivatives from the biomass. In order to overcome the recalcitrant structure of the biomass for effective reducing sugar recovery, a pretreatment stage is normally required. Currently, one of the most novel forms of biomass pretreatment is using energy irradiation methods such as electron beam, gamma ray, pulsed electrical field, microwave and ultrasound. In general, these technologies are often used together with other more conventional chemical and/or biological pretreatment techniques for enhancing sugar recovery. Nevertheless, energy irradiation offers significant improvement in terms of possible cost reduction opportunities and reduced toxicity. Hence, this review highlights the recent studies of using energy irradiation for pretreating biomass as well as the industrial applications of reducing sugars in biotechnological, chemical and fuel sectors. In short, more research needs to be done at the scientific, engineering and economic levels to make energy irradiation one of the front runners in the field of biomass pretreatment.

Keywords Biomass valorization · Electron beam · Gamma ray · Pulsed electrical field · Microwave · Ultrasound

Introduction

Lignocellulosic biomass is one of the most abundant bioresources in the world. According to the Union of Concerned Scientists (2012), in the US alone, the production rate of biomass was projected to reach

Y.-L. Loow · T. Y. Wu (✉) · G. H. Yang
Chemical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan,
47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia
e-mail: wu.ta.yeong@monash.edu;
tayeong@hotmail.com

G. H. Yang
Undergraduate Research Opportunities Program (UROP), School of Engineering, Monash University, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

J. Md. Jahim · A. W. Mohammad
Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi,
Selangor Darul Ehsan, Malaysia

W. H. Teoh
Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

nearly 680 million tons per year by 2030. In order to overcome the recalcitrance and alter the structural hindrance of biomass for effective digestibility and component utilization, a pretreatment stage is often required. Basically, the stage of biomass pretreatment is considered to be the most expensive stage within a biorefining facility, taking up to 20–48 % of the total operational cost (Ofori-Boateng and Lee 2014a). Mechanical communition techniques such as chipping, milling and grinding have been used to increase the surface area of biomass to render it more amenable to enzymatic hydrolysis (Chen et al. 2012b; Zheng et al. 2009). However, these typical techniques are also energy intensive and time consuming, making the process uneconomic and seldom used as an exclusive pretreatment method (Kim et al. 2011; Zheng et al. 2009). As such, both constraints of excessive energy consumption and low effectiveness prevent the application of most mechanical pretreatment systems to be used widely in industries (Bak et al. 2009). Only conventional chemical and biological pretreatments have been effectively applied at reasonable cost. On the other hand, some of the more novel energy irradiation methods not only require less energy, but they are also known to limit the production of inhibitors during the pretreatment process (Kim et al. 2011). Recently, advanced technologies such as gamma ray (Hong et al. 2014), electron beam (Karthika et al. 2012; Sundar et al. 2014), pulsed electrical field (Zbinden et al. 2013), microwave (Darji et al. 2015; Karunanithy et al. 2014) and ultrasound (Ninomiya et al. 2013; Rehman et al. 2014) have been gaining attention because of their fast and effective results in pretreatment of lignocellulosic biomass. Thus, this review re-evaluates the uses of reducing sugars obtained from the biomass and, most importantly, provides an overview on the recent use of high-intensity energy irradiation as a form of biomass pretreatment technique.

Current and future trends of biomass valorization

High energy demand around the globe has exerted excessive stress over the usage of depleting non-renewable resources such as fossil fuels and various minerals. Due to its renewable nature and abundant availability, the utilization of lignocellulosic biomass could be a potential sustainable solution to the aforementioned issue. The conversion of biomass into various value-added biochemicals is generally termed as biomass valorization (Iqbal et al. 2013). Over the past decades, active research is ongoing in exploring innovative and effective processes to improve the present bioconversion processes.

Complete transformation of biomass into value-added products can be divided into two stages, consisting of pretreatment of biomass, followed by either thermochemical (liquefaction, combustion, gasification, pyrolysis and torrefaction) or biological processing (fermentation) of biomass. The pretreatment of biomass is particularly vital in the biomass valorization process as it serves to break down the resistance of biomass because of the presence of hemicellulose (20–40 %), lignin (20-30 %) and extractives in large quantities, which serve as a protective layer (Lam et al. 2015). By applying an appropriate pretreatment stage, a more energy-efficient and simpler downstream process can be ensured. The type of biomass pretreatments can be further broken down into three major approaches, which are biological, chemical and physical/mechanical pretreatments (Loow et al. 2015).

The history of the pretreatment process for biomass valorization began with acid hydrolysis and steam explosion, which were developed in the 1920s (Kurian et al. 2013). As a practice to improve the existing method, different solvents and chemicals have since been developed and deployed as catalysts for the pretreatment process. Until now, various pretreatment techniques such as supercritical water treatment, alkaline hydrolysis, ozonolysis, densification and fungal digestion have been explored (Lam et al. 2015). Recently, the advances in energy irradiation have given a new impetus to the exhaustive research in this area, with methods such as electron beam, gamma ray, ultrasound, pulsed electrical field and microwave garnering attention across the research field. According to Grewell and Montalbo-Lomboy (2013), energy irradiation improved mass transport by enhancing mixing and improving the surface area for greater reaction sites. As the benefits associated with energy irradiation in the pretreatment process are significant, one of the future trends in biomass valorizations may involve the integration between energy irradiation and more conventional pretreatment methods for improving reducing sugar recovery from the lignocellulosic biomass.

Applications of reducing sugars

Any sugar that acts as a reducing agent because of the presence of free aldehyde or ketone groups can be defined as a reducing sugar. The diverse applications of reducing sugars in various industries have encouraged innovations in extracting the simplest form of sugar carbohydrates such as glucose, xylose and arabinose from the lignocellulosic biomass. Some of the major derivatives of reducing sugars as well as their applications in the industry are shown in Table 1. Therefore, the wide applications of reducing sugars for industrial purposes warrant the continuous development of more efficient and sustainable biomass pretreatment technologies.

Energy irradiation pretreatment of lignocellulosic biomass

Electron beam

Electron beam (EB) is a multi-stage process that is widely applied for polymer degradation and modification in which the pretreatment effects are caused by irradiation alone via minimization of temperature effects at high doses (Gryczka et al. 2014). As compared to gamma rays, EB is usually used at higher dosages but offers very limited penetration into materials whereby the high energy electrons are deposited in relatively thin layers of material (Duarte et al. 2012). This ionizing radiation technique has been successfully applied in the treatment of industrial effluents because the species produced from the radiation and water reaction (OH radicals, e-aq and H) were able to remove organic pollutants (Duarte et al. 2012). In the field of biomass pretreatment, EB was effective in removing the hemicellulose and lignin content, as these components retained a greater chance to be hit by the beam (Bak et al. 2009). This mode of pretreatment focused on the changes in internal structure of the substrates through the action of chain scission due to electron bombardment (Bak 2014; Shin and Sung 2008).

Generally, the dosage of EB radiation plays a significant role in pretreatment efficiency. Radiation-induced chain scission of the glucoside bond by β-cleavage of radicals was found to be proportional to the irradiation dose (Shin and Sung 2008). It is worth highlighting that the lower dosage was insufficient for effective breakage of bonds, but excessive dosage might lead to the decrease in glucose recovery since the glucose monomer was further decomposed by the excess energy (Kim et al. 2011; Xin and Kumakura 1993). For instance, Gryczka et al. (2014) reported that radiation effects were visible at 25 kGy, but severe destruction of the surface structure and breakage of cell walls was more apparent at 300 kGy as shown in Fig. 1. Using the same enzymatic hydrolysis duration, 450 kGy of radiation imposed a more profound effect on glucose yield than 150 kGy, with an increase in sugar recovery of 6.2 and 3.4 %, respectively, over the control (Shin and Sung 2008). The partial tearing that occurred at the fibers and cell walls caused the increase of the total wall area, whereas the pores progressively expanded and agglomerated into larger structures during the pretreatment process (Gryczka et al. 2014). The performance of EB-assisted sugar recoveries from various lignocellulosic biomasses is summarized in Table 2.

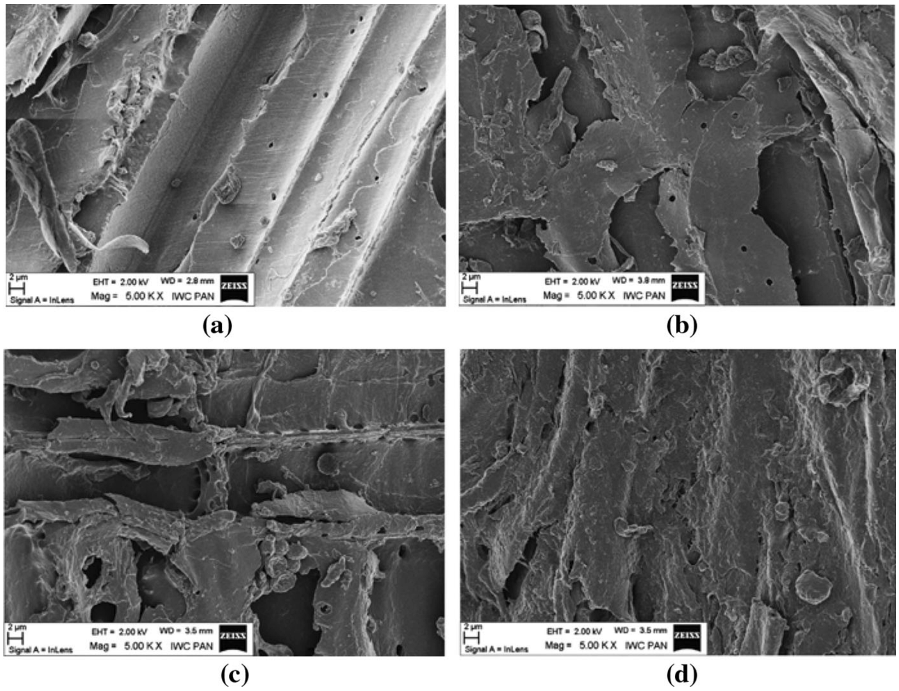
The ionizing radiation from EB had the capability of altering the lignocellulose structure within a short exposure time (Karthika et al. 2013). Besides, the pretreatment also increased the crystallinity index (CrI) because of the transformation of the intermediate para-crystalline phase of cellulose polymer between the diverse forms of crystalline and amorphous cellulose (Karthika et al. 2013). Bak et al. (2009) increased the intensity of the crystalline region from 54.5 to 58.0 % when EB was radiated at 80 kGy, attributed to the removal of hemicellulose and lignin amorphous regions. Kim et al. (2011) concurred with the result that the increase in beam dosage promoted the crystalline surface modification of biomass into the rugged surface, resulting in an increase of CrI. However, Karthika et al. (2012) and Sundar et al. (2014) observed contradictory results in which the CrI decreased along with the molecular weight, but the surface area was increased. The longitudinal fibers and vessels of the wood external layer were partially destroyed (Gryczka et al. 2014), coupled with the formation of degraded cracks and non-spherical protrusions (Bak 2014) after undergoing EB radiation. Hence, the reduction in the degree of polymerization (Shin and Sung 2008; Sung and Shin 2011) and disruption of the recalcitrant structure facilitated the reagents' accessibility as well as enzymatic saccharification (Karthika et al. 2013; Sundar et al. 2014). For

Table 1 Summary of the production of derivative from a reducing sugar

Derivative	Reducing sugar	Method of production	Market size	Commercial use	References
Acetic acid	Glucose	Fermentation	11.8 Million tons/year	Derived into polyvinyl acetate used for paints, adhesives and plastics	Pike et al. (2008)
				Derived into acetic anhydride for manufacture of paper sizing agents, bleach activator and aspirin	
				Derived into acetates and esters as solvent for coatings, inks, resins, gums, flavorings and perfumes	
				Derived into terephthalic acid (TPA) for polyethylene terephthalate (PET) bottles and fiber manufacturing	
Arabitol	Arabinose	Hydrogenation	Limited because of no real commercial interest	Anticariogenic agent that inhibits growth of oral bacteria	Koganti and Ju (2013)
				Potential food sweetener and sugar substitutes for diabetic patients	
				Potential candidate for produce biodegradable and biocompatible polymers	Loman and Ju (2014)
Ethanol	Xylose and glucose	Fermentation	86 Million tons/year	Solvent application	Choi et al. (2015)
				Liquid biofuel for motor vehicles	Sarkar et al. (2012)
				Domestic fuel for boiler's operation and cogeneration of electricity	
				Intermediate chemical for production of esters, glycol ethers, acetic acid, acetaldehyde and ethyl chloride	Sheldon (2014)
Furfural	Xylose	Dehydration with presence of acidic catalyst	250,000 tons/year	Production of plastic, pharmaceuticals and agrochemical products	Mamman et al. (2008)
				Intermediate chemical for production of furfuryl alcohol, tetrahydrofurfuryl alchohol and resin	Choi et al. (2015), Karinen et al. (2011), Mamman et al. (2008)
Hydroxy-methyfurfural (HMF)	Glucose or fructose	Dehydration with presence of acidic catalyst	Limited because of insignificant industrial uses	Synthesis of formic acid, which is used as road salt, catalysts, fuel cells and in the textile industry	Mukherjee et al. (2015)
				Synthesis of ethoxymethylfurfural as potential biofuel	
				Platform chemical for furandicarboxylic acid (FDCA), which replaces TPA in the PET industry	Teong et al. (2014)
Lactic acid	Glucose	Fermentation	400,000 tons/year	Synthesis of poly l-lactic acid (PLLA), which is used in goods packaging industry, cardiovascular (stents and grafts), dental and intestinal applications	Abdel-Rehman et al. (2011), Buruiana et al. (2013)
				Feedstock for polylactic acid, which is used in the medical field, such as surgical sutures, orthopedic implants, drug delivery systems and disposable consumer products	Abdel-Rehman et al. (2011), Sheldon (2014)

Table 1 continued

Derivative	Reducing sugar	Method of production	Market size	Commercial use	References
				Surfactant, additive, foaming agent and detergent	Akhtar et al. (2014)
				Ion chelator to prevent corrosion and pitting in metals	
				Acidulate, pH regulator, antimicrobial and flavoring agent in the food industry	
				Production of vitamins, antibiotics and amino acids in the pharmaceutical field	
				Intermediate chemical for 1,4-butanediol, tetrahydrofuran, polyester polyols and γ-butyrolactone, adipic acid	Akhtar et al. (2014), Choi et al. (2015)
				Platform chemical for succinonitrile, which is another precursor for the production of diaminobutane	Choi et al. (2015)
				Monomer for production of bio-based polymer such as polybutylene succinate and PET materials	
Sorbitol	Glucose	Hydrogenation	1.7 Million tons/year	Intermediate chemical for isosorbide, which is used to synthesize polymers, biomedicine and cosmetic products	Choi et al. (2015)
				Intermediate chemical for short chain alkanes for biofuel application	
				Intermediate chemical for polyols to be used in food, drugs, cosmetics and toothpaste	Zhang et al. (2013)
				As a food additive such as sweeteners, humectants and excipients	
				As catalyst modification media	
Xylitol	Xylose	Hydrogenation	Limited because of high production costs	Polymer for biomedical application	Loman and Ju (2014)
				Used extensively in production of toothpaste and chewing gum	
				Food sweetener (alternative to sucrose)	Albuquerque et al. (2014)
				Pharmaceutical application to prevent tooth decay and tooth calcification	
				Intermediate chemical for production of xylaric acid, ethylene glycol and propylene glycol	Choi et al. (2015)
				Medical interest to treat ear infections in children	Rafiqul and Sakinah (2013)



(a) (b) (c) (d)

Fig. 1 Scanning electron micrographs at ×5000 magnification of **a** untreated and pretreated willow plant fibers using an electron beam up to **b** 25 kGy, **c** 100 kGy and **d** 300 kGy (Gryczka et al. 2014)

instance, Sundar et al. (2014) successfully increased the overall glucose recovery by approximately fourfold when EB was applied before enzymatic hydrolysis.

Using mild radiation doses, the content of hemicellulose showed a decreasing trend with increases in dosage from 0 to 150 kGy, even though cellulose and lignin were not affected (Karthika et al. 2013). The loss of hemicellulose implied that it has been partially depolymerized and cleaved from its linkages with cellulose and lignin, rendering it easier to be solubilized (Sundar et al. 2014). Interestingly, the pretreatment effects were more pronounced when EB was integrated with other conventional methods. For instance, Karthika et al. (2013) reported that the cellulose was more sensitive to radiation with an addition of mild acid (1 % of H_2SO_4) or alkali (1 % of NaOH). Also, rice straw showed a remarkable improvement of glucose recovery after combining EB irradiation and 4 % of NaOH, with approximately 200 % higher yield than the pretreatment process consisting of alkali soaking alone (Xin and Kumakura 1993). On the other hand, Chosdu et al. (1993) improved the glucose yield of corn stalk from 20 to 43 % by incorporating both 500 kGy of EB and 2 % of NaOH. As such, the modification in structural state and mechanical strength promoted biomass hydrolysis. Nevertheless, a huge variation was observed for the sugar extraction because of the cleavage of macromolecules into soluble fractions, as well as the possible formation of intermolecular bonds (Karthika et al. 2013). Thus, high doses of EB have been reported to cause both polymerization and depolymerization in macromolecules (Karthika et al. 2013).

Gamma ray

The gamma ray (γ-ray) mechanism involves the generation of phenoxy radical intermediates, offering an efficient way to permit access of enzymes to cellulose (Chung et al. 2012). In the presence of water, γ-ray irradiation promoted the degradation of polysaccharides via breakage of glycosidic bonds in the biomass (Orozco et al. 2012; Yoon et al. 2012). High activity radicals were produced through the rapid delocalization of the absorbed energy within the molecules of cellulosic materials. Chemical reactions such as chain scission caused secondary degradation of these materials (Yoon

Table 2 Performance of the electron beam in pretreatment of various lignocellulosic biomasses

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	References
Corn stalk	*Alkali* $T = 25$ °C 2 % NaOH	*Electron beam* 500 kGy, 10 cm scan *Enzymatic hydrolysis* Cellulase (Onozuka R-10) 5000 U/g dry substrate T = 40 °C, time = 48 h	Solid fraction: 43 % glucose yield	Chosdu et al. (1993)
Industrial hemp biomass	*Electron beam* 450 kGy, 5 m/min stream velocity electron beam	*Enzymatic hydrolysis* Cellulase (ATCC 26921) 20 FPU/g biomass, β-glucosidase (Novozyme 342) 25 % of Celluclast $T = 50$ °C, time = 72 h	Solid fraction: ~36.5 % glucose yield, 18.4 % xylose yield	Shin and Sung (2008)
Napier grass x bajra	*Electron beam* 250 kGy, 1 m scan, 0.1 m/min stream velocity electron beam	*Enzymatic hydrolysis* Cellulase (ATCC 26921) 30 FPU/g cellulose, β-glucosidase (Novozyme 188) 0.5 % (p/p) $T = 50$ °C, time = 144 h	Solid fraction: ~32.0 % glucose yield, 79 % final reducing sugar yield (~350 mg reducing sugar/g biomass)	Karthika et al. (2012)
Napier grass × bajra	*Acid* Time = 48 h *L*/*S* ratio = 2:1 (v/w) 1 % H_2SO_4 soaking	*Electron beam* 150 kGy, 1 m scan, 1 m/min stream velocity electron beam *Enzymatic hydrolysis* Cellulase (ATCC 26921) 15 FPU/g biomass $T = 50$ °C, time = 120 h	Solid fraction: ~52 % glucose yield (~550 mg reducing sugar/g biomass)	Karthika et al. (2013)
	Alkali Time = 48 h *L*/*S* ratio = 2:1 (v/w) 1 % NaOH soaking	*Electron beam* 150 kGy, 1 m scan, 1 m/min stream velocity electron beam *Enzymatic hydrolysis* Cellulase (ATCC 26921) 15 FPU/g biomass $T = 50$ °C, time = 120 h	Solid fraction: ~59 % glucose yield (~575 mg reducing sugar/g biomass)	
Rice straw	*Electron beam* 80 kGy, 0.12 mA, 1 MeV	*Enzymatic hydrolysis* Cellulase (Celluclast 1.5L) 60 FPU/g glucan, β-glucosidase (Novozyme 188) 30 CBU/g glucan $T = 50$ °C, time = 132 h	Solid fraction: 52.1 % glucose yield Liquid fraction: 1.25 ± 0.09 % monomeric sugars yield Liquid fraction: HMF and furfural undetected, <0.002 % (w/w) acetic acid	Bak et al. (2009)
Rice straw	*Alkali* $T = 60$ °C Time = 24 h *L*/*S* ratio = 12:1 15 % ammonia	*Electron beam* 3 kGy, 150 mm scan, 1 m/min stream velocity electron beam *Enzymatic hydrolysis* Cellulase (Celluclast 1.5 L) 60 FPU/g glucan, β-glucosidase (Novozyme 188) 10 CBU/g glucan $T = 50$ °C, time = 48 h	Solid fraction: 89 % glucose recovery	Kim et al. (2011)

Table 2 continued

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	References
Rice straw	*Alkali* $T = 25$ °C Time = 48 h L/S ratio = 30 % (w/w) 4 % NaOH	*Electron beam* 50 kGy, 9.5 cm scan, 2.26 m/min stream velocity electron beam *Enzymatic hydrolysis* Cellulase (Onozuka R-10) 5000 U/g dry substrate $T = 40$ °C, time = 48 h	Solid fraction: 36 % glucose yield	Xin and Kumakura (1993)
Sugarcane bagasse	*Electron beam* 50 kGy, 112 cm scan, 6.72 m/min stream velocity electron beam	*Hydrothermal* $T = 180$ °C Time = 60 min L/S ratio = 12.5:1 (v/w) Distilled H_2O *Acid hydrolysis* $T = 180$ °C Time = 60 min L/S ratio = 0.1 % (w/w) H_2SO_4 *Enzymatic hydrolysis* Cellulase (Celluclast 1.5L) 5 FPU/g cellulose, β-glucosidase (Novozyme 188) 0.5 % (p/p) $T = 50$ °C, time = 48 h	Solid fraction: 71.89 % glucose recovery, 97.00 % xylose recovery	Duarte et al. (2012)
Switchgrass	*Electron beam* 1000 kGy, 3 m/min stream velocity electron beam	*Hydrothermal* $T = 150$ °C time = 3 h L/S ratio = 20:1 (v/w) *Enzymatic hydrolysis* Cellulase (ATCC 26921) 5 FPU/g cellulose and β-glucosidase (CAS 9001-22-3) 7.80 U/mg $T = 50$ °C, time = 144 h	Solid fraction: 22.8 % glucose yield	Sundar et al. (2014)

et al. 2012) by breaking down the crystalline cellulose regions and modifying the lignin structure (Hong et al. 2014). Thus, the generation of phenoxy radicals via ionizing radiation, which are important radical intermediates in lignin formation, would subsequently transform into lignin O-quinonoid structures (Chunping et al. 2008). This structure might enable enzymes to access the biomass more easily. Orozco et al. (2012) argued that γ-rays degraded lignocellulose components via three mechanisms, namely (1) weakening of van der Waals force, (2) production of free radicals through cleavage of hydrogen bonds and (3) hydrolysis of glycoside bonds. Consequently, cell wall degradation was assisted by the weakening of cell wall constituents, as well as fiber depolymerization and delignification (Yoon et al. 2012). Even after the termination of radiation, some of the radicals that were trapped in crystalline and semi-crystalline regions of the cellulose could decay over time to cause further biomass degradation (Hong et al. 2014).

Surface morphology studies indicated that the even and smooth surface of wheat straw became rugged with a broken structure after undergoing γ-ray radiation. In fact, the effect was further enhanced when γ-ray radiation was combined with dilute acid pretreatment in which the surface appeared to be severely damaged with leaf split up to many pieces as shown in Fig. 2 (Hong et al. 2014). Wang et al. (2012) also observed a similar change in lignocellulosic structure after undergoing γ-ray radiation, as the rough surface indicated destructuralization of fibers and hence an increase in cellulose reactive area. Furthermore, small droplets were observed on the uneven surface, ascribed to the melting and wider distribution of lignin at 1000 kGy of γ-ray irradiation (Wang et al. 2012).

Previous studies showed that the recovery of sugars increased with γ-ray dosage, especially when γ-ray irradiation was integrated with other pretreatment systems, particularly dilute acid hydrolysis. For instance, the reducing sugar concentration experienced a steady rise from 0.017 (without γ-ray) to 0.048 g/l (500 kGy of γ-ray), which was further enhanced to 0.235 g/l when γ-ray irradiation was implemented with dilute acid pretreatment (Yoon et al. 2012). In another study conducted by Hong et al. (2014), a cellulose-enriched solid portion was produced because of the complete removal of xylose content, promoting more efficient enzymatic hydrolysis. When γ-ray irradiation was increased from 0 to 1000 kGy, the glucose yield improved from 24.9 to 40.2 %. However, when 1000 kGy of γ-ray was combined with 3 % of (w/w) H_2SO_4, 69.7 % of sugar recovery could be achieved because of the faster and greater release of soluble glucose (Hong et al. 2014). The combination of 1000 kGy and 3 % (w/w) of γ-ray and H_2SO_4, respectively, showed a remarkable fermentable sugar yield of 83.0 %, which was greater than the individual pretreatment of γ-rays (51.5 %) or dilute acid pretreatment (56.1 %) (Chung et al. 2012). The enhancement in sugar recovery was correlated with the greater disruption of cellulose crystalline structure, alteration in polymeric lignin structures as well as removal of hemicellulose (Hong et al. 2014). Furthermore, the integration of γ-rays with dilute acid pretreatment drastically decreased the CrI of poplar bark, reaching the lowest value of 4.5 % at 1000 kGy (Chung et al. 2012). However, excessive irradiation caused a decrease in the total reducing sugar concentration, as proven by Wang et al. (2012), when the radiation dosage was increased from 800 to 2000 kGy. Orozco et al. (2012) stated that the biomass degradation was irrelevant at a low dosage of <600 kGy, but further increased beyond 1800 kGy causing glycolytic degradation of sugars. Hence, the results implied that excessive γ-ray dosage above a certain threshold could have an adverse effect on sugar recovery because of monomeric sugar degradation. The performance of γ-rays in assisting sugar recoveries from various lignocellulosic biomass sources is summarized in Table 3.

Pulsed electrical field

Pulsed electrical field (PEF) is a form of electroporation or electropermeabilization in which the cell suspensions are basically subjected to high electric fields over a short period of time to increase the membrane permeability of the cells (Zbinden et al. 2013). A very short burst (∼100 μs) of high voltage is applied from electrodes in order to induce the critical electrical potential, leading to rapid electrical breakdown and local structural changes of the plant tissue (Kumar et al. 2011). This technology is relatively established in the fields of biology, biotechnology and medicine for microorganism access. The application of an external electrical field above the transmembrane potential created very evident signs of cell polarity and produced charge separation as well as a dipole moment parallel to the external field (Zbinden et al.

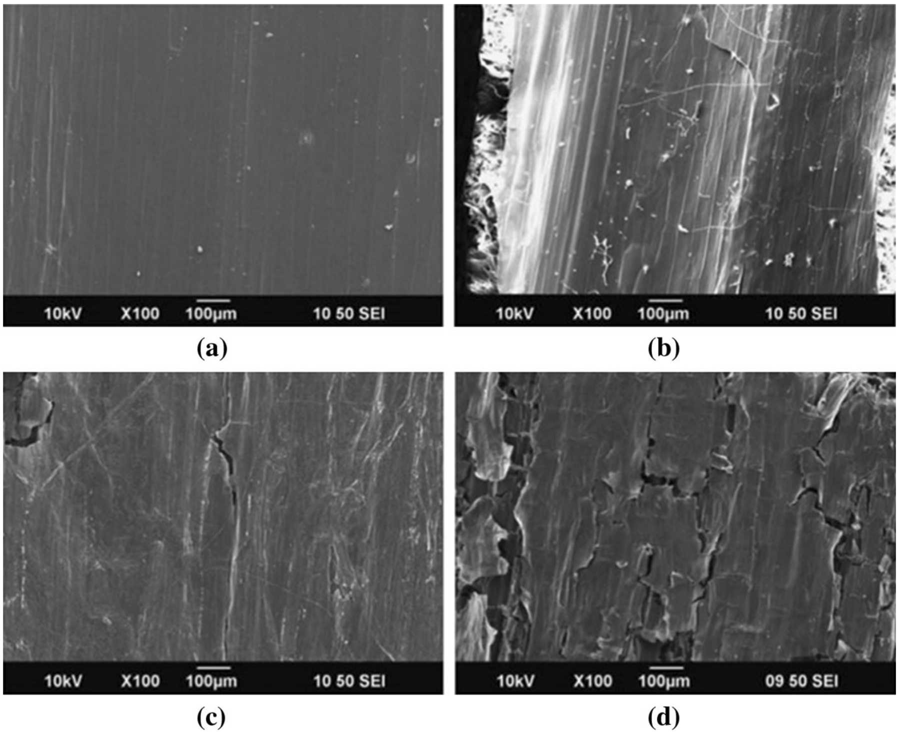


Fig. 2 Scanning electron micrographs at ×100 magnification of **a** untreated and pretreated wheat straw using **b** 1000 kGy gamma ray, **c** 3 % H_2SO_4 and **d** 3 % H_2SO_4 + 1000 kGy gamma ray (Hong et al. 2014)

2013). The formation of pores was even more visible using PEF at short duration pulses, whereas above the critical applied field, irreversible pore formation might result from dielectric rupture because of high electrocompressive forces (Zbinden et al. 2013). Field strength, pulse duration, number of pulses and type of electrical pulses (rectangular or exponential decay) were identified as several important parameters during PEF operation (Zbinden et al. 2013).

To date, PEF has not been directly used to recover sugars from lignocellulosic biomass. Instead, it was used as a pretreatment strategy for intensifying lipid extraction from the biomass (Zbinden et al. 2013) as well as algae on an industrial scale (Eckelberry et al. 2011; Kempkes et al. 2011). Nevertheless, PEF has the potential to be used as an alternative irradiation pretreatment of biomass for recovering sugars. This is because the phospholipids and peptidoglycan, which make up cell membranes and walls, contain polar molecules that give a net negative charge on the outer surface of cells (Stumm and Morgan 1996). Hence, the polar nature of the cell membranes and walls could make them more susceptible to the action of strong electrical fields. Zbinden et al. (2013) found that PEF was able to disrupt cells in the biomass to provide better access of enzymes to the biomass structure to improve sugar conversion. To prove this, Kumar et al. (2011) investigated the rate of colored dye in PEF-treated wood chips and switchgrass caused by the change of porosity during the pretreatment. The permeabilization of wood chips and switchgrass was significantly improved when the lignocellulosic biomass was pretreated with PEF at 8 and 10 kV/cm, respectively (Kumar et al. 2011). Thus, high PEF strengths in the range of 5–20 kV/cm might be able to facilitate the transportation of chemicals or enzymes into the lignocellulose structure for more efficient degradation, resulting in more desirable enzymatic or acid hydrolysis rates (Kumar et al. 2011).

Microwave

A microwave (MW) is defined as an electromagnetic wave that interacts with polar molecules such as water (Xia et al. 2013) and ions in a material to drive reactions (Diaz et al. 2015; Pang et al. 2012). MW

Table 3 Performance of gamma rays in pretreatment of various lignocellulosic biomass

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Marine algae biomass	*Gamma irradiation* $T = 22 \pm 0.5$ °C Dose rate = 10 kGy/h, 500 kGy	*Acid* $T = 121$ °C Time = 180 min 1 % H_2SO_4	Liquid fraction: 0.235 g/l total reducing sugar concentration	Yoon et al. (2012)
Poplar bark	*Acid* $T = 121$ °C Time = 60 min 3 % (w/w) H_2SO_4 *Gamma irradiation* Dose rate = 1000 kGy	*Enzymatic hydrolysis* Cellulase (Onozuka R-10) 2900 U/g biomass, β-glucosidase (Novozyme 188) 63.9 U/g biomass, endo-β-(1-4) xylanase (X2753) 2500 U/g biomass $T = 37$ °C, time = 96 h	Solid fraction: 83.1 % (w/w) reducing sugar yield	Chung et al. (2012)
Rice straw	*Gamma irradiation* $T = 25$ °C Dose rate = 2.0 kGy/h, 800 kGy *Acid* $T = 124$ °C Time = 60 min L/S ratio = 10:1 (v/w) 1.0 % (w/v) H_2SO_4	*Enzymatic hydrolysis* Cellulase (ZC-1700) 2000 U/g substrate $T = 50$ °C, time = 48 h	Solid fraction: 43.281 ± 0.001 mg glucose/g biomass, 47.074 ± 0.003 mg xylose/g biomass	Wang et al. (2012)
Wheat straw	*Acid* $T = 121$ °C Time = 60 min L/S ratio = 25:1 3 % (w/w) H_2SO_4 *Gamma irradiation* $T = 25$ °C (Ambient) Dose rate = 12 kGy/h, 1000 kGy	*Enzymatic hydrolysis* Cellulase 3.2 mg/g biomass, β-glucosidase 540 μg/g biomass, endo-β-(1-4) xylanase 540 μg/g biomass $T = 37$ °C, time = 96 h	Solid fraction: 69.7 % (w/w) glucose yield	Hong et al. (2014)

energy is able to couple with the molecules in a pretreatment mixture in order to provide more volumetric and energy-efficient internal heating of a substrate. The polar molecules and disordered ions are spun by the oscillating electric field component in MW, dissipating heat via molecular friction for uniform and rapid heating (Chen et al. 2012b; Xia et al. 2013). Besides, materials containing dielectrics that were heated by electromagnetic energy could create non-thermal effects that enhanced the degradation of lignocellulose, which is more efficient than superficial heat transfer in conventional heating systems (Chen et al. 2012a; Xia et al. 2013). According to Lai and Idris (2013), MW irradiation did not cause local overheating, which might decompose the product, substrate or reagent during the pretreatment process.

When MW was used for lignocellulose pretreatment, MW radiation selectively heated the more polar regions of the biomass, generating “hot spots” to create explosion effects among the heterogeneous material particles. Subsequently, the crystalline structure in lignocellulose was disrupted (Vani et al. 2012). In a study conducted by Marx et al. (2014), pretreatment with MW heating was able to convert up to 100 % cellulose and 58.5 % hemicellulose into hexose and pentose sugars, respectively. Besides, MW could be easily combined with chemicals such as acid, alkali or other reagents for enhancing reaction rates (Binod et al. 2012). For example, remarkable results were achieved when MW was integrated with alkali, as the electrolyte solution acted as a microwave sensitizer for energy absorption (Tsubaki and Azuma 2013). The use of 2.5 M of NaOH with MW enabled the cleavage of inter- and intra-molecular hydrogen bonds within the lignin and hemicellulose matrix of biomass (Lai and Idris 2013). Higher sugar recovery was also achieved via MW acid (36.84 %) in comparison with ultrasonic acid (30.76 %) because of more effective lignocellulose degradation during MW heating (Gabhane et al. 2014a). Moreover, MW was used to intensify the fractionation of rice straw components in a $FeCl_3$ solution, resulting in 2.9-fold reducing sugar production (Lu and Zhou 2011). Darji et al. (2015) and Mai et al. (2014) also successfully implemented ionic liquid with MW heating as the highly ionic and polar nature of the medium promoted rapid and effective dissolution during MW heating. As a result, the collision frequency between anions and cations of ionic liquid and biomass macromolecules intensified the breakage of hydrogen bonds within the biomass matrix (Darji et al. 2015). The performance of MW-assisted sugar recoveries from various lignocellulosic biomass sources is summarized in Table 4.

MW heating had the capability to form cracks and tiny cavities on the initially smooth, compact and rigid fibrils of raw biomass (Lai and Idris 2013; Vani et al. 2012). It was also able to damage and remove the silica waxy surface (Lu and Zhou 2011; Xia et al. 2013) of biomass, but changes were more significant when MW was used together with acid, whereby many channels and various sizes of pores were formed after undergoing the combined pretreatments (Xia et al. 2013). Chen et al. (2012b) claimed that an MW temperature of $\geq$130 °C caused the swelling of biomass when MW was assisted with ammonia, but the effects were barely noticeable below 130 °C. Lai and Idris (2013) also added that the exposure of the cellulose structure allowed for better enzyme accessibility, indicated by the enhanced CrI in oil palm trunks (42.07–56.08 %) and oil palm fronds (37.21–44.20 %). Similar trends were observed by Lu and Zhou (2011) and Vani et al. (2012), whereby the CrI of the biomass increased from 28.3 to 43.0 % and 45.3 to 60.0 %, respectively, after the removal of amorphous components that prevented the non-productive binding of enzymes and intensified cellulose digestion. According to Chen et al. (2011), the destruction of biomass structure became increasingly pronounced when the MW temperature was increased from 130 to 190 °C. Fragmentation and swelling were observed on the bagasse surface at 130 °C, while more severe disruptions were reported at 160 °C as shown in Fig. 3 (Chen et al. 2011). However, the effect of MW radiation seemed to be more apparent on the amorphous regions of the biomass rather than the crystalline regions (Binod et al. 2012).

High MW power and time favored the dissolution of extractives in the biomass, along with the condensation of lignin (Pang et al. 2012). Likewise, increases in these parameters improved glucose and xylose yields. For example, Janker-Obermeier et al. (2012) recorded greater removals of hemicellulose (80 %) and lignin (90 %) with higher power input due to the cleavage of inter-unit linkages in lignin that formed smaller molecular compounds, leading to a significant reduction in pretreatment time as compared to using alkaline pretreatment at ambient conditions. However,

Table 4 Performance of microwave in pretreatment of various lignocellulosic biomass

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Banana pith waste	*Alkali + Microwave* $T = 180$ °C Time = 30 min L/S ratio = 10:1 (v/w) 1 % (w/v) NaOH Power = 700 W	*Enzymatic hydrolysis* Cellulase (ONOZUKA-R10) 50 FPU/g cellulose $T = 50$ °C, time = 48 h	Solid fraction: 35.96 % reducing sugar yield	Gabhane et al. (2014a)
	Acid + Microwave $T = 121$ °C Time = 30 min L/S ratio = 10:1 (v/w) 5 % (v/v) H_2SO_4 Power = 700 W	*Enzymatic hydrolysis* Cellulase (ONOZUKA-R10) 50 FPU/g cellulose $T = 50$ °C, time = 48 h	Solid fraction: 36.84 % reducing sugar yield	
Big bluestem	*Extrusion + Microwave* Time = 2.5 min Power = 450 W	*Enzymatic hydrolysis* Cellulase (Spezyme CP) 70 FPU/g glucan, β-glucosidase (Novozyme 188) 250 CBU/g glucan $T = 50$ °C, time = 72 h	Solid fraction: 83.2 % glucose, 92.1 % xylose, 68.1 % total sugar recovery Solid fraction: 0.11 g/l acetic acid	Karunanithy et al. (2014)
Cashew apple bagasse	*Alkali* $T = 28$ °C Time = 10 min L/S ratio = 10:3 (v/w) 0.2 mol/l NaOH *Microwave* Time = 15 min Power = 600 W	*Enzymatic hydrolysis* Cellulase (Celluclast 1.5L) 134.63 FPU/ml mixture, β-glucosidase (Novozyme 188) 5.0 CBU/mm mixture $T = 45$ °C, time = 72 h	Solid fraction: 372 ± 12 mg glucose/g glucan yield	Rodrigues et al. (2011)
Corn stover	*Steam explosion* $T = 190$ °C Time = 5 min *Microwave* Time = 5 min Power = 540 W	*Enzymatic hydrolysis* Cellulase (Celluclast 1.5L) 60 FPU/g glucan, β-glucosidase (Novozyme 188) 60 CBU/g glucan $T = 50$ °C, time = 72 h	Liquid fraction; 5.80 g glucose, 5.94 g xylose (per 100 g biomass) 0.29 g furfural, 0.89 g HMF (per 100 g biomass)	Pang et al. (2012)

Table 4 continued

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Cotton plant residue	*Alkali* + *Microwave* Time = 6 min *L*/*S* ratio = 100:17.5 (v/w) Power = 300 W	*Enzymatic hydrolysis* Cellulase (Zytex) 45 FPU/g glucan $T = 50$ °C	Solid fraction: 0.495 g maximum reducing sugar yield/g biomass	Vani et al. (2012)
Green tea residue	*Alkali* + *Microwave* $T = 200$ °C Time = 5 min *L*/*S* ratio = 20:1 (v/w) 1 % NaOH	*Enzymatic hydrolysis* Cellulase (Meicelase) 1.0 % (w/w) $T = 37$ °C, time = 48 h	Liquid fraction: 51.8 ± 8.6 % glucose, 4.8 ± 3.8 % xylose, 19.2 ± 1.1 % arabinose composition Solid fraction: 58.7 ± 6.1 % glucose, 10.8 ± 3.2 % xylose, 4.9 ± 0.4 % arabinose composition	Tsubaki and Azuma (2013)
Rice hulls	*Alkali* + *Microwave* Time = 22.50 min *L*/*S* ratio = 30 g/l 2.75 %	*Enzymatic hydrolysis* Spore suspension (*Aspergillus heteromorphus*) $T = 30$ °C, time = 9 days	Solid fraction: ~27.0 mg reducing sugars/g biomass	Singh et al. (2011)
Rice straw	*Inorganic salt* + *Microwave* $T = 160$ °C Time = 19 min *L*/*S* ratio = 10:1.09 (v/w) 0.14 mol/l $FeCl_3$ Power = 800 W	*Enzymatic hydrolysis* *Bacillus pumilus* spore (1 ml/100 ml medium), *Trichoderma viride* spore (2 ml/100 ml medium) $T = 30$ °C, time = 72 h	Solid fraction: 6.62 g/l reducing sugars	Lu and Zhou (2011)
Rice straw	*Alkali* + *Microwave* Time = 22.50 min *L*/*S* ratio = 30 g/l 2.75 %	*Enzymatic hydrolysis* Spore suspension (*Aspergillus heteromorphus*) $T = 30$ °C, time = 9 days	Solid fraction: ~37.5 mg reducing sugars/g biomass	Singh et al. (2011)
Rubber wood biomass	*Ionic liquid* + *Microwave* *L*/*S* ratio = 20:1 $[C_4mim][OAc]$ Power = 200 W	*Enzymatic hydrolysis* Cellulase (Spezyme CP) 52 FPU/g glucan, β-glucosidase (Novozyme 188) 130 CBU/g glucan $T = 48$ °C, time = 72 h	Solid fraction: 52 % glucose yield	Darji et al. (2015)
Sago bark waste	*Acid* + *Microwave* Time = 30 s *L*/*S* ratio = 4:1 (w/w) 3 % (v/v) H_2SO_4 Power = 1100 W	*Enzymatic hydrolysis* α-amylase 2.0 g, glucoamylase 0.10 g $T = 50$ °C, time = 6 h	Solid fraction: 62.6 % maximum sugar yield	Kannan et al. (2013)

Table 4 continued

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Sorghum bagasse	*Alkali + Microwave* $T = 130$ °C Time = 60 min L/S ratio = 10:1 (v/w) 28 % (v/v) NH_4OH	*Enzymatic hydrolysis* Cellulase (Spezyme CP) 60 FPU/g glucan, β-glucosidase (Novozyme 188) 64 CBU/g glucan $T = 55$ °C, time = 72 h	Solid fraction: 4.2 g glucose/10 g dry biomass yield Solid fraction: 0.7 g/l acetic acid, < 0.1 g/l HMF, < 0.1 g/l furfural	Chen et al. (2012a)
Sorghum liquor waste	*Microwave* Time = 3 min L/S ratio = 10:1 (v/w) 1 N HCl Power = 800 W	*Enzymatic hydrolysis* Cellulase (*Trichoderma reesei*) 25 FPU/g dry biomass, cellobiase (*Aspergillus niger*) 30 IU/g dry biomass $T = 50$ °C, time = 48 h	Solid fraction: 90.5 % reducing sugar recovery (341.3 mg reducing sugar/g biomass) Solid fraction: ~0.19 mg acetic acid/g dry biomass	Su et al. (2010)
Sugarcane bagasse	*Alkali + Microwave* Time = 4 min L/S ratio = 10:1 (v/w) 1 % NaOH Power = 600 W *Acid + Microwave* Time = 4 min L/S ratio = 10:1 (v/w) 1 % H_2SO_4 Power = 600 W	*Enzymatic hydrolysis* Cellulase (Zytex) 30 FPU/g biomass $T = 50$ °C, time = 72 h	Solid fraction: 0.83 g reducing sugar yield/g dry biomass	Binod et al. (2012)
Sugarcane baggase	*Acid + Microwave* $T = 180$ °C Time = 30 min L/S ratio = 10:1 (v/w) 0.005 M H_2SO_4 Power = 900 W	None	Liquid fraction: ~38 % xylose, ~6.4 % glucose recoveries Liquid fraction: ~7 % furfural, ~0.6 % HMF	Chen et al. (2012b)
Switch-grass	*Extrusion + Microwave* Time = 2.5 min Power = 450 W	*Enzymatic hydrolysis* Cellulase (Spezyme CP) 70 FPU/g glucan, β-glucosidase (Novozyme 188) 250 CBU/g glucan $T = 50$ °C, time = 72 h	Solid fraction: 52.6 % glucose, 75.5 % xylose, 59.2 % total sugar recovery Solid fraction: 0.12 g/l acetic acid	Karunanithy et al. (2014)

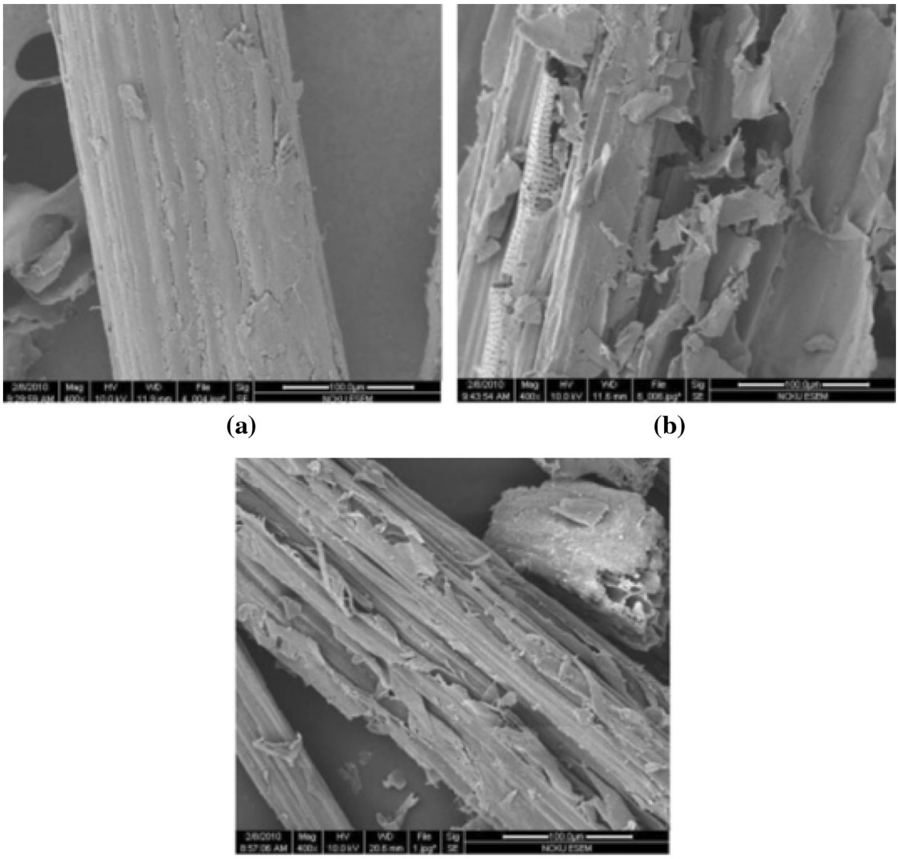
Table 4 continued

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Water hyacinth	*Acid + Microwave* $T = 140$ °C Time = 15 min L/S ratio = 50:1 (v/w) 1 % H_2SO_4	*Enzymatic hydrolysis* Cellulase (*Trichoderma reesei*) $T = 45$ °C, time = 60 h	Liquid fraction: 94.6 % reducing sugar yield	Xia et al. (2013)
Wheat straw	*Alkali + Microwave* $T = 140$ °C Time = 10 min L/S ratio = 9:1 (w/w) 5 wt % NaOH	None	100 % glucose, 97 % xylose, 57 % arabinose recovery	Janker-Obermeier et al. (2012)

Rodrigues et al. (2013) confirmed the reduction of glucose recovery from 355 to 307 mg/g glucan when the power was raised excessively from 600 to 900 W. According to Xia et al. (2013), the hydrolysis of hemicellulose also markedly increased with temperature, as the biomass attained a low residual hemicellulose content of 16.93 % at 120 °C and complete degradation at 160 °C. On the other hand, a temperature of 180 °C assisted crystalline structure degradation and cellulose hydrolysis to achieve maximum glucose recovery of 8.74 g/100 g biomass, but the glucose was found to be degraded beyond 180 °C (Xia et al. 2013). Short pretreatment durations could be compensated with higher MW power. For instance, maximum reducing sugar yield was obtained using 3 and 24 min of pretreatment at 850 and 100 W, respectively (Binod et al. 2012). Nonetheless, Pang et al. (2012) affirmed that lower power and shorter times were recommended in pretreatment of lignocellulosic biomass because less severe conditions reduced both energy consumption and potential generation of degradation products because of localized overheating (Pang et al. 2012; Vani et al. 2012).

Ultrasound

An application of energy in the form of sound waves is known as ultrasonication, usually applied with a frequency of >20 kHz for the intention of cell disruption (Ofori-Boateng and Lee 2014b). Depending on the frequency, ultrasound (US) can be generally categorized into three classes, namely power (16–100 kHz), high frequency (0.1–1 MHz) and diagnostic (1–10 MHz) (Kang et al. 2013). US ranging from 20 to 100 kHz is usually used in chemically important systems in which chemical and physical changes are desired as it has the ability to cause cavitation of bubbles (Wu et al. 2013). During US, energy is simultaneously provided by means of cavitation, turbulence, agitation as well as heating (Rehman et al. 2014). When US is applied to liquid slurry, 4–300 micron bubbles can be generated (Luo et al. 2014). As a result, nearby particles are disintegrated for improved diffusivity or mass transfer because of vigorous hydromechanical shear forces (Luo et al. 2014; Rehman et al. 2014), which depolymerize the macropolymers in lignocellulosic biomass (Velmurugan and Muthukumar 2011). US has been used to assist many thermo- and biochemical



(a) (b)

(c)

Fig. 3 Scanning electron micrographs at ×400 magnification of **a** untreated and pretreated sugarcane bagasse using H_2SO_4 plus 900-W microwave at the reaction temperature of **b** 130 °C and **c** 160 °C (Chen et al. 2011)

reactions with increased sugars, bioethanol and gas products up to 10–300 % when US was combined with the proper solvents (Luo et al. 2014). However, the difficulty in calculating acoustic properties induced by US leads to very few studies being conducted to evaluate the effect of US pretreatment on the biomass (Hodnett and Zeqiri 1997).

Even though US alone was incapable of hydrolyzing polysaccharides to monomeric sugars (Villa-Velez et al. 2015; Yunus et al. 2010), it could assist the breaking of lignocellulosic linkages while producing fewer impurities in the process (Kang et al. 2013). As such, similar to enzymatic hydrolysis, US did not obtain remarkable recoveries when used on its own, but only when US was used as an auxiliary or before other pretreatments (Placido et al. 2013). Biomass pretreated by US was more easily hydrolyzed for extraction of cellulose, hemicellulose and lignin compounds (Luo et al. 2014) because of the increased accessible surface area and improved mass transfer of reactants (Kang et al. 2013; Placido et al. 2013). Gabhane et al. (2014b) successfully recovered more reducing sugars (59.56 %) via US-assisted alkali pretreatment, which was more than alkali alone (32.76 %). Also, Subhedar and Gogate (2014) reported that US caused a twofold increase in the extent of biomass delignification as compared to only using alkaline pretreatment. US was used to facilitate the diffusion of 1-allyl-3-methylimidazolium chloride ionic liquid into the structure of biomass (Liu et al. 2013). When the transient cavitation bubbles shrank or collapsed, high local temperatures and compressed air were formed to generate violent shock waves and jet streams to promote the binding of 1-allyl-3-methylimidazolium chloride to the biomass cellulose structures as shown in Fig. 4 (Liu et al. 2013). Moreover, the conversion of cellulose to glucose reached a maximum of 95.48 % when 1-methyl-3-methylimidazolium

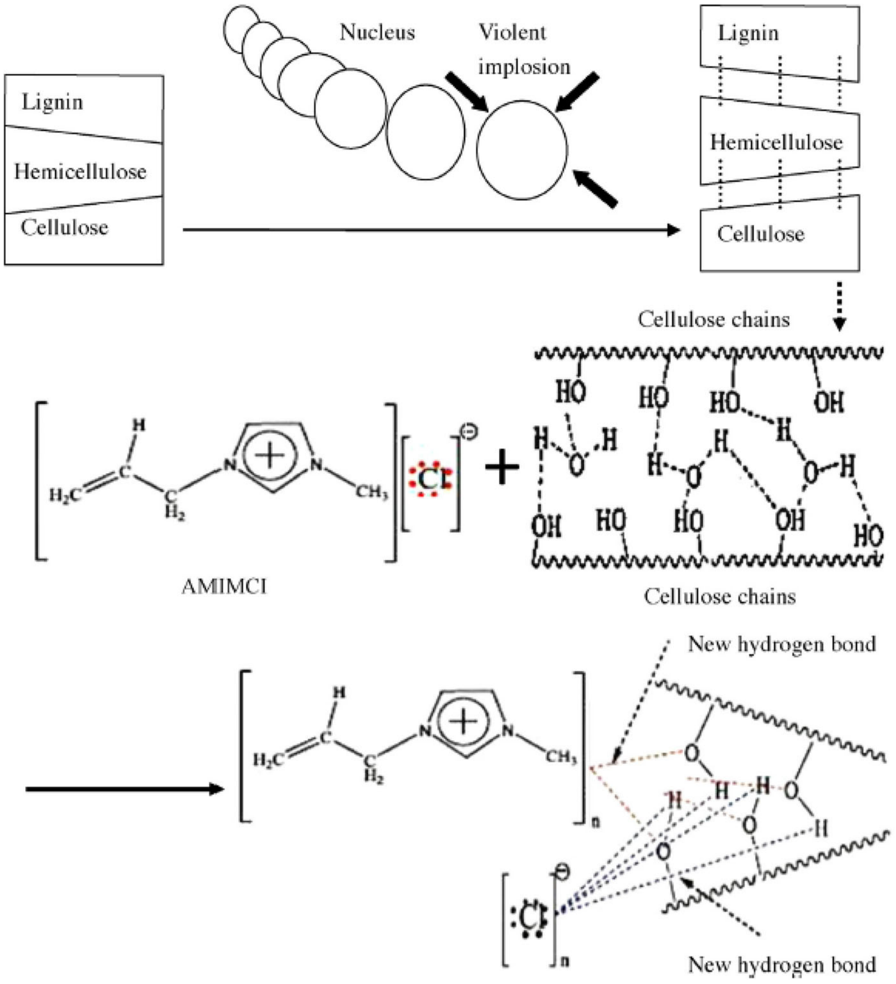


Fig. 4 Mechanism of cellulose dissolution in 1-allyl-3-methylimidaolium chloride with ultrasound energy (Liu et al. 2013)

dimethylphosphate was used in conjunction with US (Yang et al. 2010). Hence, the result from the ionic liquid-US integrated pretreatment was significantly higher than the control (42.77 %) and cellulose treated with mere conventional heating (75.57 %). Velmurugan and Muthukumar (2011) found that US also facilitated contact between reactants during acid hydrolysis, subsequently hydrolyzing significant amounts of cellulose in a shorter period of time. Better catalyst-reactant contact during US was contributed by the phenomenon of micro-streaming, thereby improving mass and heat transfer (Luo et al. 2014). Therefore, faster reactions or a change of kinetics due to disengagement of heterogeneous reactants, intermediates and products could be achieved (Luo et al. 2014). The performance of US-assisted sugar recoveries from various lignocellulosic biomass sources is summarized in Table 5.

Some of the important parameters during US include the temperature and concentration of the medium (Ofori-Boateng and Lee 2014b). For example, US was proven to work well at low temperature ranges in any concentration of NaOH (Kang et al. 2013). Specifically, the enzymatic digestibility of biomass after undergoing NaOH pretreatment increased by 27 % when the pretreatment was coupled with US at a low temperature of 30 °C, but the effects were diminished at high temperature of around 80 °C (Kang et al. 2013). Yang and Fang (2014) observed comparable trends in which the total sugar yields reached a peak of 65.05 % at 50 °C. At lower temperature, cavitational effects were dominant in assisting the diffusion of enzymes into substrate networks. Furthermore, Villa-Velez et al. (2015) mentioned that the biomass could behave like a liquid to allow the spread of shock waves from bubble

Table 5 Performance of ultrasound in pretreatment of various lignocellulosic biomass

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Bamboo	*Ultrasound-Ionic liquid* $T = 25$ °C Time = 60 min L/S ratio = 10:1 (w/w) ChOAc, 0.5wt % water Ultrasound = 24 kHz, 35 W	*Enzymatic hydrolysis* Cellulase (*Trichoderma viride*, Meicelase) 6200 FPU/g $T = 50$ °C, time = 48 h	Solid fraction: 92.4 ± 7.1 % glucose recovery	Ninomiya et al. (2013)
Cotton gin trash	*Ultrasound* L/S ratio = 10:1 *Autohydrolysis* $T = 121$ °C, $P = 15$ psi Time = 1 h L/S ratio = 10:1	*Enzymatic hydrolysis* Cellulase complex (Accellerase 1500) 2200–2800 CMC U/g and 525–775 pNPG U/g, hemicellulase complex (Accellerase XY) 20,000–30,000 ABXU/g $T = 50$ °C, time = 96 h	Solid fraction: 23.4 % glucose yield	Placido et al. (2013)
Garden biomass	*Ultrasound-Alkaline* $T = 45$–50 °C Time = 60 min L/S ratio = 50:1 (v/w) 1.0 % NaOH Ultrasound = 25 kHz, 150 W	*Enzymatic hydrolysis* Commercial cellulase (ONOZUKAR-10) 50 FPU/g biomass $T = 50$ °C, time = 48 h	Solid fraction: 59.56 ± 2.60 % reducing sugar yield	Gabhane et al. (2014b)
Oil palm fronds	*Ultrasound-Organosolv* $T = 76.82$ °C Time = 30.64 min L/S ratio = 20:1 (v/w) 1.39 % NaOH Ultrasound = 37 kHz, 200 W *Liquid peroxide* $T = 25$ °C Time = 16 h 3.42 % H_2O_2	*Enzymatic hydrolysis* Cellulase (Celluclast 1.5L) 15 FPU/g cellulose, β-glucosidase (Novozyme 188) 15 IU/g cellulose $T = 50$ °C, time = 48 h	Solid fraction: 26.51 g/l glucose, 8.63 g/l xylose Liquid fraction: 15.15 g/l xylose	Ofori-Boateng and Lee (2014a)

Table 5 continued

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Oil palm empty fruit bunch (OPEFB)	*Ultrasound* $T = 25$ °C Time = 45 min L/S ratio = 10:1 (v/w) 2 % H_2SO_4 Ultrasound = 20 kHz, 2000 W	*Acid* $T = 100$ °C Time = 200 min L/S ratio = 25:1 2 % H_2SO_4	Liquid fraction: ~53 % xylose yield, ~5 % glucose yield	Yunus et al. (2010)
Rapeseed-straw	*Ultrasound-Alkaline* $T = 75.0$ °C Time = 6.8 h L/S ratio = 10:1 (v/w) 7.0 % (w/w) NaOH Ultrasound = 40 kHz, 300 W	*Enzymatic hydrolysis* Cellulase 30 FPU/g cellulose, β-glucosidase 30 CBU/g cellulose $T = 50$ °C, time = 72 h	Solid fraction: 98.9 ± 0.3 % enzymatic digestibility	Kang et al. (2013)
Rice straw	*Ultrasound-Acid* $T = 80$ °C Time = 50 min L/S ratio = 10:1 10 % H_2SO_4 Ultrasound = 20 kHz, 750 W, 20 % amplitude	None	Solid fraction: 31.78 g reducing sugar/100 g dry biomass	Rehman et al. (2014)
Rice straw	*Ultrasound-Ionic liquid* $T = 60$ °C Time = 180 min L/S ratio = 25:1 (w/w) 5 % (w/w) [CH][OH] Ultrasound = 40 kHz, 300 W	*Enzymatic hydrolysis* Commercial cellulase (*T. reesei* ATCC 26921) 700 EGU/g cellulose $T = 50$ °C, time = 240 min Ultrasound = 40 kHz, 300 W	Solid fraction: 96.22 % reducing sugar yield	Yang and Fang (2014)
Sugarcane bagasse	*Ultrasound-Alkaline* $T = 50 \pm 10$ °C Time = 20 min L/S ratio = 20:1 (v/w) 2 % NaOH Ultrasound = 24 kHz, 100 % amplitude	*Ultrasound-Acid* $T = 50 \pm 10$ °C Time = 45 min L/S ratio = 20:1 (v/w) 2 % H_2SO_4 Ultrasound = 24 kHz, 50 % cycle control system	Liquid fraction: 69.06 % total hexose recovery (76.65 % glucose yield), 81.35 % total pentose recovery Liquid fraction: 0.1 g/l furfural, 0.95 g/l acetic acid	Velmurugan and Muthukumar (2011)

Table 5 continued

Lignocellulosic biomass	Initial pretreatment	Subsequent pretreatment	Key findings	Reference
Sweet sorghum	*Ultrasound* Time = 25 min *Autohydrolysis* T = 150 °C Time = 30 min L/S ratio = 9:1 (w/w)	*Enzymatic hydrolysis* Cellulase (Accellerase 1500) 2200–72,800 CMC U/g and 525–775 pNPG U/g, xylanase/cellulase (Accellerase XC) 1000–1400 CMC U/g and 2500–3800 ABXU/g T = 50 °C, time = 96 h	Solid fraction: 89 % glucose recovery, 48 % total xylose and arabinose recovery	Imam and Capareda (2012)
Triticale meal	*Ultrasound* T = 60 °C Time = 5 min L/S ratio = 3:1 H_2O Ultrasound = 40 kHz, 125 W	*Liquefaction* Automated mashing water bath L/S ratio = 3:1 T = 60 °C, time = 65 min	Solid fraction: 55.98 ± 0.46 g fermentable sugars/100 g dry matter	Pejin et al. (2012)
Z. Japonica grass	*AFEX* T = 120 °C, P = 200psi Time = 30 min	*Ultrasound-Ionic liquid* T = 80 °C, time = 30 min L/S ratio = 25:1 (w/w) Synthesized AMIMCI Ultrasound = 110 W	Liquid fraction: 52 % (w/w) cellulose solubility, 97 % (w/w) cellulose regeneration rate for recycling AMIMCI	Liu et al. (2013)

collapse throughout the entire volume of medium at low biomass concentration. High solid-to-liquid ratios could be detrimental to US effects, as proven by Bussemaker et al. (2013). They reported that the cavitation was hindered at 1:15 (g/ml) concentration of wheat straw, leading to inefficient physico-chemical effects. The concentrations of solid substrates were ranged between 2 and 5 wt%, as 5–10 wt% would require the addition of acid/base to improve the efficiency of US (Luo et al. 2014).

More importantly, the frequency, time and power of US also play significant roles in ultrasonication efficiency (Ofori-Boateng and Lee 2014b). Jiang et al. (2011) found that biomass exposure to low-intensity US for longer duration was similar to that of high intensity for shorter duration. According to Ofori-Boateng and Lee (2014b), low-intensity US could facilitate the disintegration of the biomass cell wall. Ashokkumar et al. (2008) highlighted that low- (20–100 kHz) and high-frequency (>100 kHz) US favored physical disruption and radical generation, respectively. High frequency US could be unsuitable for cavitation because of insufficient time, radial motion and bubble collapse (Luo et al. 2014). Besides, the smaller volume change of bubbles also contributed to rapid decay of acoustic energy (Luo et al. 2014). For example, US caused significant physical damage such as pits and cracking at 40 kHz and major carbohydrate solubilization due to enhanced radical attacks at 995 kHz (Bussemaker et al. 2013). In a detailed investigation conducted by Suresh et al. (2014), it was concluded that the contribution of US through micro-streaming was more significant for increasing sugar content as opposed to micro-turbulence and acoustic waves generated by the cavitation (Suresh et al. 2014). US at spatial and temporal scales was ineffective in opening biomass structure, and the US only facilitated the transport of monosaccharides out from the biomass matrix (Suresh et al. 2014). Basically, the majority of the US was beneficial in extracting carbohydrates within the first 20–30 min of pretreatment (Bussemaker et al. 2013). Rehman et al. (2014) enhanced the sugar yields by twofold when the sonication time was increased from 30 to 50 min. On the other hand, Yunus et al. (2010) attained a maximum xylose yield of 52 %, as compared to the control (22 %), when 90 % amplitude was applied for 45 min. However, contradictory results were reported by Subhedar and Gogate (2013), whereby lower sonication time was recommended for minimizing energy consumption and lignin condensation. Glucose recovery from starchy materials was improved using US for 5–10 min, while 10–20 min was more suitable for lignocellulosic materials (Subhedar and Gogate 2013). Pejin et al. (2012) also added that while US for short periods might be effective in destroying amorphous regions, the compact crystalline regions could not be degraded easily even at longer sonication durations. In addition, US power greatly affected the number and lifetime of cavitation bubbles as well as the cavitation intensity. Particularly, bubbles that were formed at the transducer during US at high power levels might obstruct the transfer of energy to the medium, adversely affecting the cavitational effects (Subhedar and Gogate 2014). Villa-Velez et al. (2015) found that the morphology of the biomass changed in accordance with the power: the cellulose structure was altered at 300 W; a homogeneous structure with compact and shorter fibrils was formed at 900 W; cellulose microstructure particle size was significantly reduced at 1500 W. Regardless, yields were found to be proportional to the power, but the US power and time were inversely related (Imai et al. 2004). Stirring during US was not recommended as it could interrupt the cavitation field around the solid surface in the solid–liquid system, causing the liquid jet force to be abated and thus decreasing the radical production (Bussemaker et al. 2013).

According to Ninomiya et al. (2013), the biomass became rougher after introducing choline acetate pretreatment, but was further disordered with the implementation of US. Alkali pretreatment that was assisted with US showed that the surface of sugarcane bagasse became rough and porous because of the combined effects of NaOH swelling and free radicals formed by US (Velmurugan and Muthukumar 2011). The effect of US on biomass surface morphology is shown in Fig. 5 (Kim and Han 2012). In addition, the physicochemical effects induced by dilute acid microbubbles during US created a microporous surface that enabled easier access to the biomass interior structure (Rehman et al. 2014). The cavitation phenomenon during US even caused surface pitting with severe surface erosion (Luo et al. 2014) and bumps on the surface, along with the reduced silica content from 5.94 to 0.94 %, which promoted hydrolysis (Yang and Fang 2014). Yunus et al. (2010) deduced that the perforation of the silica crater contributed to better penetration of water molecules into the biomass

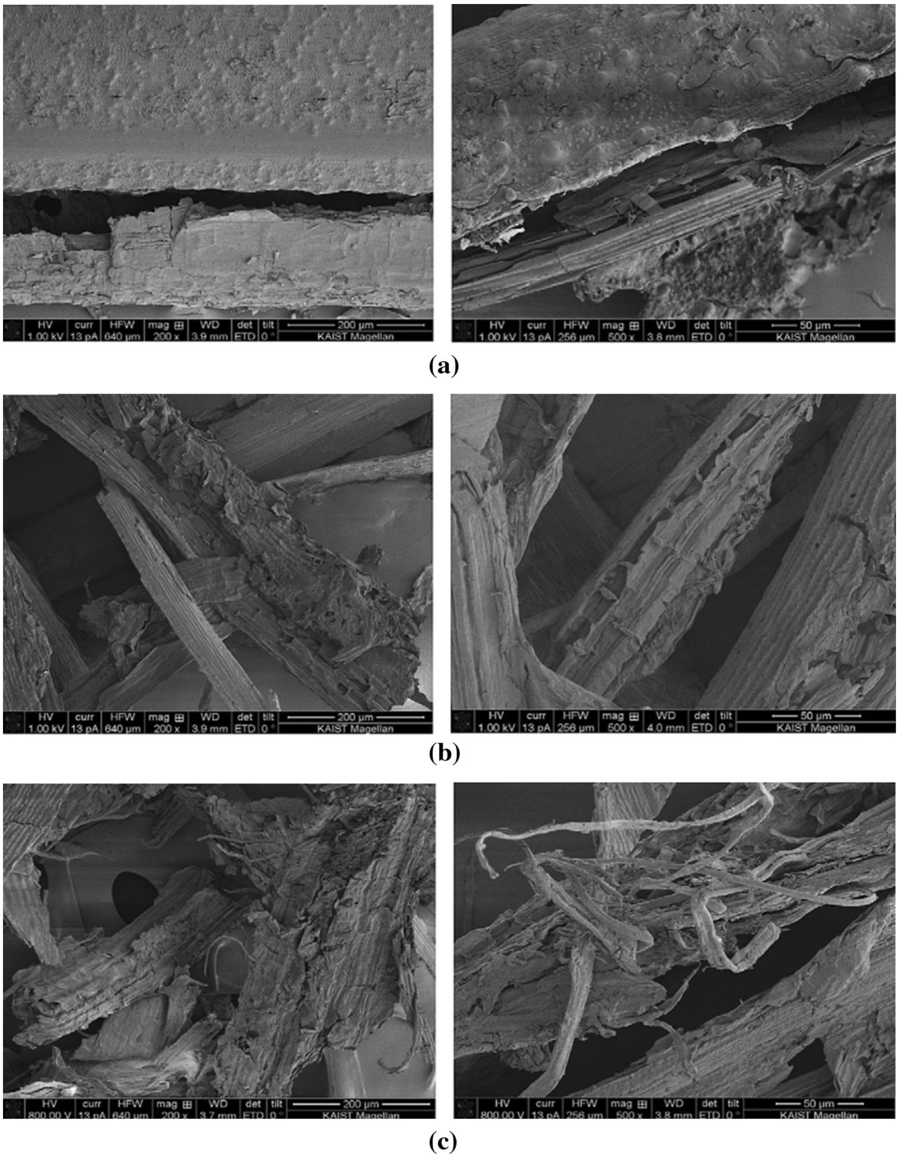
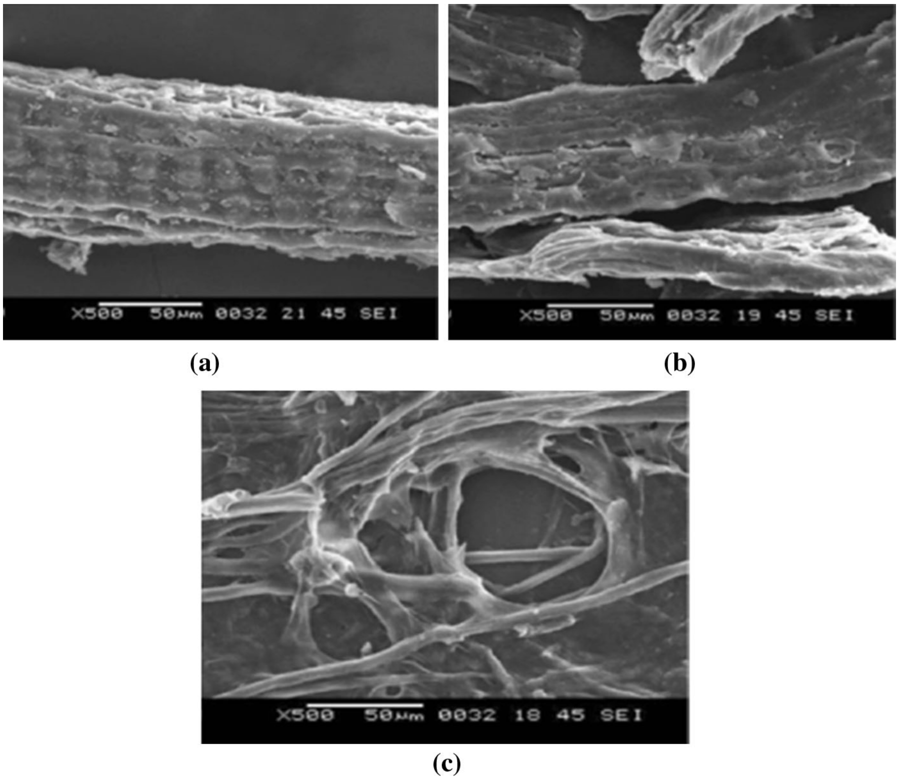


Fig. 5 Scanning electron micrographs at ×200 (*left*) and ×500 (*right*) magnifications of **a** untreated and pretreated rice straw using **b** 2.0 % NaOH and **c** 2.0 % NaOH + 300 W ultrasound (Kim and Han 2012)

during US-assisted acid hydrolysis. Also, acid hydrolysis increased the CrI of sugarcane bagasse from 50 to 66 % and was further enhanced to 70.7 % when the pretreatment was integrated with US (Velmurugan and Muthukumar 2011). Gabhane et al. (2014b) reported a decrease in the degree of biomass polymerization after undergoing US irradiation, exhibited by an increase of CrI from 72.9 to 82.8 %. In comparison with MW irradiation, which formed fragmentation at 200 °C, US caused fibrillation to the biomass surface, in which the cellulose fibrils appeared as forks and fine fibrils with major cracks on the cell wall, as shown in Fig. 6 (Gabhane et al. 2014b). In this aspect, US appeared to be more advantageous as the fibrillation would ease enzymatic hydrolysis, whereas the complete tissue collapse after undergoing MW resulted in less space for microbial activities (Gabhane et al. 2014b). Also, US energy was capable of causing particle size reduction for improving solubilization (Bussemaker et al. 2013). For instance, when US was used with hot



(a) (b)

(c)

Fig. 6 Scanning electron micrographs at ×500 magnification of **a** untreated and pretreated garden biomass using **b** 1 % NaOH + 700 W microwave and **c** 1 % NaOH + 150 W ultrasound (Gabhane et al. 2014b)

water, the surface area was enhanced with a reduction of average particle size of biomass from 1000 to 10 µm (Imam and Capareda 2012).

Prospect of energy irradiation pretreatment

Advantages of energy irradiation

One of the main advantages of energy irradiation is the reduced toxicity during biomass pretreatment as the use of reagents is not essential, though the combination between energy irradiation and chemicals usually gives higher sugar recovery. Thus, the need to set up a wastewater treatment system for the spent chemicals may be eliminated, which is economically viable especially in large-scale operations. Furthermore, according to Karthika et al. (2012) and Sundar et al. (2014), certain ionizing radiation methods such as EB had the advantage of disrupting complex lignocellulosic structures without forming any inhibitory components since extreme temperature was not required during the energy irradiation pretreatment (Bak et al. 2009). The negligible production of major inhibitors such as acetic acid, furfural and HMF content contributed to better bioconversion rates in the later stages (Bak 2014). Duarte et al. (2012) confirmed that the combination of energy irradiation and enzymatic hydrolysis managed to decrease pretreatment severity, preventing both excessive sugar degradation and generation of toxic by-products.

Additionally, some irradiation technologies offer vast opportunities for cost reduction during biomass pretreatment because of less severe operating conditions and ease of operation. For example, PEF could be carried out under ambient conditions with low energy usage, since processing could be done at relatively short pulse times as well as at ambient temperature (25 °C) and pressure (1 atm) (Kumar et al. 2011). PEF is a very energy-efficient technique, as the rupturing of cells is contributed by the presence of the electrical field and not temperature effects. Particularly, PEF showed remarkable energy savings of 50, 80 and 95 % in comparison with traditional mechanical, enzymatic and thermal pretreatment technologies, respectively (Zbinden et al. 2013). In addition, no moving part is involved in the equipment, which simplifies the equipment operation. On the other hand, MW irradiation offers lower process energy and time requirements, consistent processing, better control and flexibility in process operation, high reaction rates as well as reductions of equipment size and waste reagents (Darji et al. 2015; Rodrigues et al. 2011). Kannan et al. (2013) claimed that the energy input using MW pretreatment contributed to only 7 % of the total energy needed during bioethanol production from sago barks. Moreover, the energy consumption of MW-alkali pretreatment was reported to be approximately 108 kJ, which was five times less than using high pressure pretreatment (Vani et al. 2012). Thus, MW is a cost-effective and easy alternative that may offer better yields than conventional pretreatments at a commercial level (Binod et al. 2012; Kannan et al. 2013). Moreover, the reduction in energy demands for γ-ray irradiation ($ 0.48/kg) led to lower pretreatment costs than traditional physical pretreatments such as ball milling ($ 5.82/kg) and roller milling ($ 14.0/kg) (Fan et al. 1981).

In fact, the process time required for biomass pretreatment and enzymatic saccharification could be reduced significantly when energy irradiation is coupled with other conventional pretreatments such as dilute acid and alkali hydrolysis. A case in point, hydrolysis of rice straw was 22 times faster when 1-ethyl-3-methylimidazolium acetate-dimethlysulfoxide was used together with MW, resulting in four times higher sugar productions than untreated rice straw (Mai et al. 2014). The carbon-rich biomass also acted as a good MW energy absorber and required less energy to generate hydrothermic conditions for polysaccharide hydrolysis (Diaz et al. 2015; Tsubaki and Azuma 2013). In fact, MW could selectively heat polar molecules after penetrating into the inner particles, resulting in reduced heating time by a factor of over ten as compared to conventional heating, which usually utilizes conduction and convection (Xia et al. 2013). Bak (2014) further demonstrated the potential for energy/time saving during the subsequent fermentation process, as the fermentability of biomass treated with EB was around 2.1 times higher than the untreated biomass. The sugar yield from rice straw radiated with EB achieved 65.5 % after 10 days of biodegradation, which was similar to that of unradiated rice straw (64.8 %), which took a longer biodegradation period of 15 days to achieve similar results (Bak 2014).

Challenges faced in energy irradiation

One of the major bottlenecks for most energy irradiation technologies lies in the scaling-up of irradiation systems for industrial application. This may be due to the difficulty in handling and inefficient irradiation at large volumes, such as the scaling up of MW technology (Zheng et al. 2014, Vani et al. 2012). In addition, MW irradiation cannot be carried out indefinitely without a loss of liquid at atmospheric pressure, since the pretreatment time is only limited to the boiling point of the sugar broth (Marx et al. 2014). In order to minimize the loss of sugar broth, the duration of MW at atmospheric pressure could be limited, but with lower liberation of sugars from the biomass. Therefore, Diaz et al. (2015) have successfully implemented the use of high-boiling-point glycerol as the hydrolysis medium so that it could be maintained at liquid state during MW heating. US also faces some challenges as the use of an incorrect sonochemical reactor and parameter choices could cause poor sonification and unfavorable economics, leading to low efficiency especially in scaled equipment (Luo et al. 2014). According to Kim and Han (2012), the sonication effect may sometimes be insufficient to warrant the use of US for biomass pretreatment, since the improved digestibility could be attributed to the temperature rise instead of the physical and chemical changes due to the US itself. Nevertheless, Bussemaker and Zhang (2013) insisted that the use of US to pretreat biomass in biorefinery and biofuel applications promised significant benefits, possibly in the form of reduced energy requirements and higher accessibility of microorganisms during enzymatic hydrolysis and fermentation. Hence, irradiation technologies such as US in biomass pretreatment provide various opportunities for cost reduction in other aspects, such as reduction in enzyme loading as well as shorter treatment times (Sabarez et al. 2014).

Furthermore, the efficiency of energy irradiation strongly depends on the type of biomass sample. In the case of MW heating, polarizable components were preferred for dipole orientation in the electrical field (Janker-Obermeier et al. 2012). Hence, a modification of the direction and strength of the electrical field would be essential to rotate the dipoles and induce effective biomass heating. Also, Wang et al. (2012) highlighted that γ-rays appeared to be strongly selective toward certain biomass species, working more favorably for pretreatment of cellulosic materials for ethanol conversion purposes. Moreover, the efficiency of PEF was also largely dependent on the type of biomass used during the pretreatment process, as the degree of electropolaration was observed to be lower for biomass with higher lignin content since it was harder to be broken down (Kumar et al. 2011). Therefore, even if an irradiation technique was proven to be effective in pretreating a certain type of biomass, it might not be suitable for another biomass.

Conclusion

Generally, irradiation is free of toxicity since reagents or additives are not required, making it more environmentally friendly and simpler in comparison with conventional pretreatment methods such as dilute acid and alkaline hydrolysis (Yoon et al. 2012). Additionally, radiation has the capability to cause polymer degradation reproducibly and quantitatively (Orozco et al. 2012). However, the high intensity of energy associated with the majority of irradiation methods contradicts the main purpose of the pretreatment, which is to induce a cost reduction for an effective downstream transformation process. As such, the increasing demand for environmental sustainability warrants more research efforts to be done in utilizing energy irradiation for biomass pretreatment, despite concerns regarding the cost in technology. The use of reducing sugars as building blocks for value-added products holds great promise for sustainable development. Therefore, improvements need to be done at a scientific level to fully understand the mechanism involved during radiation pretreatment. Studies at the tissue and cellular scale will hence be pivotal so that better optimization works can be done for the development of cost-effective pretreatments (Loow et al. 2016). Also, more studies need to be conducted at the engineering level in terms of reactor design and process optimization as well as the economic level via cost reduction and improvement in energy efficiency.

Acknowledgments The funding of this study is supported by the Ministry of Higher Education, Malaysia, under the Long Term Research Grant Scheme (LRGS/2013/UKM-UKM/PT/01) and University of Malaya Research Grant (RP002D-13AET). In addition, the authors would like to thank Monash University Malaysia for providing Y.-L. Loow with a postgraduate scholarship.

References

Abdel-Rehman MA, Tashiro Y, Sonomoto K (2011) Lactic acid production from lignocellulose-derived sugars using lactic acid bacteria: overview and limits. J Biotechnol 156:286–301

Akhtar J, Idris A, Aziz RA (2014) Recent advances in production of succinic acid from lignocellulosic biomass. Appl Microbiol Biotechnol 98:987–1000

Albuquerque TLD, Silva IJD Jr, Macedo GRD, Rocha MV (2014) Biotechnological production of xylitol from lignocellulosic wastes: a review. Process Biochem 49:1779–1789

Ashokkumar M, Sunartio D, Kentish S, Mawson R, Simons L, Vilkhu K, Versteeg CK (2008) Modification of food ingredients by ultrasound to improve functionality: a preliminary study on a model system. Innov Food Sci Emerg 9:155–1560

Bak JS (2014) Process evaluation of electron beam irradiation-based biodegradation relevant to lignocellulose bioconversion. SpringerPlus 3(487):1–6

Bak JS, Ko JK, Han YH, Lee BC, Choi IG, Kim KH (2009) Improved enzymatic hydrolysis yield of rice straw using electron beam irradiation pretreatment. Bioresour Technol 100:1285–1290

Binod P, Satyanagalakshmi K, Sindhu R, Janu KU, Sukumaran RK, Pandey A (2012) Short duration microwave assisted pretreatment enhances the enzymatic saccharification and fermentable sugar yield from sugarcane bagasse. Renew Energy 37:109–116

Buruiana CT, Garrote G, Vizireanu C (2013) Bioethanol production from residual lignocellulosic materials: a review—part I. Food Technol 37(1):9–24

Bussemaker MJ, Zhang D (2013) Effect of ultrasound on lignocellulosic biomass as a pretreatment for biorefinery and biofuel applications. Ind Eng Chem Res 52:3563–3580

Bussemaker MJ, Xu F, Zhang D (2013) Manipulation of ultrasonic effects on lignocellulose by varying the frequency, particle size, loading and stirring. Bioresour Technol 148:15–23

Chen WH, Tu YJ, Sheen HK (2011) Disruption of sugarcane bagasse lignocellulosic structure by means of dilute sulfuric acid pretreatment with microwave-assisted heating. Appl Energy 88:2726–2734

Chen C, Boldor D, Aita G, Walker M (2012a) Ethanol production from sorghum by a microwave-assisted dilute ammonia pretreatment. Bioresour Technol 110:190–197

Chen WH, Ye SC, Sheen HK (2012b) Hydrolysis characteristics of sugarcane bagasse pretreated by dilute acid solution in a microwave irradiation environment. Appl Energy 93:237–244

Choi S, Song CW, Shin JH, Lee SY (2015) Biorefineries for the production of top building block chemicals and their derivatives. Metab Eng 28:223–239

Chosdu R, Hilmy N, Erizal Erlinda TB, Abbas B (1993) Radiation and chemical pretreatment of cellulosic waste. Radiat Phys Chem 42:695–698

Chung BY, Lee JT, Bai HW, Kim UJ, Bae HJ, Wi SG, Cho JY (2012) Enhanced enzymatic hydrolysis of poplar bark by combined use of gamma ray and dilute acid for bioethanol production. Radiat Phys Chem 81:1003–1007

Chunping Y, Zhiqiang S, Guoce Y, Jianlong W (2008) Effect and aftereffect of γ radiation pretreatment on enzymatic hydrolysis of wheat straw. Bioresour Technol 99:6240–6245

Darji D, Alias Y, Som FM, Razak NHA (2015) Microwave heating and hydrolysis of rubber wood biomass in ionic liquids. J Chem Technol Biotechnol 90:2050–2056

Diaz AB, Moretti MMDS, Bussoli CB, Nunes CDCC, Blandino A, Silva RD, Gomes E (2015) Evaluation of microwave-assisted pretreatment of lignocellulosic biomass immersed in alkaline glycerol for fermentable sugars production. Bioresour Technol 185:316–323

Duarte CL, Ribeiro MA, Oikawa H, Mori MN, Napolitano CM, Galvao CA (2012) Electron beam combined with hydrothermal pretreatment for enhancing the enzymatic convertibility of sugarcane bagasse. Radiat Phys Chem 81:1008–1011

Eckelberry ND, Green MP, Fraser, SA, United States Patent Application Publication (2011) Systems, apparatuses, and methods for extracting non-polar lipids from an aqueous algae slurry and lipids produced therefrom. USA Patent US 2011/0095225 A1

Fan LT, Gharpuray MM, Lee YH (1981) Evaluation of pretreatments for enzymatic conversion of agricultural residues. Biotechnol Bioeng Symp 11:29–45

Gabhane J, Prince William SPM, Gadhe A, Rath R, Vaidya AN, Wate S (2014a) Pretreatment of banana agricultural waste for bio-ethanol production: individual and interactive effects of acid and alkali pretreatments with autoclaving, microwave heating and ultrasonication. Waste Manag 34:498–503

Gabhane J, Prince William SPM, Vaidya AN, Anand D, Wate S (2014b) Pretreatment of garden biomass by alkali-assisted ultrasonication: effects on enzymatic hydrolysis and ultrastructural changes. J Environ Health Sci Eng 12:76

Grewell D, Montalbo-Lomboy M (2013) Ultrasonics for enhanced fluid biofuel production. In: Xie H, Gathergood N (eds) The role of green chemistry in biomass processing and conversion. Wiley, Hoboken, pp 375–405

Gryczka U, Migdal W, Chmielewska D, Antoniak M, Kaszuwara W, Jastrzebska A, Olszyna A (2014) Examination of changes in the morphology of Lignocellulosic fibers treated with e-beam irradiation. Radiat Phys Chem 94:226–230

Hodnett M, Zeqiri B (1997) A strategy for the development and standardisation of measurement methods of high power/cavitation ultrasonic fields: a review of high power field measurement techniques. Ultrason Sonochem 4:273–288

Hong SH, Lee JT, Lee S, Wi SG, Cho EJ, Singh S, Lee SS, Chung BY (2014) Improved enzymatic hydrolysis of wheat straw by combined use of gamma ray and dilute acid for bioethanol production. Radiat Phys Chem 94:231–235

Imai M, Ikari K, Suzuki I (2004) High-performance hydrolysis of cellulose using mixed cellulase species and ultrasonication treatment. Biochem Eng J 17:79–83

Imam T, Capareda S (2012) Ultrasonic and high-temperature pretreatment, enzymatic hydrolysis and fermentation of lignocellulosic sweet sorghum to bio-ethanol. Int J Ambient Energy 33(3):152–160

Iqbal HMN, Kyazze G, Keshavarz T (2013) Biotech applications of biomass. Bioresources 8(2):3157–3176

Janker-Obermeier I, Sieber V, Faulstich M, Schieder D (2012) Solubilization of hemicellulose and lignin from wheat straw through microwave-assisted alkali treatment. Ind Crop Prod 39:198–203

Jiang J, Zhao Q, Wei L, Wang K, Lee DJ (2011) Degradation and characteristic changes of organic matter in sewage sludge, using microbial fuel cell with ultrasound pretreatment. Bioresour Technol 102:272–277

Kang KE, Jeong GT, Park DH (2013) Rapeseed-straw enzymatic digestibility enhancement by sodium hydroxide treatment under ultrasound irradiation. Bioproc Biosys Eng 36:1019–1029

Kannan TS, Ahmed AS, Ani FN (2013) Energy efficient microwave irradiation of sago bark waste (SBW) for bioethanol production. Adv Mater Res 701:249–253

Karinen R, Vilonen K, Niemela M (2011) Biorefining: heterogeneously catalyzed reactions of carbohydrates for the production of furfural and hydroxymethylfurfural. ChemSusChem 4:1002–1016

Karthika K, Arun AB, Rekha PD (2012) Enzymatic hydrolysis and characterization of lignocellulosic biomass exposed to electron beam irradiation. Carbohydr Polym 90:1038–1045

Karthika K, Arun AB, Melo JS, Mittal KC, Kumar M, Rekha PD (2013) Hydrolysis of acid and alkali presoaked lignocellulosic biomass exposed to electron beam irradiation. Bioresour Technol 129:646–649

Karunanithy C, Muthukumarappan K, Gibbons WR (2014) Sequential extrusion-microwave pretreatment of switchgrass and big bluestem. Bioresour Technol 153:393–398

Kempkes MA, Roth I, Gaudreau MPJ, United States Patent Application Publication (2011) Pulsed electrical field (PEF) method for continuous enhanced extraction of oil and lipids from small aquatic plants. USA Patent US 2011/0107655 A1

Kim I, Han JI (2012) Optimization of alkaline pretreatment conditions for enhancing glucose yield of rice straw by response surface methodology. Biomass Bioenergy 46:210–217

Kim SB, Kim JS, Lee JH, Kang SW, Park C, Kim SW (2011) Pretreatment of rice straw by proton beam irradiation for efficient enzyme digestibility. Appl Biochem Biotechnol 164:1183–1191

Koganti S, Ju LK (2013) *Debaryomyces hansenii* fermentation for arabitol production. Biochem Eng J 79:112–119

Kumar P, Barrett DM, Delwiche MJ, Stroeve P (2011) Pulsed electrical field pretreatment of switchgrass and wood chip species for biofuel production. Ind Eng Chem Res 50:10996–11001

Kurian JK, Nair GR, Hussain A, Raghavan GSV (2013) Feedstocks, logistics and pre-treatment processes for sustainable lignocellulosic biorefineries: a comprehensive review. Renew Sustain Energy Rev 25:205–219

Lai LW, Idris A (2013) Disruption of oil palm trunks and fronds by microwave-alkali pretreatment. Bioresources 8(2):2792–2804

Lam WC, Kwan TH, Budarin VL, Mubofu EB, Fan J, Lin CSK (2015) Pretreatment and thermochemical and biological processing of biomass. In: Clark J, Deswarte F (eds) Introduction to chemicals from biomass, 2nd edn. Wiley, Chishester, pp 53–88

Liu L, Ju M, Li W, Hou Q (2013) Dissolution of cellulose from AFEX-pretreated zoysia japonica in AMIMCl with ultrasonic vibration. Carbohydr Polym 98:412–420

Loman AA, Ju L-K (2014) Arabitol production from glycerol by fermentation. In: Brentin RP (ed) Soy-based chemicals and materials. American Chemical Society, Washington, pp 109–126

Loow Y-L, Wu TY, Tan KA, Lim YS, Siow LF, Jahim JMd, Mohammad AW, Teoh WH (2015) Recent advances in application of inorganic salt pretreatment for transforming lignocellulosic biomass into reducing sugars. J Agric Food Chem 63:8349–8363

Loow Y-L, Wu TY, Jahim JMd, Mohammad AW, Teoh WH (2016) Typical conversion of lignocellulosic biomass into reducing sugars using dilute acid hydrolysis and alkaline pretreatment. Cellulose 23:1491–1520

Lu J, Zhou P (2011) Optimization of microwave-assisted $FeCl_3$ pretreatment conditions of rice straw and utilization of *Trichoderma viride* and *Bacillus pumilus* for production of reducing sugars. Bioresour Technol 102:6966–6971

Luo J, Fang Z, Smith RL Jr (2014) Ultrasound enhanced conversion of biomass to biofuels. Prog Energy Combust 41(1):56–93

Mai NL, Ha SH, Koo YM (2014) Efficient pretreatment of lignocellulose in ionic liquids/co-solvent for enzymatic hydrolysis enhancement into fermentable sugars. Process Biochem 49:1144–1151

Mamman AS, Lee JM, Kim YC, Hwang IT, Park NJ, Hwang YK, Chang JS, Hwang JS (2008) Furfural: hemicellulose/xylose-derived biochemical. Biofuel Bioprod Biorefining 2:438–454

Marx S, Ndaba B, Chiyanzu I, Schabort C (2014) Fuel ethanol production from sweet sorghum bagasse using microwave irradiation. Biomass Bioenergy 65:145–150

Mukherjee A, Dumont MJ, Raghavan V (2015) Review: sustainable production of hydroxymethylfurfural and levulinic acid: challenges and opportunities. Biomass Bioenergy 72:143–183

Ninomiya K, Ohta A, Omote S, Ogino C, Takahashi K, Shimizu N (2013) Combined used of completely bio-derived cholinium ionic liquids and ultrasound irradiation for the pretreatment of lignocellulosic material to enhance enzymatic saccharification. Chem Eng J 215–216:811–818

Ofori-Boateng C, Lee KT (2014a) Sono-assisted organosolv/H_2O_2 pretreatment of oil palm (*Elaeis guineensis* Jacq.) fronds for recovery of fermentable sugars: optimization and severity evaluation. Fuel 115:170–178

Ofori-Boateng C, Lee KT (2014b) Ultrasonic-assisted simultaneous saccharification and fermentation of pretreated oil palm fronds for sustainable bioethanol production. Fuel 119:285–291

Orozco RS, Hernandez PB, Ramirez NF, Morales GR, Luna JS, Montoya AJC (2012) Gamma irradiation induced degradation of orange peels. Energies 5:3051–3063

Pang F, Xue S, Yu S, Zhang C, Li B, Kang Y (2012) Effects of microwave power and microwave irradiation time on pretreatment efficiency and characteristics of corn stover using combination of steam explosion and microwave irradiation (SE-MI) pretreatment. Bioresour Technol 118:111–119

Pejin DJ, Mojovic LV, Grujic OS, Markov SL, Nikolic SB, Markovic MN (2012) Increase in bioethanol production yield from triticale by simultaneous saccharification and fermentation with application of ultrasound. J Chem Technol Biotechnol 87:170–176

Pike RW, Sengupta D, Institute Minerals Processing Research, Hertwig TA (2008) Integrating biomass feedstocks into chemical production complexes using new and existing processes. Minerals Processing Research Institute Louisiana State University, Baton Rouge

Placido J, Imam T, Capareda S (2013) Evaluation of ligninolytic enzymes, ultrasonication and liquid hot water as pretreatments for bioethanol production from cotton gin trash. Bioresour Technol 139:203–208

Rafiqul ISM, Sakinah AMM (2013) Processes for the production of xylitol—review. Food Rev Int 29:127–156

Rehman MSU, Kim I, Kim KH (2014) Optimization of sono-assisted dilute sulfuric acid process for simultaneous pretreatment and saccharification of rice straw. Int J Environ Sci Technol 11:543–550

Rodrigues THS, Rocha MVP, Macedo GRD, Goncalves LRB (2011) Ethanol production from cashew apple bagasse: improvement of enzymatic hydrolysis by microwave-assisted alkali pretreatment. Appl Biochem Biotechnol 164:929–943

Sabarez H, Oliver CM, Mawson R, Dumsday G, Singh T, Bitto N, McSweeney C, Augustin MA (2014) Synergism between ultrasonic pretreatment and white rot fungal enzymes on biodegradation of wheat chaff. Ultrason Sonochem 21:2084–2091

Sarkar N, Ghosh SK, Bannerjee S, Aikat K (2012) Bioethanol production from agricultural wastes: an overview. Renew Energy 37:19–27

Sheldon RA (2014) Green and sustainable manufacture of chemicals from biomass: state of the art. Green Chem 16:950–963

Shin SJ, Sung YJ (2008) Improving enzymatic hydrolysis of industrial hemp (*Cannabis sativa L.*) by electron beam irradiation. Radiat Phys Chem 77:1034–1038

Singh A, Tuteja S, Singh N, Bishnoi NR (2011) Enhanced saccharification of rice straw and hull by microwave-alkali pretreatment and lignocellulolytic enzyme production. Bioresour Technol 102:1773–1782

Stumm W, Morgan JJ (1996) Aquatic chemistry. Wiley, New York

Su MY, Tzeng WS, Shyu YT (2010) An analysis of feasibility of bioethanol production from Taiwan sorghum liquor waste. Bioresour Technol 101:6669–6675

Subhedar PB, Gogate PR (2013) Intensification of enzymatic hydrolysis of lignocellulose using ultrasound for efficient bioethanol production: a review. Ind Eng Chem Res 52:11816–11828

Subhedar PB, Gogate PR (2014) Alkaline and ultrasound assisted alkaline pretreatment for intensification of delignification process from sustainable raw material. Ultrason Sonochem 21:216–225

Sundar S, Bergey NS, Cardona LS, Stipanovic A, Driscoll M (2014) Electron beam pretreatment of switchgrass to enhance enzymatic hydrolysis to produce sugars for biofuels. Carbohydr Polym 100:195–201

Sung YJ, Shin SJ (2011) Compositional changes in industrial hemp biomass (*Cannabis sativa L.*) induced by electron beam irradiation pretreatment. Biomass Bioenerg 35:3267–3270

Suresh K, Ranjan A, Singh S, Moholkar VS (2014) Mechanistic investigations in sono-hybrid techniques for rice straw pretreatment. Ultrason Sonochem 21:200–207

Teong SP, Yi G, Zhang Y (2014) Hydroxymethylfurfural production from bioresources: past, present and future. Green Chem 16:2015–2026

Tsubaki S, Azuma J (2013) Total fractionation of green tea residue by microwave-assisted alkaline pretreatment and enzymatic hydrolysis. Bioresour Technol 131:485–491

Union of Concerned Scientists (2012) The promise of biomass. Clean power and fuel—if handled right. http://www.ucsusa.org/sites/default/files/legacy/assets/documents/clean_vehicles/Biomass-Resource-Assessment.pdf. Accessed on 14th July 2016

Vani S, Binod P, Kuttiraja M, Sindhu R, Sandhya SV, Preeti VE, Sukumaran RK, Pandey A (2012) Energy requirement for alkali assisted microwave and high pressure reactor pretreatments of cotton plant residue and its hydrolysis for fermentable sugar production for biofuel application. Bioresour Technol 112:300–307

Velmurugan R, Muthukumar K (2011) Utilization of sugarcane bagasse for bioethanol production: sono-assisted acid hydrolysis approach. Bioresour Technol 102:7119–7123

Villa-Velez HA, Vaquiro HA, Telis-Romero J (2015) The effect of power-ultrasound on the pretreatment of acidified aqueous solutions of banana flower-stalk: structural, chemical and statistical analysis. Ind Crop Prod 66:52–61

Wang KQ, Xiong XY, Chen JP, Chen L, Su X, Liu Y (2012) Comparison of gamma irradiation and steam explosion pretreatment for ethanol production from agricultural residues. Biomass Bioenerg 46:301–308

Wu TY, Guo N, Teh CY, Hay JXW (2013) Advances in ultrasound technology for environmental remediation. Springer, Dordrecht. doi:10.1007/978-94-007-5533-8

Xia A, Cheng J, Song W, Yu C, Zhou J, Cen K (2013) Enhancing enzymatic saccharification of water hyacinth through microwave heating with dilute acid pretreatment for biomass energy utilization. Energy 61:158–166

Xin LZ, Kumakura M (1993) Effect of radiation pretreatment on enzymatic hydrolysis of rice straw with low concentrations of alkali solution. Bioresour Technol 43:13–17

Yang CY, Fang TJ (2014) Combination of ultrasonic irradiation with ionic liquid pretreatment for enzymatic hydrolysis of rice straw. Bioresour Technol 164:198–202

Yang F, Li L, Li Q, Tan W, Liu W, Xian M (2010) Enhancement of enzymatic in situ saccharification of cellulose in aqueous-ionic liquid media by ultrasonic intensification. Carbohydr Polym 81:311–316

Yoon M, Choi JI, Lee JW, Park DH (2012) Improvement of saccharification process for bioethanol production from *Undaria* sp. by gamma irradiation. Radiat Phys Chem 81:999–1002

Yunus R, Salleh SF, Abdullah N, Biak DRA (2010) Effect of ultrasonic pre-treatment on low temperature acid hydrolysis of oil palm empty fruit bunch. Bioresour Technol 101:9792–9796

Zbinden MDA, Sturm BSM, Nord RD, Carey WJ, Moore D, Shinogle H, Stagg-Williams SM (2013) Pulsed electrical field (PEF) as an intensification pretreatment for greener solvent lipid extraction from microalgae. Biotechnol Bioeng 110(6):1606–1615

Zhang J, Li JB, Wu SB, Liu Y (2013) Advances in the catalytic production and utilization of sorbitol. Ind Eng Chem Res 52:11799–11815

Zheng Y, Pan Z, Zhang R (2009) Overview of biomass pretreatment for cellulosic ethanol production. Int J Agric Bio Eng 2(3):51–68

Zheng Y, Zhao J, Xu F, Li Y (2014) Pretreatment of lignocellulosic biomass for enhanced biogas production. Prog Energy Combust 42:35–53