

An application of ultrasonication in lignocellulosic biomass valorisation into bio-energy and bio-based products

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ABSTRACT

The industrial revolution has caused a tremendous impact on our modern way of life. It shapes the economic, social and culture of many modern societies around the world. However, the world's heavy dependence on fossil fuels has exacerbated the effect of modernisation, causing a detrimental effect to the world climate. Recently, the scientific community has shifted their focus to the valorisation of lignocellulosic biomass as a renewable and clean source of energy. Lignocellulosic biomass is a potential substitute for fossil fuel as it could be transformed to various bio-energy and bio-based products by biorefineries. However, the recalcitrant nature of lignocellulosic biomass hinders the commercialisation at large scale due to the processing difficulties and economically not viable. Hence, ultrasound has been utilised as an auxiliary energy to intensify pretreatments as well as biorefinery processes in the productions of bio-fuels and fine chemicals. In this review, the background information of lignocellulosic biomass and ultrasound is provided. Furthermore, the applications of ultrasound as a complement to existing pretreatments and bioprocessing technologies are discussed by highlighting the importance of mechanoacoustic and sonochemical effect produced by the ultrasound. Lastly, technoeconomic analysis and socioeconomic impact of utilising ultrasound in the biomass processing are elaborated to provide a holistic view on the novel and environmentally friendly green technique.

1. Introduction

There has been a huge global effort to reduce consumption of crude oil with renewable sources. However, the progress is sluggish as crude oil is still the global primary energy source since 2005 up to 2018, with a total consumption of 37.21% and 33.62% respectively [1]. With the current total oil world reserves to be only 239.4 thousand million tonnes, our undeterred global production will only be sufficient to sustain our lifestyle for another 50 years [2]. This is an alarming data as our current renewable energy sources only account to 9.57% in 2015, and is projected to only be able to substitute less than 5% of oil consumption within the next five years [1]. As such, an effective and comprehensive renewable energy is needed. Among them, lignocellulosic biorefineries have attracted researchers' attentions due to the abundance of lignocellulosic biomass feedstock and its renewable nature.

Lignocellulosic biomass feedstock in biorefineries can be categorised into three categories: agricultural products such as corn, waste from

agro-food or forestry industry such as oil palm fronds, and lastly specialised energy crops such as willow [3]. While all the raw materials mentioned above are viable feedstocks, debates have been rising over the use of food crop as an energy resource, as well as land use for dedicated energy crop [4]. Hence, the utilisation of already existing waste from an agricultural industry as a feedstock is widely studied because it is regarded as being a "waste-free" approach [5]. Some examples of agriculture lignocellulosic residues generated during the processing of crops include plant fibers, leaves, and husks [6]. In Malaysia alone, approximately 96.54 million metric tons of agro-wastes are projected to be generated annually. These massive quantities of lignocellulosic rich biomass are commonly left to rot as mulches or directly combusted as fuel for boiler. This practice is underutilising the potential of agro-waste to be reused in a biorefinery to manufacture various value added products such as biochemical and renewable source of fuel [7].

Pretreatment is a crucial stage during the valorisation of

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lignocellulosic biomass in any biorefineries. This is because an effective pretreatment process will overcome the recalcitrant nature of the biomass. However, biomass pretreatment stage is considered to be the most costly biorefinery process, often taking up 20–48% of the total operational expenditure [8]. Therefore, due to the constraints of cost and effectiveness, the uses of typical mechanical comminution methods such as milling, chipping and grinding during the pretreatment stages have been limited [9]. Recently, the usage of sequential ultrasonic irradiation has gained traction within the research community as an auxiliary energy to lower energy cost and increase effectiveness in biomass valorisation [10]. Thus, this review will be evaluating the utilisation of ultrasonic irradiation in assisting lignocellulosic biomass valorisation.

2. Lignocellulosic biomass in biorefineries

In the United States of America, it was projected that 991 million dry tons of lignocellulosic biomass will be produced annually by the year 2030 [11]. The huge production of lignocellulosic biomass was also observed in the European Union, where 1 billion tons of lignocellulosic biomass was estimated to be produced annually by the year 2030 [12]. This highlights the advantages of valorising lignocellulosic biomass due to its availability worldwide. Lignocellulosic biomass comprised of mainly lignin, polysaccharides such as cellulose and hemicellulose and small quantity of ash (Fig. 1). The major load bearing of a plant cell wall is cellulose and it is also one of the most abundant biopolymer on earth [13]. Cellulose microfibrils are insoluble carbohydrate made up of α -D-glucose linear chain bonded by β (1, 4) linkage. The cellulose microfibrils are made up of cellulose chains (20–300) held together by hydrogen bonds and van der Waals forces [14]. Cellulose polymers commonly exist as a crystalline structure in nature. However, amorphous region of cellulose also exists when the crystalline structure has not formed during cell synthesis or the structure has been disrupted by the pretreatments. The amorphous region of cellulose is a region of microfibrils with nonordered β (1, 4) linked glucose molecules that are detectable by X-ray diffraction. The amorphous region is soluble in water and are more susceptible to enzyme hydrolysis in comparison to the crystalline structure [15]. Cellulosic biorefineries typically focus on the saccharification of cellulose to obtain monomeric glucose. The glucose produced is then fermented to produce second generation bio-ethanol [16].

Hemicellulose is a type of polysaccharide that is composed of different sugar monomers such as D-xylose, L-arabinose, D-galactose, D-mannose and D-glucose. Hemicelluloses are a diverse and branched polymer that have differing composition depending on the plant species, tissues, and the plant's maturity. Although hemicelluloses have a potentially large pool of fermentable sugar, they also present homogeneity challenges during biomass processing. As a result, this complicates pretreatment strategies and requires highly tailored biorefinery processing for a specific type of lignocellulosic biomass [17]. In a plant cell, hemicelluloses are bonded to the surface of cellulose microfibrils by hydrogen bond, and linked to lignin by covalent bonds [18].

Lignin is a polymer of phenylpropane monomers that provides mechanical rigidity and acts as a protective barrier around the polysaccharides. The three main lignin monomers (monolignols) are synapyl alcohol (S), p-hydroxyphenyl alcohol (H) and coniferyl alcohol (G). During plant growth, these monolignols are secreted into the polysaccharide matrix to be polymerised through free radical process, leading to a highly randomised lignin structure that varies from species to species of plant [19]. The covalent linkages between lignin and polysaccharide form a lignin carbohydrate complex which lead to the recalcitrance nature of lignocellulosic biomass [20]. The recalcitrant nature of lignocellulosic biomass provides a protection to the plant cell from mechanical, chemical and biological degradation. Hence, making the lignocellulosic biomass difficult to be utilised directly without a proper pretreatment [21]. Most of the biological processing platforms for the production of biofuel will produce large amount of waste lignin stream. This lignin waste is commonly combusted as an energy source in a plant. However, the high carbon to oxygen ratio of lignin makes it suitable for the production of aromatics such as benzene, toluene and phenol [22]. Thus, the combustion of lignin for energy will reduce the economic competitiveness of the biorefinery plant, and undermine the potential of converting lignin to biomaterials or liquid fuels [16].

3. Use of ultrasonic irradiation in lignocellulosic biomass valorisation

3.1. Background information of ultrasound irradiation

The term biomass valorisation generally means conversion of biomass into value added biochemical or biomaterial [10]. Recently, researchers have begun to employ various type of energy irradiation,

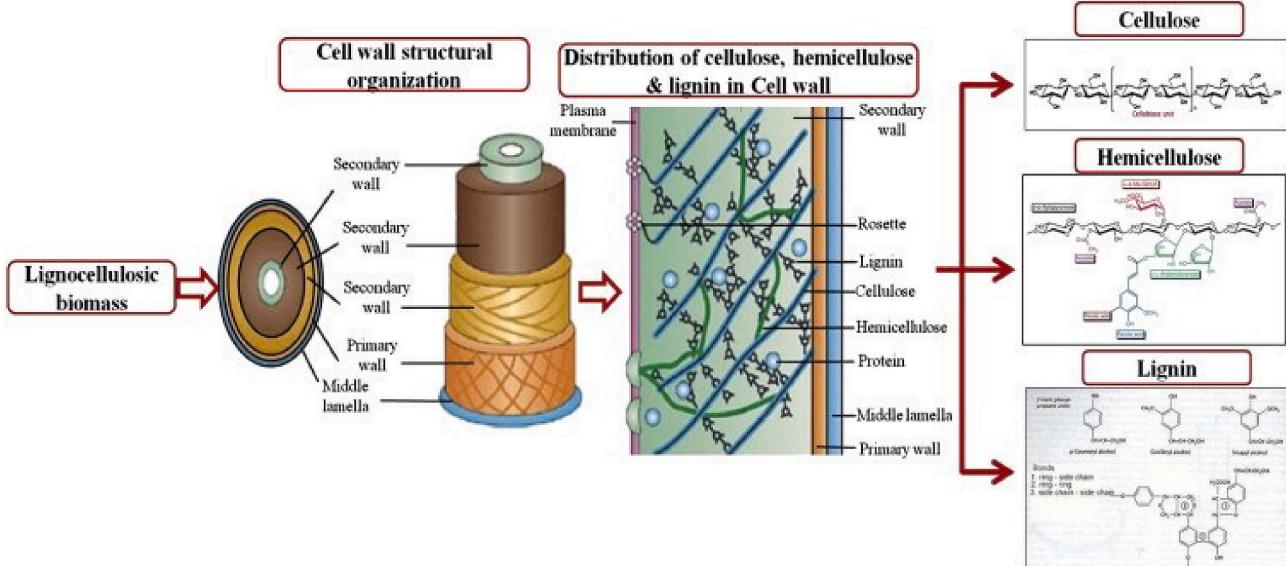


Fig. 1. Structure of lignocellulosic biomass comprised of cellulose, hemicellulose and lignin.
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such as electron beam, microwave, gamma ray, pulse electrical field and ultrasound to assist in bioprocessing (Table 1). The uses of ultrasonic irradiation technology have garnered the attention of researchers due to the phenomena of mechanoacoustic (physical) and sonochemical (chemical) effect. During ultrasound, the compression and rarefaction of acoustic pressure in liquid will cause a decrease in local pressure. When the local pressure in liquid falls below the saturated vapour pressure, it will lead to the formation of microbubbles. The microbubbles present in the liquid will undergo growth phase by absorbing ultrasonic energy and eventually collapsing upon reaching a critical size (Fig. 2). The violent collapse of microbubbles is known as cavitation [24].

The working principle of ultrasound delignification is through acoustic cavitation of numerous microbubbles within the medium. During cavitation of microbubbles, the physical effect experienced by the biomass is a vigorous hydromechanical shear force from shockwave and microjet. Furthermore, the cavitation of microbubbles is also able to generate turbulence and agitation within the liquid as a secondary effect [10]. The chemical effect of ultrasound, which is occurred during the implosion of microbubbles, will promote the decomposition of water molecules into hydroxyl radicals. The free radicals, which are generated during the cavitation, aid in the cleavage process of lignin and xylan networks [25]. Both physical and chemical effects of microbubbles cavitation increase the extent of delignification, assist in breakdown of crystalline nature of cellulose, enhance the heat and mass transfer through vigorous agitation, and improve the solubilisation of organic matters [26–28]. A complete transformation of lignocellulosic biomass into value added products can be categorised into two stages: pretreatment stage, and thermochemical or biological processing of biomass. This review will discuss in depth the effect of ultrasound synergism on various stages of lignocellulosic biomass conversion.

3.2. Ultrasonication irradiation in lignocellulosic pretreatment

Pretreatment stage is an essential process to overcome the recalcitrance of lignocellulosic biomass. The removal of hemicellulose and lignin component will ensure a more efficient and higher sugar yield in downstream processes [33]. Hence, an effective pretreatment should reduce the amount of lignin and hemicellulose to increase the accessibility of cellulose. Furthermore, the hydrophobicity of crystalline cellulose prevents the ease of dissolution and hydrolysis. Therefore, lignocellulosic pretreatment could also disrupt the crystallinity structure of cellulose to enhance the hydrolysis of polysaccharide into its monomeric sugar. Finally, a higher surface area of cellulose will achieve greater extent of enzymatic hydrolysis of cellulose into glucose [26].

Table 1
Type of energy irradiation and effect on lignocellulosic biomass.

Type of irradiation	Effect on lignocellulosic biomass	Ref.
Electron beam	High energy electrons degrading internal structure of biomass through chain scission due to electron bombardment	[29]
Microwave	Oscillating electromagnetic wave interact with polar molecules which leads to dissipation of heat via molecular friction. Generating “hot spots” to create rapid expansion to disrupt crystalline structure of cellulose and lignin.	[30]
Gamma ray	Generation of high activity radicals through rapid localisation of the absorbed energy within lignocellulosic biomass	[31]
Pulse electrical field	High electric fields increase cell permeability to pretreatment solvent and enzymes	[32]
Ultrasound	Mechanoacoustic effect: Cavitation bubbles generate intense stream of liquid which physically disrupts the surface of biomass Sonochemical effect: Extreme temperature and pressure from cavitation leading to the generation of highly reactive radicals	[10]

Therefore, a successful pretreatment of lignocellulosic biomass could break down the lignin structure and disrupt the crystalline structure of cellulose for enhancing the enzymes accessibility on the cellulose during hydrolysis step [34]. The requirements needed for an effective pretreatment will undoubtedly increase the energy input during pretreatment. However, milder conditions such as room temperature, neutral pH condition, atmospheric pressure, and shorter pretreatment duration are preferred for the purpose of atom efficiency [35]. These contradictory demands during the pretreatment can be solved through the integration of ultrasonic irradiation as an auxiliary technique.

3.2.1. Dilute acid pretreatment

Dilute acid pretreatment has the advantage of solubilising hemicellulose fraction into simple sugars for ease of fermentation. Furthermore, dilute acid pretreatment also has the ability to disrupt hydrogen, covalent and van der Waals forces which reduces the requirement of enzymatic hydrolysis step [36]. However, the utilisation of dilute acid for pretreatment is limited due to the inability in removing lignin [37]. Therefore, an auxiliary irradiation energy such as ultrasound is recommended to maximise the efficiency of dilute acid pretreatment [36]. Past studies have found that the combination of ultrasound and dilute acid pretreatment was able to increase delignification of grass from 33% to 80.4%. This phenomenon was also observed by Tao et al. [38], whereby the greatest lignin removed was achieved when dilute hydrochloric acid pretreatment was combined with ultrasound irradiation. Mohapatra et al. [39] reported that the high delignification rate was attributed to high power ultrasound. During cavitation of microbubbles, microjet was formed and directed towards the surface of biomass. This led to significant disruptions on the surface of biomass which reduced the particle size of biomass and removed the layer of wax. Furthermore, it was also suggested that silica and lignin were removed from surface of lignocellulosic biomass. The combined morphological transformation increased the surface area for greater effectiveness of dilute acid pretreatment.

3.2.2. Alkaline pretreatment

Alkaline pretreatment is extensively studied due to many desirable advantages. Alkaline pretreatment is highly efficient in selectively removing lignin and hemicellulose without degrading cellulose. The end product of alkaline pretreated lignocellulose is an enriched cellulose biomass. Furthermore, alkaline pretreatment has been shown to be just as effective in delignification when conducted in a mild pretreatment condition [40–42]. However, the disadvantages of mild alkaline pretreatment is the long pretreatment duration and high consumption of alkali [43]. The usage of a suitable irradiation energy such as ultrasound could be introduced to rectify the drawbacks of mild alkaline pretreatment. Ultrasound irradiation was found to be able to intensify alkaline pretreatment, due to the production of cavitation bubbles. These cavitation bubbles were able to disrupt the hydrophobic layer of wax on the surface of lignocellulosic biomass. Thus, increasing available surface area for pretreatment by alkaline solution. Furthermore, cavitation of microbubbles was found to be able to weaken the covalent bonds between lignin-hemicellulose, which facilitated the penetration of alkaline solution into the raw material [28]. In a study conducted by Wu et al. [44], the intense heat generated from cavitation of microbubbles, was sufficient to substitute external heating required during alkaline pretreatment. The lignin content of rice straw after alkaline pretreatment for external heating and ultrasound only was 4.70% and 4.60%, respectively. The utilisation of heat energy dissipated from cavitation bubble demonstrated a novel energy saving strategy which could be employed to increase the economic viability of ultrasound irradiation during the pretreatment.

3.2.3. Alkaline hydrogen peroxide

According to Ho et al. [45], aerobic saprophytes commonly seen in nature utilises oxidative deconstruction of lignocellulosic biomass as an effective pretreatment method. Alkaline hydrogen peroxide

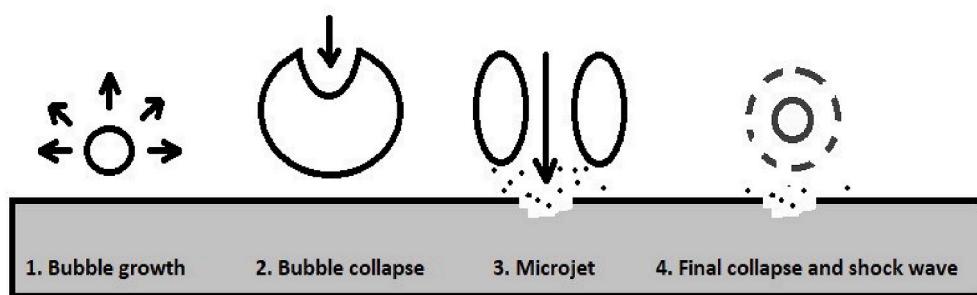


Fig. 2. Growth and collapse of microbubbles during ultrasonication.

pretreatment closely resembles the natural process by producing hydroperoxyl anion ($\text{HO}^{\cdot -}$), which is attributed to the oxidation of carbonyl and ethylene groups found in the lignin. The production of $\text{HO}^{\cdot -}$ anion is also crucial to initiate the production of radicals [46]. The pretreatment method could be further enhanced through exposure to ultrasound. During an ultrasonication, the cavitation of microbubbles will generate large amount of radicals through splitting of H_2O_2 , NaOH , and H_2O . The hydroxyl ($\text{HO}^{\cdot -}$) and superoxide anion ($\text{O}_2^{\cdot -}$) radicals are crucial in the dissolution of lignin and hemicellulose through disruption of intermolecular bond between lignin and cellulose [47]. The radicals

produced are able to effectively cleave phenolic α -O-4 and non phenolic β -O-4 linkages found in the lignin molecule. Furthermore, radicals could also remove lignin fractions via disruption of the carbon-carbon linkages to produce low lignin content biomass. In a study conducted by Ovalle-Serrano et al. [46], it was found that ultrasound assisted alkaline hydrogen peroxide pretreatment was able to achieve a maximum lignin removal of 88% for fique fibers and tow, while lignin removal of fique pulp was found to be 79%.

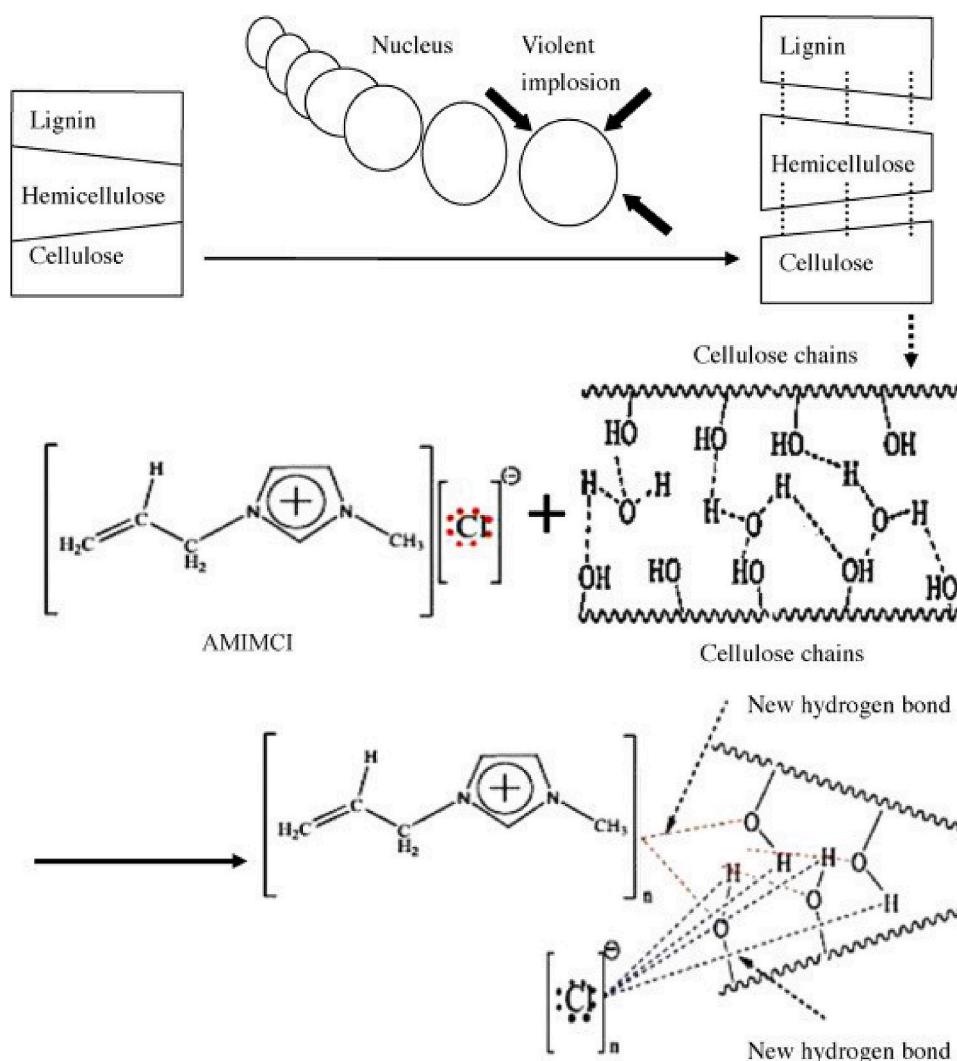


Fig. 3. Working mechanism of ultrasound assisted ionic liquid pretreatment.
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3.2.4. Ionic liquid

Ionic liquid is defined as organic salt that has melting point below 100 °C, high thermal stability, low volatility, non-flammable, and able to solubilise polar, non-polar organic, inorganic, and polymeric compounds [48]. As ionic liquid has the capability in dissolving and fractionate lignocellulosic biomass, the pretreatments using ionic liquid have been utilised in multiple studies involving delignification of lignocellulosic biomass. The utilisations of ionic liquid and ultrasound have been found to enhance the delignification due to the extreme shear force and high temperature generated in the area around the collapsed bubble. A study conducted by Han et al. [49] demonstrated that the introduction of ultrasound to assist BmimCl-HCl and AmimCl-HCl ionic liquid pretreatment of rice straw was able to enhance lignin removal rate of unsonicated ionic liquid pretreatment by 18.06–19.33%. Additionally, this observation was supported by another study on ultrasound assisted ionic liquid pretreatment when the lignin content of Eucalyptus saw dust was reduced from 26.3% to 15.38% [50]. In another study done by Liu et al. [51], it was found that the use of ultrasound was able to enhance the dissolution of cellulose by ionic liquid. The improvement was largely contributed by enhanced agitation by cavitation of micro-bubbles which promoted contact between Z. japonica and the AMIMCl ionic liquid solvent (Fig. 3). However, Ninomiya et al. [52] reported that the use of BmimCl, AmimCl, EmimCl, EmimDep, and EmimOAc ionic liquid resulted in equal removal of cellulose, hemicellulose and lignin from kenaf powder into the supernatant. Hence, the selection of a suitable ionic liquid is highly dependent for the type of biomass and its intended use (e.g., for delignification or dissolution of polysaccharide).

3.2.5. Deep eutectic solvent

Deep eutectic solvent is a type of environmentally friendly solvent that is formed from the mixture of two salts that act as either the hydrogen bond donor or hydrogen bond acceptor [53]. While deep eutectic solvent and ionic liquid have very similar physical properties such as low volatility and melting point, deep eutectic solvent is able to

address key issues of ionic liquid such as high production cost, high toxicity, and non-biodegradability [54]. Although deep eutectic solvent is able to solubilise lignin through the cleavage of ether or ester bond between hemicellulose and lignin quite effectively, the use of ultrasound to assist lignin removal in deep eutectic solvent pretreatment system has been found to further enhance the delignification through synergism. The synergism was due to ultrasonic energy's effect on the structural integrity of lignocellulose. In a study conducted by Malaek et al. [55], it was found that ultrasound enhanced deep eutectic solvent system by solubilising lignin up to 48.15% (w/w). The high solubility of lignin was attributed to ultrasound treatment in removing and destroying waxy layers and silica deposited onto surface of lignocellulosic biomass. Recently, Ong et al. [56] also found that the synergistic effect of sequential deep eutectic solvent pretreatment with ultrasound irradiation was able to enhance lignin removal up to 36.42%, in comparison to unsonicated pretreatment lignin removal of 14.02%. The synergism was postulated to be the degradation of lignin matrix due to the application of ultrasound during the first stage of pretreatment. The physical disruption of ultrasound was shown through pitting on the surface of biomass, which, increased the surface area for deep eutectic solvent pretreatment (Fig. 4). Furthermore, this study also found that excessive ultrasonication reduced pretreatment efficiency [56].

3.2.6. Organosolv

Organosolv pretreatment is normally performed with an organic or aqueous organic solvent that is heated to a temperature of up to 150–250 °C using high pressure. Low molecular weight alcohols such as ethanol and methanol are favoured in organosolv pretreatment due to the ease of recovery [57]. Under high temperature and pressure, organosolv pretreatment has been found to be able to cleave various functional groups such as α-O-4 and β-O-4 ethers found in the lignin. The combined pretreatment of organosolv and ultrasound pretreatment showed slight improvement in delignification of rapeseed straw [58]. The minor improvement of ultrasound combined pretreatment was also

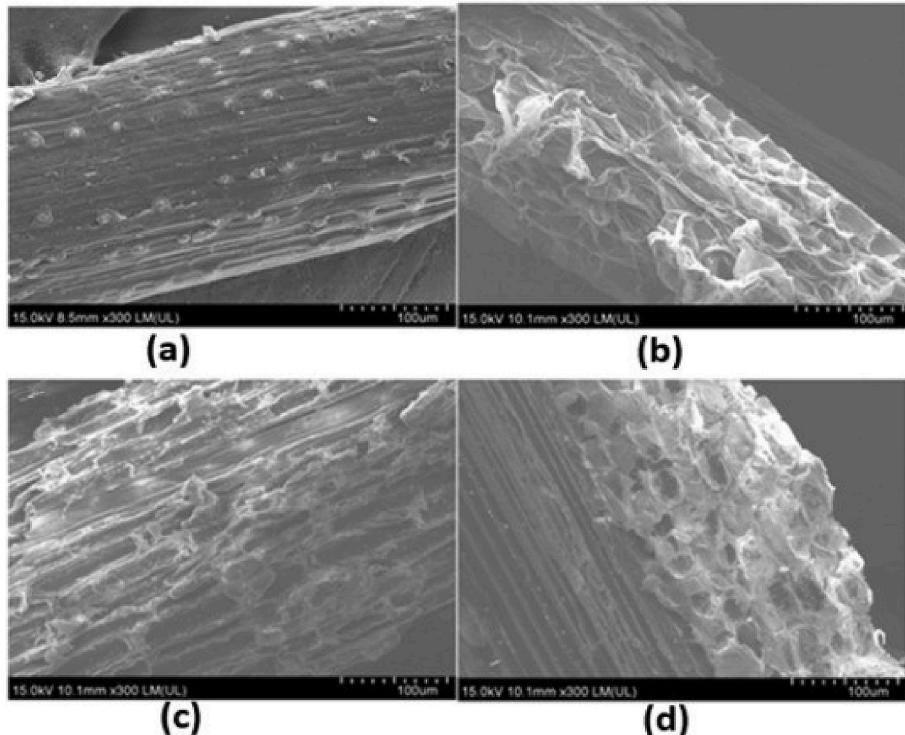


Fig. 4. Scanning electron micrograph for (A) Raw OPF (B) ChCl:urea pretreated only OPF (C) ultrasound pretreated only OPF (D) ultrasound assisted deep eutectic solvent pretreated OPF.

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observed by Xu et al. [59], where delignification efficiency of unsonicated sample increased marginally from 76.5% to 77.2% after ultrasonication. These results suggested that the application of ultrasound irradiation might not be a suitable technique used with organosolv pretreatment in a delignification of biomass.

Pretreatment is a key step in ensuring effective biological conversion of lignocellulosic biomass to ethanol and other bio-based products. Thus, choosing a suitable pretreatment method based on the type of feedstock is vital to ensure economic viability [60]. As a whole, lignocellulosic biomass pretreatment can be divided into three major approaches, which are chemical, mechanical and biological [61]. However, most studies involving ultrasound assisted pretreatments have only been integrated widely in chemical pretreatment method (Table 2).

3.3. Ultrasonication irradiation in bio-methane production

Bio-methane production from lignocellulosic biomass has been widely studied as a method of biomass conversion to bio-energy.

However, the recalcitrance nature of lignocellulosic biomass prevents accessibility of anaerobic microorganisms to convert the useable sugars. Therefore, a pretreatment of biomass is essential to increase the efficiency of downstream bio-methane production [62]. In a study conducted by Dong et al. [63], it was found that the use of dual frequency ultrasound combined with alkali pretreatment was able to enhance biogas production yield from corn stalk feedstock by 56.5% in comparison to untreated group. This phenomenon was observed due to the ultrasound capability in eroding the cell wall of corn stalk. Thus, allowing the organic matter to be in constant contact with anaerobic microorganism for higher reaction rate [63]. The higher biogas production rate was also observed by Lamb et al. [64]. It was found that the use of steam-explosion pretreatment followed by sequential ultrasonication was able to increase the rate of biogas production up to 77.26 mL/gVS/day in comparison to the control of 72.11 mL/gVS/day. The increase of biogas production rate was crucial to ensure a shorter retention time in a biogas process plant which led to an overall increase in biogas capacity without incurring extra capital cost to increase size of

Table 2

Type of ultrasound assisted pretreatment methods.

Chemical pretreatment	Lignocellulosic biomass	Ultrasonic parameter	Ultrasound assisted pretreatment	Key findings	Reference
Dilute acid pretreatment	Triarrhena lutarioriparia	Probe, 20 kHz, 200 W, 30 min,	Subsequent dilute acid pretreatment Solid loading = 1:10 (w/v) HCl concentration = 10% (w/v) Temperature = 120 °C Duration = 1 h	1. Sequential ultrasound and dilute acid pretreatment removed lignin content from 17.6% to 15.56% 2. Increased total reducing sugar from 79.4 mg/g to 111.2 mg/g	[38]
	Grass	100 W, duty cycle of 70%, 50 min, 80 °C	Simultaneous dilute acid pretreatment Solid loading = 1:10 (w/v) HCl concentration = 1.5%	1. Without ultrasound Delignification = 33% Combined pretreatment with ultrasound Delignification = 80.4% 2. FTIR and autofluorescence analyses revealed enhanced cellulose exposure	[39]
Alkaline	hardy sugar cane giant reed narrow-leaved cattail pink morning glory	Probe, 24 kHz, 400 W, 30 min	Simultaneous ultrasound assisted Alkaline pretreatment Solid loading = 1:20 (w/v) NaOH concentration = 0.5% (w/v)	1. Total lignin removal ranging from 80% to 85% 2. Ethanol and water extractives removed ranging from 75% to 85%	[28]
	Rice straw	Probe, 22 kHz, 300 W, 1 h	Simultaneous ultrasound assisted Alkaline pretreatment Solid loading = 1:20 (w/v) NaOH concentration = 1% (w/v)	1. Lignin% reduced from 8.33% to 4.6% 2. Use of heat dissipated from ultrasound was sufficient to achieve similar delignification as external heating	[44]
Alkaline hydrogen peroxide	Fique fibers Fique tow Fique pulp	Bath, 22 kHz, 130 W, 1 h, 40 °C	Subsequent ultrasound assisted Alkaline hydrogen peroxide pretreatment Solid loading = 1:10 (w/v) H ₂ O ₂ concentration = 2% pH = 11.5 Duration = 2 h Temperature = 70 °C	1. Highest lignin removal achieved was 88% for fique fibers and tow, while 79% for fique pulp 2. XRD analysis showed increased crystallinity index, while FTIR showed removal of both lignin and cellulose	[46]
	Sunn hemp	Bath, 50 Hz, 50 °C, 1 h	Simultaneous ultrasound assisted Alkaline hydrogen peroxide pretreatment Solid loading = 1:40 (w/v) H ₂ O ₂ concentration = 2%	1. Optimum condition reduced lignin% from 7.04% to 4.995% 2. Ultrasound reduced pretreatment duration from 5 h to 1 h	[47]
Ionic liquid	Rice straw	Bath, 70 °C, 1 h	Subsequent ionic liquid pretreatment Solid loading = 1:20 Duration = 15 min	1. Ultrasonication enhanced lignin removal of ionic liquid pretreatment by 18.06–19.33% 2. Enhanced total sugar recovery by 20.13–28.96%	[49]
	Eucalyptus saw dust	360 W, 60 °C, 30 min	Simultaneous ionic liquid pretreatment Solid loading = 1:10 (w/v) Solvent = 20% [TBA][OH] solution	1. Removed lignin from 26.3% to 15.38%, while increased cellulose from 41.35% to 53.07% 2. FTIR analysis showed violent delignification due to ultrasonication	[50]
Deep eutectic solvent	Oil palm frond	Cup horn, 70% amplitude, 30 min	Subsequent deep eutectic solvent pretreatment Solid loading = 1:10 (w/v) ChCl:Urea molar ratio = 1:2	1. Ultrasound assisted deep eutectic solvent achieved lignin removal of 36.42% while improving xylose recovery by 58% 2. Negative impact of excessive ultrasound irradiation due to aggregation of particles	[56]
	Pine sawdust	Bath, 42 kHz, 100 W, 3 h	Initial organosolv pretreatment Solid loading = 1:10 (w/v) Temperature = 190 °C Stirring speed = 400 rpm Duration = 4 h	1. Ultrasound pretreatment increased delignification efficiency marginally from 76.5% to 77.2%	[59]

the reactor. While there have been an abundant of research demonstrating the positive effect of ultrasound as a pretreatment for enhancing bio-methane production, there is a lack of research on ultrasound assisted anaerobic digestion. Simultaneous ultrasonication and anaerobic digestion might yield positive effect on the production of bio-methane by agitating the medium to ensure suspension of substrate [65].

3.4. Ultrasonication irradiation in bio-hydrogen production

The decomposition of organic material by microbes without the presence of light to produce bio-hydrogen is known as dark fermentation. The process of dark fermentation could be improved due to the breakdown of lignocellulosic biomass during the ultrasonic pretreatment. As shown in a study conducted by Wang et al. [66], corn stalk (CS) pretreated with ultrasound irradiation and sulphuric acid, when it was used as a substrate in bio-hydrogen production, was able to achieve specific hydrogen accumulation of $142.59 \text{ mLg}^{-1}\text{-CS}$ and hydrogen production rate of $17.03 \text{ mLg}^{-1}\text{-CS h}^{-1}$. The specific hydrogen accumulation and hydrogen production rate were 9.3 times and 6.1 times higher than the untreated corn stalk, respectively. The limiting factors in bio-hydrogen production are mainly dominated by substrate transport and bacterial activities. In the past studies, ultrasound was utilised as an auxiliary energy to overcome the limiting factors during fermentation. For example, Budiman et al. [67] found that the use of intermittent ultrasound irradiation during photo-fermentation was able to improve bio-hydrogen production rate up to $4.219 \text{ mL H}_2/\text{mL}_{\text{medium}} \text{ h}$. The significant increase in production rate might occur due to the enhancement in substrate transport and bacterial enzymatic activities. Furthermore, in a separate study conducted by Budiman and Wu [68], the use of ultrasound as a pretreatment step of effluents was able to improve bio-hydrogen production from 467 to 872.4 mL of H_2 . This phenomenon was observed due to ultrasound ability in enhancing solubilisation of organic matters in the combined effluents. This led to enhanced bacteria activity due to increase bioavailable substrates for bacteria to degrade.

3.5. Ultrasonication irradiation in lignocellulosic conversion to bio-ethanol

Bio-ethanol, or chemically known as ethyl alcohol is produced from the microorganism's fermentation of plant source sugar, such as glucose from cellulose. Lignocellulosic biomass could be valorised into fuel substitute through the following main steps: pretreatment of biomass, hydrolysis of polysaccharide, fermentation of sugars obtained, and purification of bio-ethanol produced [26].

3.5.1. Ultrasonication irradiation in enzymatic hydrolysis

Enzymatic hydrolysis of long chain polysaccharide into fermentable sugar is a crucial step in enabling bio-ethanol production. Conventional enzymatic hydrolysis presents multiple advantages such as mild operating condition, inherently safe process, as well as the absence of by-products. However, enzymatic hydrolysis has the disadvantage of requiring a long hydrolysis duration to achieve satisfactory level of sugar yield [69]. Multiple studies have been conducted to overcome such issues through the usage of auxiliary energy source. One of the up and coming technologies is the application of ultrasound during enzymatic hydrolysis.

In a study conducted by Subhedar and Gogate [70], the use of direct ultrasonication probe during enzymatic hydrolysis was able to achieve a total reducing sugar yield of 370.86 g/kg , in comparison to conventional mechanical stirring total reducing sugar yield of only 75.5 g/kg . The huge improvement in sugar yield could be contributed by ultrasound induced enhancement in activity of cellulase by modifying the shape of hydrolytic enzyme. Conformational changes in the enzyme molecule could be attributed to the generation of microturbulence and cavitation of microbubble during the ultrasonication.

The same result was also reported by Lunelli et al. [71], where ultrasound assisted hydrolysis of sugarcane bagasse increased the fermentable sugar yield by more than double when compared to unsonicated hydrolysis. Interestingly, in the same study conducted, the efficiency of ultrasound assisted enzymatic hydrolysis was found to be affected by moisture content. At high moisture content, the higher water content promoted excessive cavitation microbubble which resulted in a decrease of enzyme stability. However, at low moisture content, mass transfer in the medium was impeded which also resulted in lower hydrolysis efficiency. An intermediate moisture content was necessary to obtain an equilibrium between enzyme stability during the ultrasound irradiation and mass transfer effect within the system [71].

In a separate study on the application of ultrasound during enzymatic hydrolysis of *Parthenium hysterophorus*, the total reducing sugar yield achieved was 711.3 mg/g after 14 h of ultrasound assisted hydrolysis; whereas, unsonicated hydrolysis only managed to achieve a sugar yield of 593 mg/g after 96h [72]. Besides achieving an improvement of sugar yield by approximately 20%, the kinetics of enzymatic hydrolysis was found to have been enhanced by almost 6 times [72]. The enhancement of reaction kinetics was found to be contributed by the improved mass transfer of hydrolysis product into the bulk liquid. The diffusion of product in the medium reduced the probability of the product (glucose) from binding to the active site of enzyme (cellulase), resulting in an inhibition due to the competition [73]. Furthermore, during cavitation of microbubbles, the generation of intense microturbulence also enhanced the conversion of enzyme/substrate complex into the product. Thus, splitting the enzyme-substrate complex and allow the enzyme to bind with another substrate faster [72].

In a study conducted by Brahim et al. [74], it was found that the use of different irradiation pretreatments such as microwave, ultrasound and high voltage electrical discharge were able to improve enzymatic hydrolysis of rapeseed straw. It is interesting to note that the ultrasound pretreatment conducted at shorter duration and lower temperature was able to yield higher concentration of hydrolysed sugar in comparison to other irradiation techniques (Fig. 5). This result was in agreement to a past study done by Ong et al. [56], in which a severe ultrasound pre-treatment would result in a gentler collapse of microbubbles. Therefore, it is crucial to select a suitable irradiation technology based on operating condition.

3.5.2. Ultrasonication irradiation in fermentation to bio-ethanol

Ultrasound has been applied extensively to increase ethanol yield through the pretreatment of biomass [28,75–77], and in assisting hydrolysis of polysaccharide to fermentable sugar [25,78]. Ultrasound assisted fermentation has also been found to successfully enhance the ethanol yield (Table 3). In a study conducted by Borah et al. [79], it was found that an application of ultrasound during the fermentation of invasive weed feedstock was able to produce a total ethanol yield of 220 g/kg , while unsonicated fermentation only produced an ethanol yield of 147 g/kg . Furthermore, it was also reported that ultrasound assisted fermentation was able to reduce fermentation period by 50%, from 24 h to 12 h [79]. According to Neel et al. [80], fermentation was enhanced by ultrasound due to the factors such as desorption of CO_2 from the fermentation broth, alterations in the permeability of cell membrane and increase in mass transfer through the boundary layer from bulk liquid to the surface of yeast cell. The effect of rapid desorption of inhibitory CO_2 from the medium was found to have contributed to an increase in cell growth. Hence, increasing ethanol production by the yeast cell during the fermentation [81]. Besides, the ultrasound provided a more effective microstirring and, thus, might augment the effects of regular stirring. The stirring could help remove the ethanol from the yeast surface and facilitate the fermentation process. [80]. Fig. 6 shows the schematic diagram of yeast cell during the fermentation process.

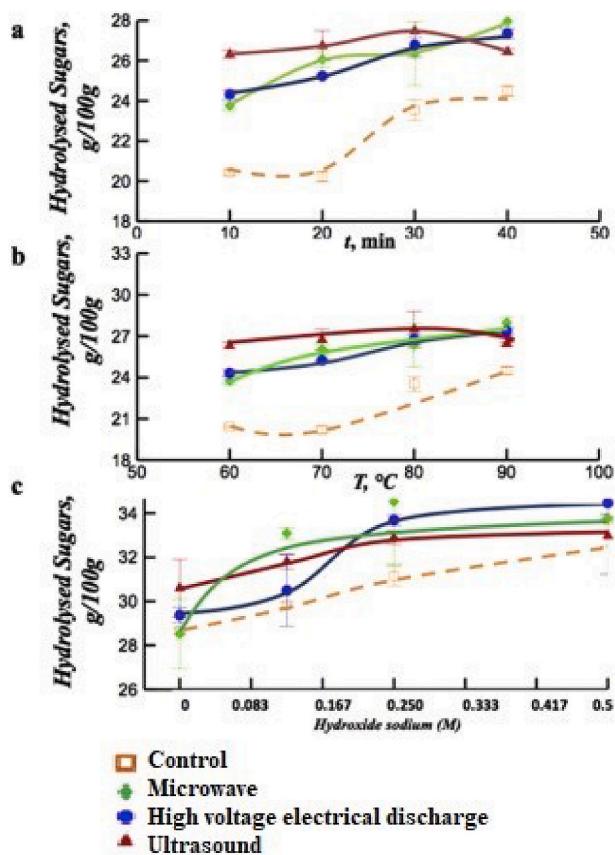


Fig. 5. Effect of various irradiation pretreatment on enzymatic hydrolysis of pretreated rapeseed straw with pretreatment condition of (a) $T = 60^{\circ}\text{C}$, $\text{NaOH} = 0\text{ M}$ (b) $t = 20\text{ min}$, $\text{NaOH} = 0\text{ M}$ and (c) $t = 20\text{ min}$, $T = 60^{\circ}\text{C}$.

Reprinted with permission from Brahim et al. [74]. Copyright 2016 Elsevier.

3.6. Ultrasonication irradiation in lignocellulosic conversion to bio-based product

The formation and extraction of bio-based product from lignocellulosic biomass will require specific condition and in the presence of chemical reagents. The incorporation of ultrasonication during organic reaction will allow greater efficiency of biomass conversion to fine chemicals. The enhancement is attributed to the mechanoacoustic and sonochemical effect produced during cavitation of bubbles.

The effectiveness of ultrasound was its ability to reduce the reaction condition required for a reaction to occur. In a study to produce furfural from rice husk, sugar cane straw, yerba-mate waste, grass and wood waste through ultrasound assisted acid hydrolysis, the highest furfural yield of 72.4 mg/g was obtained from grass under the mild condition of 30°C , 50% amplitude and 60 min of ultrasonication [83]. Interestingly, no furfural was produced when the reaction was repeated under the same condition by using mechanical stirring instead of ultrasonication. It was postulated that the use of ultrasound contributed for overcoming lignin barrier and allowed glucose protonation to produce 2,3 unsaturated aldehyde intermediate, and further reaction to produce furfural. Furthermore, the reaction was able to proceed under a mild condition due to the production of radicals and generation of intense heat and pressure during the cavitation of microbubbles [83]. Marullo et al. [84] investigated the transformations of fructose, glucose and sucrose into 5-hydroxymethylfurfural (5-HMF) through sonochemical activation in ionic liquid catalysed by HY zeolite. Comparable conversion of 5-HMF was obtained for both sonicated and unsonicated samples but the both reaction duration and temperature were reduced drastically from 5 h to 0.5 h, and from 80°C to 40°C after undergoing an ultrasonication. The

same study estimated a net reduction in energy consumption per mass of materials to be up to 99% when the reaction was performed under sonochemical activation [84]. Nomura et al. [85] found that the 19.5 kHz ultrasonic welding method could reduce the time of cellulose decomposition by an addition of cellulase. By adding cellulase in the welding process, cellulose from a filter paper was decomposed into glucose, 5-HMF, furfural, and oligosaccharides. Glucose was produced only when the cellulase was added. Although 5-HMF could be produced by using ultrasonic irradiation alone, the production of 5-HMF was further enhanced by adding cellulase at higher power of 200 W. [85]. Besides production of furanic derivatives, ultrasound has also been employed in the production of volatile fatty acid in grass clipping. The amount of volatile fatty acid produced from sonicated and unsonicated samples were 3.32 g/L and 1.64 g/L, respectively. The enhanced production of volatile fatty acid was due to ultrasound by disrupting the surface of biomass and creating erosion traces [86]. The disrupted structure promoted the accessibility of enzymes and microorganisms to the substrate within the biomass.

The mechanoacoustic effect of ultrasound has been found to be crucial in the production of nanocrystalline cellulose. The bonding inside cellulose polymer can be broken by a process known as solvo-dynamic shear. Solvo-dynamic shear is the nucleation, growth and collapse of microbubbles which will impose huge amount of mechanical and thermal energy on the cellulose fiber. The vigorous interaction between cellulose fiber and cavitation bubble will eventually disintegrate the fibers into smaller particle size [87]. According to Cui et al. [88], the application of ultrasound assisted enzyme hydrolysis technique was able to increase nanocrystalline cellulose yield from 17.58% to 22.57%. Also, the usage of ultrasound yielded nanocrystalline cellulose with higher crystallinity index. The higher crystallinity index is an important factor in determining the mechanical strength and thermal stability [88].

Ultrasound has also been utilised in assisting the extraction of fine chemicals from lignocellulosic biomass. Ultrasound assisted extraction of bioactive compound was found to be higher because of rupturing the matrix bond, increasing the solubility of the target compound, solvent diffusion rate, heat and mass transfer while reducing solvent viscosity [89]. In a study conducted by Lama-Muñoz et al. [89], the application of ultrasound was able to increase oleuropein and luteolin-7-glucoside extraction yield by 6.6% and 37.9%, respectively, when compared to conventional Soxhlet extraction method. Higher extraction yield was also observed by Corrales et al. [90], where the utilisation of ultrasound was able to increase the total phenolic compound recovery of grape by-products by two-fold in comparison to the control samples.

Recent application of ultrasound in various bio-based product synthesis and extraction demonstrated a wide range of usefulness. Each chemical reaction employs a different type of ultrasound working mechanism that enhances the reaction process. Through past studies, it was found that the synergy between ultrasound and the chemical reagent for reaction was able to enhance the product yield significantly (Table 4). Overall, ultrasound is a promising technique in lignocellulosic conversion to bio-based products because there are still countless number of bio-based fine chemical reactions that ultrasound has yet to be explored.

4. Advantages and disadvantages of ultrasound irradiation

In the present review, past studies utilising ultrasound integrated process have shown positive impact throughout the reaction course. During ultrasonication, the mechanoacoustic and sonochemical effect have various role in enhancing reactions throughout the biorefinery stages. During the pretreatment of biomass, the cavitation of microbubbles generate an intense stream of liquid which clean and remove wax layer, silica, and lignin from the surface of lignocellulose. This process is crucial in ensuring pretreatment solvent is delivered effectively to the surface of biomass for proper delignification process. The physical disruption of cavitation bubble also includes reduction in

Table 3

Ultrasonically assisted transformation of lignocellulosic biomass to bio-energy.

Bio-energy	Lignocellulosic biomass	Operation condition	Key findings	Reference
Bio-methane	Corn stalk	52 g of feedstock ultrasonicated in dual frequency sonoreactor (57 kHz/50 W and 20 kHz/50 W and 30 min) followed by 2% NaOH alkali pretreatment time of 36 h	1. Combined ultrasound and alkali pretreatment enhanced bio-gas yield by 56.5% in comparison to untreated biomass 2. The use of ultrasound as agitator during pretreatment increase net energy produced by 114.9% in comparison to shaker as agitator	[63]
Bio-methane	Birchwood	10 g of steam-exploded feedstock ultrasonicated in ultrasonic transducer (24 kHz, 30 W and 2 h) in 200 ml of pH 4 water	1. Steam explosion pretreatment with sequential ultrasound pretreatment was able to increase the rate of biogas production to 77.26 mL/gVS/day 2. Biogas production rates was found to be higher in milder ultrasound pretreatments in comparison to harsher sonication	[64]
Bio-hydrogen	Cornstalk	Feedstock ultrasonicated (25 kHz and 1.5 h) in 2.0% sulphuric acid solution at a liquid-solid ratio of 20:1	1. The specific hydrogen accumulation and hydrogen production rate were 9.3 times and 6.1 times higher than untreated cornstalk, respectively 2. Scanning electron microscope image of ultrasound pretreated biomass found to be more porous, which allowed acid pretreatment to penetrate deeper	[66]
Bio-hydrogen	Palm oil mill effluent Pulp and paper mill effluent	Fermentation broth ultrasonicated intermittently in ultrasound cuphorn (20 kHz, amplitude 20% and 10 min) at every hour for first 6 h of fermentation	1. The use of ultrasound was estimated to have a potential net saving of $\$4.05 \times 10^{-4}$ in comparison to unsonicated fermentation process 2. Excessive intermittent ultrasonication had adverse effect on bio-hydrogen production due to damage of bacterial cells	[67]
Bio-hydrogen	Palm oil mill effluent Pulp and paper mill effluent	Feedstock ultrasonicated in ultrasonic transducer (20 kHz, amplitude 70% and 45 min) as a pretreatment prior to fermentation	1. Ultrasound pretreatment enhanced bio-hydrogen production from 467 to 872.4 mL H ₂ 2. Increased of COD _{soluble} /COD _{total} from 0.25 to 0.85 implied more bioavailable substrate for bacteria activity	[68]
Bio-ethanol	Invasive weeds	50 ml of feedstock fermentation hydrolysate ultrasonicated in ultrasound bath (35 kHz, 35 W and 10% duty cycle) for 12 h	1. Total ethanol yield was increased from 147 g/kg to 220 g/kg after the implementation of ultrasound 2. Kinetics of pentose and hexose fermentation were enhanced by 2 fold after ultrasonication	[79]
Bio-ethanol	Defatted rice bran	Feedstock ultrasonicated in ultrasound bath (37 kHz, 132 W, 15 min and 50% duty cycle) for every 2 h for 10 h	1.60% of total bio-ethanol was produced after only ultrasound exposure during 4 h of fermentation 2. Ultrasound enhanced transport of nutrients and oxygen to yeast cell membrane, which led to improved microorganism growth	[82]

particle size to increase surface area for maximising contact with the pretreatment solvent. The extreme temperature generated during bubble collapse has also been cited to enhance the delignification rate. Furthermore, one study even found that heat dissipated from the cavitation bubble was sufficient to replace external heating during pretreatment process. This novel cost saving strategy is a step forward to a greener processing while increasing the competitiveness of bio-refineries. The sonochemical effect of ultrasound generates radicals which enhance delignification through disruption of intermolecular bond between lignin and cellulose. This effect is even more prevalent when alkaline hydrogen peroxide pretreatment is assisted with

ultrasound irradiation. Large amount of radicals are generated through the decomposition of H₂O₂, NaOH, and H₂O. During enzymatic hydrolysis, ultrasound enhances enzyme activity by modifying the shape of hydrolytic enzyme and increasing the rate of splitting of enzyme/substrate complex. The enhanced mass transfer ensures that hydrolysis product from the enzymatic activity will be diffused into bulk liquid. Hence, increasing the probability of substrate binding, while reducing competitiveness from products rebinding with the enzymes. In a fermentation process to produce bio-ethanol, cell growth of yeast is crucial to enhance the rate of production. Mild ultrasonication is able to promote cell growth through removal of inhibitory product from the

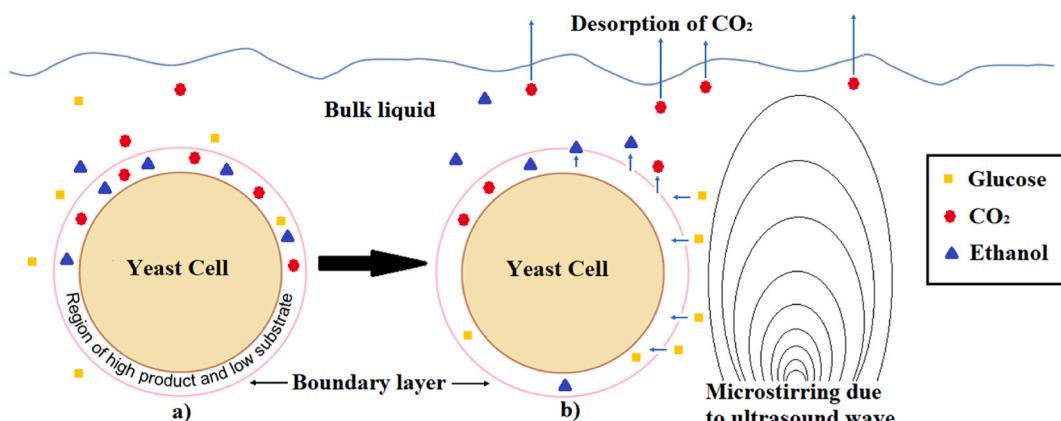
**Fig. 6.** Schematic diagram of yeast cell during fermentation: a) without ultrasound and b) with ultrasound.

Table 4

Ultrasonically assisted transformation of lignocellulosic biomass to bio-based products.

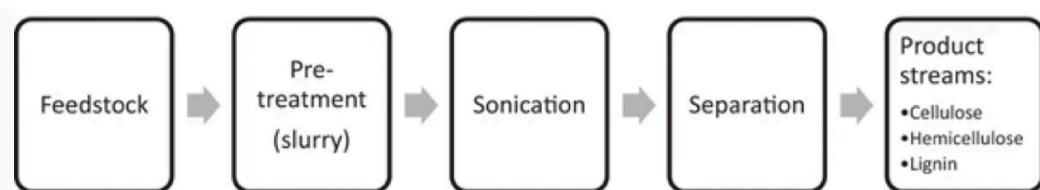
Bio-based product	Lignocellulosic biomass	Operation condition	Key findings	Reference
Furfural	Rice husk Sugar cane straw Yerba-mate waste Grass Wood waste	0.1 g feedstock ultrasonicated with cuphorn probe (50% amplitude and 60 min) in 4 mol L ⁻¹ of HNO ₃ at 30 °C	1. Production of 72.4 mg/g of furfural from grass feedstock 2. Absence of furfural production during mechanical stirring demonstrate sonochemical effect in promoting production of furfural at milder condition	[83]
5-HMF	Fructose Glucose Sucrose	50 mg of feedstock ultrasonicated with ultrasound probe in 1 g of [bmppip][Cl] _{0.5} [NTf ₂] _{0.5} ionic liquid with 100 mg of HY at 40 °C for 0.5 h	1. Reduced reaction time by 10-fold (0.5 h compared to 5 h) 2. Reduced reaction temperature from 80 °C to 40 °C 3. Net reduction of energy consumption per mass of materials processed of 99%	[84]
Furfural 5-HMF Glucose	Filter paper	200 mg of feedstock ultrasonicated with ultrasound probe (19.5 kHz, 200 W and 60 s) in 5 ml of pure water with cellulase as catalyst	1. Furfural dehydration step was successfully conducted in pure water and cellulase as catalyst 2. Use of ultrasound promoted glucose production rate from cellulose	[85]
Acetic acid Propionic acid Isobutyric acid Butyric acid	Grass clipping	Pretreatment: 2 g of feedstock ultrasonicated with ultrasonic cell crusher (25 kHz and 10 min) in 100 ml of Ca(OH) ₂ solution Volatile fatty acid production: 100 ml of biogas slurry was added to 100 ml of deionised water and placed in air-bath shaker for 12 d at 35 °C	1. US-Ca(OH) ₂ pretreated biomass produced greater volatile fatty acid during fermentation due to erosion of biomass surface	[86]
Nanocrystalline cellulose	Jute stalk	1 g of feedstock ultrasonicated (90 W and 35 min) in 20 ml of [EMIM] ⁺ Cl ⁻ at 90 °C	1. Mechanoacoustic effect of ultrasound disintegrated cellulose into smaller particle size 2. Ultrasound assisted the removal of lignin to produce high crystallinity index nanocrystalline cellulose	[87]
Oleuropein Luteolin-7-glucoside	Olive leaves	2 g of feedstock ultrasonicated in sonifier ultrasonic disruptor (40 kHz, 30% amplitude and 15 min) in 26 ml of 60% (v/v) ethanol-water solution at 40 °C	1. Enhanced extraction of oleuropein and luteolin-7-glucoside by 6.6% and 37.9%, respectively, in comparison to conventional method 2. Extraction time was significantly reduced from 4 h to 15 min	[89]
Anthocyanin Anthocyanin monoglucoside	Grape by-products	Feedstock ultrasonicated in ultrasonic bath (35 kHz and 1 h) in 50% (v/v) ethanol-water solution at 70 °C with a solid/liquid ratio of 1:4.5	1. Ultrasound assisted extraction yield two-fold higher total phenolic content 2. Ultrasound assisted extraction increased antioxidant content to 308.13 µmol TE g ⁻¹ DM in comparison to the control 187.13 µmol TE g ⁻¹ DM	[90]

fermentation. Microturbulence generated during cavitation has been found to increase desorption of CO₂ from the fermentation broth. Furthermore, an ultrasound enhances mass transfer, which contributes to cell growth through diffusion of ethanol (inhibitor to yeast cell) away from the boundary layer of yeast cell; while, glucose is able to diffuse more readily into the boundary layer.

The application of ultrasound in lignocellulose conversion is not limited to bio-ethanol production only. A reaction to produce bio-based product or fine chemical could be enhanced through an application of ultrasound. Generally, chemical reaction assisted by ultrasound is able to occur at milder condition and shorter duration. Consequently, promoting an inherently safer and greener process by reducing operation temperature, pressure and energy demand. Furthermore, the study conducted by Nomura et al. [85] showed that ultrasound irradiation alone was capable of converting cellulose to furanic derivatives. Thus, highlighting the potential of employing sonochemistry in a solvent free reaction to promote environmentally friendly chemical synthesis.

Although ultrasound generally increases the effectiveness of a pretreatment, ultrasound has limited contributions when the pretreatment is conducted in an organosolv pretreatment. This demonstrates that ultrasound is not a universal auxiliary energy for every pretreatment or

biomass valorisation method. Furthermore, energy used during ultrasonication might not be fully optimised for every reactor design. Hence, an optimisation of process parameters and reactor design is crucial to achieve a proper distribution of cavitational energy. Besides energy wastage during ultrasonication, economic competitiveness is also a major challenge in application of ultrasound in an industrial production. Production of bio-ethanol is met with huge competition due to the low cost of petroleum. However, this could be mitigated if biorefineries could fully valorise side products such as lignin to produce various fine chemicals such as furfural, 5-HMF, organic acids and phenolic compounds [91]. Thus, allowing biorefineries to profit from side products by venturing into the niche market. Additionally, it is also found that excessive severity of ultrasound energy is detrimental to the pretreatment process as the particles could aggregate to reduce pretreatment surface area. Excessive ultrasonication is also discouraged to prevent energy wastage and reduce manufacturing costs. Thus, there is a need to determine the optimised ultrasound condition, depending on the species of lignocellulosic biomass and purpose of the reaction. Lastly, cavitational activity is limited to a region that is close to the transducer probe. This limit the region of active cavitation which is detrimental to large scale production [35]. Hence, the advancement of properly designed

**Fig. 7.** Technology process model used during technoeconomic analysis of ultrasound assisted organosolv pretreatment [92].

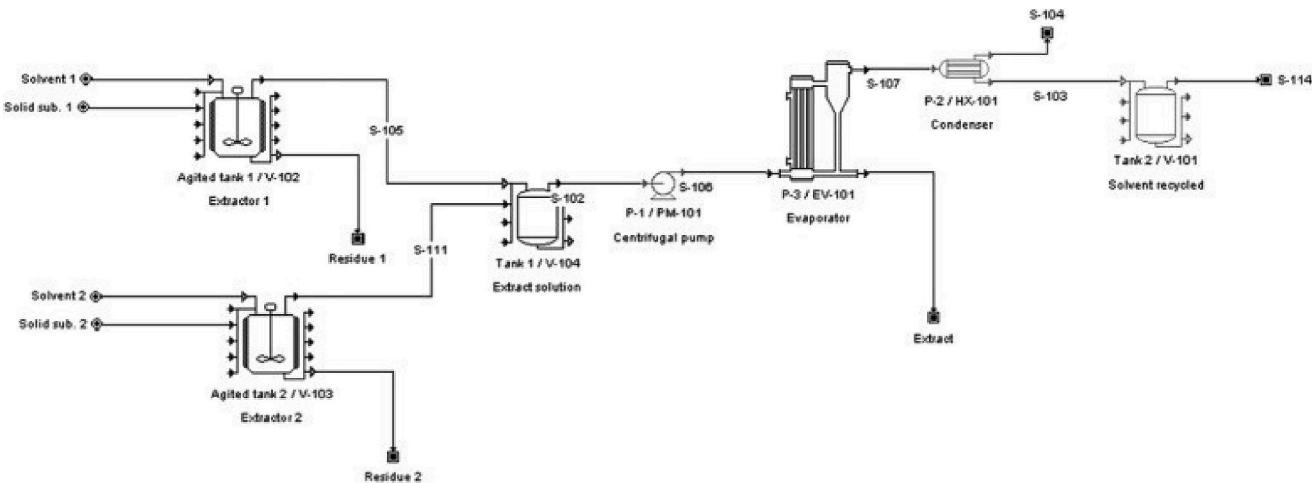


Fig. 8. Flowchart of ultrasound assisted extraction of jabuticaba skin (Ultrasonic transducers merged with tank). Reprinted with permission from Santos et al. [94]. Copyright 2010 Elsevier.

sonochemical reactor is important to fully realise the potential of using ultrasound in an industrial scale.

5. Technoeconomic analysis and socioeconomic impact of ultrasound assisted lignocellulosic biomass valorisation

Technoeconomic analysis is essential to ensure the viability of integrating ultrasound in the biorefineries. Furthermore, technoeconomic analysis provides a bigger picture on the operational and fixed cost bottlenecks of incorporating ultrasound technology in a large scale production. Once these key points are identified, it will assist future researchers in evaluating cost saving strategies and optimisation. In a case study conducted by Bussemaker et al. [92], lignocellulosic biomass was first subjected to organosolv pretreatment and followed by ultrasound pretreatment. After the pretreatment, the pretreated biomass was separated into liquid and solid stream. The solid stream rich in cellulose biomass was filtered out and dried for a subsequent processing, while the liquid stream rich in lignin and hemicellulosic sugars was further separated using aqueous and organic phase separation. The technology model was developed by Bio-Sep limited and was verified at a pilot scale (Fig. 7). The assumption made for the recovery of cellulose, hemicellulose and lignin was 98%, 72% and 94%, respectively and the product was valued at £2600, £1200 and £460, per ton respectively. The total fixed cost and an operational cost were estimated to be £753,000/year and £257/year/tonne, with a total heat and electrical energy usage of 634 kWh and 235 kWh, respectively. In the same technoeconomic analysis, 63% of the electrical cost was contributed by ultrasonic energy cost. As ultrasound technology is a relatively new technology, the high energy consumption could be due to the inefficiency and energy dissipation to the environment. This justifies the need for novel sonoreactor design to ensure successful scale up biorefineries application [93]. Furthermore, the technoeconomic analysis above identified that solvent recovery and further processing of lignocellulosic biomass for higher value product was crucial for the process to be economically feasible.

In a separate study conducted by Santos et al. [94], jabuticaba skin was subjected to ultrasound assisted extraction of phenolic compound to evaluate the economic benefits of ultrasound. In this study, the technoeconomic analysis simulation was conducted using SuperPro Designer 6.0® with the assumption that both laboratory and industrial scale up had the same performance. The detailed process flow is shown in Fig. 8. The manufacturing costs of crude extract for conventional Soxhlet extraction (acidified ethanol at pH 3) and ultrasound assisted extraction decreased significantly from US\$1001.00/kg to US\$401.21/kg, respectively. The high cost of conventional extraction method was found to be due to the long extraction time (8 h), which led to high expenses on

energy usage. Furthermore, this study reported that increasing capacity of ultrasound assisted extraction from 0.05 to 0.3 m³ was able to reduce manufacturing cost of crude extract from US\$794.46/kg to US \$401.21/kg, respectively. This phenomenon was observed due to the increase of production which led to a reduction of costs. Among all the extraction methods investigated, Santos et al. [94] found that the combined ultrasound assisted extraction and agitation bed extraction presented the smallest cost of manufacturing for the extract and for the phenolic compounds fraction. Therefore, ultrasound assisted extraction of fine chemicals could be a viable process due to increased production which reduced the portion of operational labour and capital investment cost.

The utilisation of ultrasound technology has the potential to reduce the operational cost by eliminating external heating, reducing the duration and enzyme usage for hydrolysis, and increasing yield of bio-ethanol [44,72,79]. However, for the lignocellulose derived fuel to be attractive, the cost of processing must be lower than the fossil fuel extraction. The economic competition faced by biorefineries in comparison to highly subsidised fossil fuel decreases incentives for researchers and organisation to improvise new innovation for biomass valorisation. Thus, policy changes are necessary for the continuation of research on lignocellulosic conversion and preventing further environmental crisis from burning of fossil fuel. Policy proposals such as direct subsidy could reduce the financial burden faced by biorefineries and incentivise more investors to capitalise on these green processes. Additionally, in a study conducted by Zhao et al. [95], it was proposed that tax preference should be implemented. For example, consumption tax for ethanol should be exempted, value added tax be refunded upon collection, and compulsory purchase of electricity from bio-ethanol plant by the grid. The implementation of policy favouring biorefineries could have unexpected positive externality. The commission of biorefineries will encourage the generation of green energy by various private sector, increase in employment opportunities, and increase the support for R&D in technologies related to greener productions. Furthermore, the substitution of fossil fuel by bio-energy will lead to a reduction in greenhouse gas pollution and exhaust emission, which will reduce the global climate change and improve the quality of life in a country [96].

While technoeconomic analysis is crucial to ensure the viability of implementing ultrasound technology in biorefineries, the amount of literature available is rather limited. This might discourage investors from capitalising into ultrasound assisted biorefineries due to the lack of economic analysis and statistical proofs, such as technoeconomic analysis. Furthermore, the technoeconomic analysis conducted by Bussemaker et al. [92] highlighted the costing and revenue stream of the

entire organosolv-ultrasound pretreatment process. However, the analysis above did not take into account of subsequent processes such as enzymatic hydrolysis, fermentation to bio-ethanol and the valorisation of lignin into more valuable product. Hence, a holistic techno-economic analysis for ultrasound processing should include analysis on the type of ultrasound assisted processes for every stage of biorefinery. Besides, techno-economic analysis conducted by Santos et al. [94] explored the possibility of utilising ultrasound in obtaining fine chemicals. However, the assumption that both industrial and laboratory scale ultrasonic equipment will perform at the same level should be avoided due to scaling up limitations. Industrial scaled ultrasonic processor might face limitations such as non-uniform distribution of energy intensity or inability to achieve the required amplitude. These phenomena will lead to an inefficient conversion of energy, which will ultimately increase the manufacturing cost. Thus, a pilot scale will have to be conducted to further strengthen the claim of techno-economic analysis that ultrasound assisted extraction is more economically competitive than conventional Soxhlet extraction. Lastly, various policies should be implemented to ensure the viability of ultrasound assisted biorefineries. Although the change in policy might not be economically feasible in a short term, the long term benefits such as environmental preservation, generation of clean renewable energy, and green job creation should be included as part of valuation of policy.

6. Future prospect of ultrasound irradiation in lignocellulosic biomass transformation

Ultrasound irradiation has shown significant advantages as an auxiliary energy to promote pretreatment and conversion of lignocellulosic biomass. Ultrasound effects such as mechanoacoustic and sonochemical are able to intensify pretreatment, shorten reaction duration, reduce operation condition, and enhance production of bio-energy or bio-based product. Although ultrasound could be useful to improve the process of lignocellulosic transformation, there are several challenges that need to be addressed. The major bottleneck for ultrasound technology lies in difficulty of scaling up from a laboratory to an industrial scale. Furthermore, the positive effect of ultrasound varied with respect to the type of lignocellulosic biomass and process. Thus, future research could include computer simulation to provide a more comprehensive model that could be used to predict the viability of various ultrasound assisted process. Pilot plants will need to be commissioned to prove the effectiveness of sonoreactors in biorefineries. In addition, a holistic techno-economic and cost benefit analysis will need to be conducted to ensure ultrasound technology is economically sustainable. Furthermore, future techno-economic analysis should also include economists to ensure every aspect that might influence the economic feasibility of ultrasound technology is fully covered [97]. Therefore, a multidisciplinary group will be required to fully realise the potential of using ultrasound in industrial scale biorefineries.

7. Conclusion

This review highlights the various applications of ultrasound in lignocellulosic biomass pretreatment, production of biofuel, and synthesis of fine chemicals. The limitations in fully valorising lignocellulose are the costly pretreatment process, high energy demand and efficiency in biomass conversion. Based on the past research, ultrasound was shown to be fully capable of addressing the common issues faced by biorefineries. Furthermore, ultrasound has shown promising potential due to its flexibility in adjusting irradiation condition to suit various biosynthesis process. The mechanoacoustic and sonochemical effect from cavitation bubble has been able to promote reaction kinetics while reducing severity of reaction. However, the drawbacks from applying ultrasound in large scale production are the efficiency of ultrasonication and cost of operation. Furthermore, excessive ultrasound is found to be detrimental to certain reaction condition. Hence, more in depth

technoeconomic studies have to be conducted to provide greater understanding on the feasibility of ultrasound in large scale biorefineries. Through techno-economic analysis, the application of ultrasound in a pretreatment is still not viable due to the factors such as inefficiency and cost of separation of products. However, the transition to a civilisation powered by renewable source of energy will provide many positive externalities that will benefit mankind as a whole. Therefore, archaic policy which still favours the use of fossil fuel should be gradually replaced with policy and incentives that will assist in the growth of biorefineries.

Credit author statement

Victor Zhenquan Ong – Conceptualization; Investigation; Writing - Original Draft. Ta Yeong Wu – Conceptualization; Supervision; Project administration; Funding acquisition; Writing - Review & Editing.

Declaration of competing interest

None.

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References

- [1] Ritchie H, Roser M. Energy. <https://ourworldindata.org/energy>. [Accessed 2 April 2020].
- [2] British Petroleum. BP statistical review of world energy. 2019. <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf>. [Accessed 2 April 2020].
- [3] Kucharska K, Rybarczyk P, Holowacz I, Lukajtis R, Glinka M, Kaminski M. Pretreatment of lignocellulosic materials as substrates for fermentation processes. *Molecules* 2018;23(11).
- [4] Severo IA, Siqueira SF, Deprá MC, Maroneze MM, Zepka LQ, Jacob-Lopes E. Biodiesel facilities: what can we address to make biorefineries commercially competitive? *Renew Sustain Energy Rev* 2019;112:686–705.
- [5] Mohammed NI, Kabbashi N, Alade A. Significance of agricultural residues in sustainable biofuel development. In: Aladjadiyan A, editor. Agricultural waste and residues. Intechopen; 2018.
- [6] Yusriah L, Sapuan SM, Zainudin ES, Mariatti M. Underutilized malaysian agro-wastes fiber as reinforcement in polymer composites: potential and challenges. *J Polym Mater* 2012;29(2):201–16.
- [7] Yatin P, Lin NS, Lam HL, Choy EA. Overview of the key risks in the pioneering stage of the Malaysian biomass industry. *Clean Technol Environ Policy* 2017;19(7): 1825–39.
- [8] Ofori-Boateng C, Lee KT. Sono-assisted organosolv/H₂O₂ pretreatment of oil palm (*Elaeis guineensis* Jacq.) fronds for recovery of fermentable sugars: optimization and severity evaluation. *Fuel* 2014;115:170–8.
- [9] Chen W-H, Ye S-C, Sheen H-K. Hydrolysis characteristics of sugarcane bagasse pretreated by dilute acid solution in a microwave irradiation environment. *Appl Energy* 2012;93:237–44.
- [10] Loow YL, Wu TY, Yang GH, Jahim JM, Teoh WH, Mohammad AW. Role of energy irradiation in aiding pretreatment of lignocellulosic biomass for improving reducing sugar recovery. *Cellulose* 2016;23(5):2761–89.
- [11] Langholtz MH, Stokes BJ, Eaton LM. Billion ton report: advancing domestic resources for a thriving bioeconomy, vol. 1. Economic Availability of Feedstocks; 2016. <http://energy.gov/eere/bioenergy/2016-billion-ton-report>. [Accessed 2 April 2020].
- [12] Ahorsu RF, Medina Constantí M. Significance and challenges of biomass as a suitable feedstock for bioenergy and biochemical production: a review. *Energies* 2018;11(12).
- [13] Dhyan V, Bhaskar T. Chapter 9 - pyrolysis of biomass. In: Pandey A, Larroche C, Dussap C-G, Gnansounou E, Khanal SK, Ricke S, editors. Biofuels: alternative feedstocks and conversion processes for the production of liquid and gaseous biofuels. second ed. Academic Press; 2019. p. 217–44.
- [14] Kulasiński K, Keten S, Churakov SV, Derome D, Carmeliet J. A comparative molecular dynamics study of crystalline, paracrystalline and amorphous states of cellulose. *Cellulose* 2014;21(3):1103–16.

- [15] Ravindran R, Jaiswal AK. A comprehensive review on pre-treatment strategy for lignocellulosic food industry waste: challenges and opportunities. *Bioresour Technol* 2016;199:92–102.
- [16] Sannigrahi P, Pu Y, Ragauskas A. Cellulosic biorefineries—unleashing lignin opportunities. *Curr Opin Environ Sustain* 2010;2(5):383–93.
- [17] Sorek N, Yeats TH, Szemeyei H, Youngs H, Somerville CR. The implications of lignocellulosic biomass chemical composition for the production of advanced biofuels. *Bioscience* 2014;64(3):192–201.
- [18] Sun SN, Cao XF, Xu F, Sun RC, Jones GL, Baird M. Structure and thermal property of alkaline hemicelluloses from steam exploded *Phyllostachys pubescens*. *Carbohydr Polym* 2014;101(1):1191–7.
- [19] Duval A, Lawoko M. A review on lignin-based polymeric, micro- and nano-structured materials. *React Funct Polym* 2014;85:78–96.
- [20] Iiyama K, Lam TBT, Stone BA. Covalent cross-links in the cell wall. *Plant Physiol* 1994;104(2):315.
- [21] Zhang YHP. Reviving the carbohydrate economy via multi-product lignocellulose biorefineries. *J Ind Microbiol Biotechnol* 2008;35(5):367–75.
- [22] Agarwal A, Rana M, Park JH. Advancement in technologies for the depolymerization of lignin. *Fuel Process Technol* 2018;181:115–32.
- [23] Menon V, Rao M. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. *Prog Energy Combust* 2012;38(4):522–50.
- [24] Kuna E, Behling R, Valange S, Chatel G. Sonocatalysis: a potential sustainable pathway for the valorization of lignocellulosic biomass and derivative. *Top Curr Chem* 2017;375:41.
- [25] Subhedar PB, Ray P, Gogate PR. Intensification of delignification and subsequent hydrolysis for the fermentable sugar production from lignocellulosic biomass using ultrasonic irradiation. *Ultrason Sonochem* 2017;40:140–50.
- [26] Bundhoo ZMA, Mohee R. Ultrasound-assisted biological conversion of biomass and waste materials to biofuels: a review. *Ultrason Sonochem* 2018;40:298–313.
- [27] Zhang W, Liu J, Wang Y, Sun J. Effect of ultrasound on ionic liquid-hydrochloric acid pretreatment with rice straw. *Biomass Conserv Bior* 2020.
- [28] Muthuvelu KS, Rajarathnam R, Kanagaraj LP, Ranganathan RV, Dhanasekaran K, Manickam NK. Evaluation and characterization of novel sources of sustainable lignocellulosic residues for bio-ethanol production using ultrasound-assisted alkaline pre-treatment. *Waste Manag* 2019;87:368–74.
- [29] Guo X, Zhang T, Shu S, Zheng W, Gao M. Compositional and structural changes of corn cob pretreated by electron beam irradiation. *ACS Sustainable Chem Eng* 2017;5(1):420–5.
- [30] Cantero D, Jara R, Navarrete A, Pelaz L, Queiroz J, Rodríguez-Rojo S, Cocero MJ. Pretreatment processes of biomass for biorefineries: current status and prospects. *Annu Rev Chem Biomol Eng* 2019;10(1):289–310.
- [31] Singh R, Krishna BB, Kumar J, Bhaskar T. Opportunities for utilization of non-conventional energy sources for biomass pretreatment. *Bioresour Technol* 2016;199:398–407.
- [32] Liu Y, Nie Y, Lu X, Zhang X, He H, Pan F, Zhou L, Liu X, Ji X, Zhang S. Cascade utilization of lignocellulosic biomass to high-value products. *Green Chem* 2019;21(13):3499–535.
- [33] Mudhoo A, Torres-Mayanga PC, Forster-Carneiro T, Sivagurunathan P, Kumar G, Komilis D, Sánchez A. A review of research trends in the enhancement of biomass-to-hydrogen conversion. *Waste Manag* 2018;79:580–94.
- [34] Alvira P, Tomás-Pejó E, Ballesteros M, Negro MJ. Pretreatment technologies for an efficient bio-ethanol production process based on enzymatic hydrolysis: a review. *Bioresour Technol* 2010;101(13):4851–61.
- [35] Luo J, Fang Z, Smith Jr RL. Ultrasound-enhanced conversion of biomass to biofuels. *Prog Energy Combust Sci* 2014;41(1):56–93.
- [36] Yang G, Wang J. Ultrasound combined with dilute acid pretreatment of grass for improvement of fermentative hydrogen production. *Bioresour Technol* 2019;275:10–8.
- [37] Noparat P, Prasertsan P, O-Thong S, Pan X. Dilute acid pretreatment of oil palm trunk biomass at high temperature for enzymatic hydrolysis. *Energy Procedia* 2015;79:924–9.
- [38] Tao X, Li J, Zhang P, Nabi M, Jin S, Li F, Wang S, Ye J. Reinforced acid-pretreatment of *Triarrhena lutarioriparia* to accelerate its enzymatic hydrolysis. *Int J Hydrogen Energy* 2017;42(29):18301–8.
- [39] Mohapatra S, Dandapat SJ, Thatoi H. Physicochemical characterization, modelling and optimization of ultrasono-assisted acid pretreatment of two *Pennisetum* sp. using Taguchi and artificial neural networking for enhanced delignification. *J Environ Manag* 2017;187:537–49.
- [40] Loow Y-L, Wu TY, Md Jahim J, Mohammad AW, Teoh WH. Typical conversion of lignocellulosic biomass into reducing sugars using dilute acid hydrolysis and alkaline pretreatment. *Cellulose* 2016;23(3):1491–520.
- [41] Curreli N, Agelli M, Pisut B, Rescigno A, Sanjust E, Rinaldi A. Complete and efficient enzymic hydrolysis of pretreated wheat straw. *Process Biochem* 2002;37(9):937–41.
- [42] Curreli N, Fadda MB, Rescigno A, Rinaldi AC, Soddu G, Sollai F, Vaccariu S, Sanjust E, Rinaldi A. Mild alkaline/oxidative pretreatment of wheat straw. *Process Biochem* 1997;32(8):665–70.
- [43] Kim JS, Lee YY, Kim TH. A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. *Bioresour Technol* 2016;199:42–8.
- [44] Wu H, Dai X, Zhou SL, Gan YY, Xiong ZY, Qin YH, Ma J, Yang L, Wu ZK, Wang TL, Wang WG, Wang CW. Ultrasound-assisted alkaline pretreatment for enhancing the enzymatic hydrolysis of rice straw by using the heat energy dissipated from ultrasonication. *Bioresour Technol* 2017;241:70–4.
- [45] Ho MC, Ong VZ, Wu TY. Potential use of alkaline hydrogen peroxide in lignocellulosic biomass pretreatment and valorization – a review. *Renew Sustain Energy Rev* 2019;112:75–86.
- [46] Ovalle-Serrano SA, Blanco-Tirado C, Combariza MY. Exploring the composition of raw and delignified Colombian fique fibers, tow and pulp. *Cellulose* 2018;25(1):151–65.
- [47] Baksi S, Saha S, Birgen C, Sarkar U, Preisig HA, Markussen S, Wittgens B, Wentzel A. Valorization of lignocellulosic waste (*Crotalaria juncea*) using alkaline peroxide pretreatment under different process conditions: an optimization study on separation of lignin, cellulose, and hemicellulose. *J Nat Fibers* 2019;16(5):662–76.
- [48] Cheng F, Sun J, Wang Z, Zhao X, Hu Y. Organosolv fractionation and simultaneous conversion of lignocellulosic biomass in aqueous 1,4-butanediol/acidic ionic-liquids solution. *Ind Crop Prod* 2019;138.
- [49] Han Y, Chang K, Qiu X, Liu Z, Wang X, Chen X, Deng H, Laddawan P, Huang J. Study on ultrasound assisted ionic liquid-hydrochloric acid pretreatment process for rice straw. *Huanjing Kexue Xuebao/Acta Scientiae Circumstantiae* 2018;38(1):283–90.
- [50] Wang Z, Hou X, Sun J, Li M, Chen Z, Gao Z. Comparison of ultrasound-assisted ionic liquid and alkaline pretreatment of *Eucalyptus* for enhancing enzymatic saccharification. *Bioresour Technol* 2018;254:145–50.
- [51] Liu L, Ju M, Li W, Hou Q. Dissolution of cellulose from AFEX-pretreated *Zoysia japonica* in AMIMCl with ultrasonic vibration. *Carbohydr Polym* 2013;98(1):412–20.
- [52] Ninomiya K, Kamide K, Takahashi K, Shimizu N. Enhanced enzymatic saccharification of kenaf powder after ultrasonic pretreatment in ionic liquids at room temperature. *Bioresour Technol* 2012;103(1):259–65.
- [53] Loow Y-L, New EK, Yang GH, Ang LY, Foo LY, Wu TY. Potential use of deep eutectic solvents to facilitate lignocellulosic biomass utilization and conversion. *Cellulose* 2017;24(9):3591–618.
- [54] Plechкова NV, Seddon KR. Applications of ionic liquids in the chemical industry. *Chem Soc Rev* 2008;37(1):123–50.
- [55] Malaeke H, Housaindokht MR, Monhemti H, Izadyar M. Deep eutectic solvent as an efficient molecular liquid for lignin solubilization and wood delignification. *J Mol Liq* 2018;263:193–9.
- [56] Ong VZ, Wu TY, Lee CBTL, Cheong NWR, Shak KPY. Sequential ultrasonication and deep eutectic solvent pretreatment to remove lignin and recover xylose from oil palm fronds. *Ultrason Sonochem* 2019;58:104598.
- [57] Alio MA, Tugui O-C, Vial C, Pons A. Microwave-assisted Organosolv pretreatment of a sawmill mixed feedstock for bio-ethanol production in a wood biorefinery. *Bioresour Technol* 2019;276:170–6.
- [58] Brahim M, Checa Fernandez BL, Regnier O, Boussetta N, Grimi N, Sarazin C, Husson E, Vorobiev E, Brosse N. Impact of ultrasounds and high voltage electrical discharges on physico-chemical properties of rapeseed straw's lignin and pulps. *Bioresour Technol* 2017;237:11–9.
- [59] Xu C, Liao B, Shi W. Organosolv pretreatment of pine sawdust for bio-ethanol production. *Green Energy Technol* 2013:435–57.
- [60] Yang B, Wyman CE. Pretreatment: the key to unlocking low-cost cellulosic ethanol. *Biofuels*, Bioprod Bioref 2008;2(1):26–40.
- [61] Loow YL, Wu TY, Tan KA, Lim YS, Siow LF, Jahim J Md, Mohammad AW, Teoh WH. Recent advances in the application of inorganic salt pretreatment for transforming lignocellulosic biomass into reducing sugars. *J Agric Food Chem* 2015;63(38):8349–63.
- [62] Vivekanand V, Olsen EF, Eijsink VGH, Horn SJ. Effect of different steam explosion conditions on methane potential and enzymatic saccharification of birch. *Bioresour Technol* 2013;127:343–9.
- [63] Dong C, Chen J, Guan R, Li X, Xin Y. Dual-frequency ultrasound combined with alkali pretreatment of corn stalk for enhanced biogas production. *Renew Energy* 2018;127:444–51.
- [64] Lamb JJ, Islam MH, Hjelme DR, Pollet BG, Lien KM. Effect of power ultrasound and Fenton reagents on the bio-methane potential from steam-exploded birchwood. *Ultrason Sonochem* 2019;58:104675.
- [65] Lindmark J, Thorin E, Fdhila RB, Dahlquist. Effects of mixing on the result of anaerobic digestion: Review. *Renew Sustain Energy Rev* 2014;40:1030–47.
- [66] Wang H, Zhi Z, Wang J, Ma S. Comparison of various pretreatment methods for bio-hydrogen production from cornstalk. *Bioproc Biosyst Eng* 2012;35(7):1239–45.
- [67] Budiman PM, Wu TY, Ramantan RN, Jahim J Md. Improving photofermentative bio-hydrogen production by using intermittent ultrasonication and combined industrial effluents from palm oil, pulp and paper mills. *Energy Convers Manag* 2017;132:110–8.
- [68] Budiman PM, Wu TY. Ultrasonication pre-treatment of combined effluents from palm oil, pulp and paper mills for improving photofermentative bio-hydrogen production. *Energy Convers Manag* 2016;119:142–50.
- [69] Sun Y-C, Xu J-K, Xu F, Sun R-C. Structural comparison and enhanced enzymatic hydrolysis of eucalyptus cellulose via pretreatment with different ionic liquids and catalysts. *Process Biochem* 2013;48(5):844–52.
- [70] Subhedar PB, Gogate PR. Enhancing the activity of cellulase enzyme using ultrasonic irradiations. *J Mol Catal B Enzym* 2014;101:108–14.
- [71] Lunelli FC, Sfalcin P, Souza M, Zimmermann E, Dal Prá V, Foletto EL, Jahn SL, Kuhn RC, Mazutti MA. Ultrasound-assisted enzymatic hydrolysis of sugarcane bagasse for the production of fermentable sugars. *Biosyst Eng* 2014;124:24–8.
- [72] Singh S, Agarwal M, Bhatt A, Goyal A, Moholkar VS. Ultrasound enhanced enzymatic hydrolysis of *Parthenium hysterophorus*: a mechanistic investigation. *Bioresour Technol* 2015;192:636–45.
- [73] Holtzapple MT, Caram HS, Humphrey AE. The HCH-1 model of enzymatic cellulose hydrolysis. *Biotechnol Bioeng* 1984;26(7):775–80.
- [74] Brahim M, Kantar SE, Boussetta N, Grimi N, Brosse N, Vorobiev E. Delignification of rapeseed straw using innovative chemo-physical pretreatments. *Biomass Bioenergy* 2016;95:92–8.

- [75] Terán Hilares R, Kamoei DV, Ahmed MA, da Silva SS, Han J-I, Santos JCd. A new approach for bio-ethanol production from sugarcane bagasse using hydrodynamic cavitation assisted-pretreatment and column reactors. *Ultrason Sonochem* 2018; 43:219–26.
- [76] Sharma V, Nargotra P, Bajaj BK. Ultrasound and surfactant assisted ionic liquid pretreatment of sugarcane bagasse for enhancing saccharification using enzymes from an ionic liquid tolerant Aspergillus assutensis VS34. *Bioresour Technol* 2019.
- [77] Chang K-L, Han Y-J, Wang X-Q, Chen X-M, Leu S-Y, Liu J-y, Peng Y-P, Liao Y-L, Potprommanee L. The effect of surfactant-assisted ultrasound-ionic liquid pretreatment on the structure and fermentable sugar production of a water hyacinth. *Bioresour Technol* 2017;237:27–30.
- [78] John I, Pola J, Appusamy A. Optimization of ultrasonic assisted saccharification of sweet lime peel for bio-ethanol production using Box-Behnken method. *Waste Biomass Valorization* 2019;10(2):441–53.
- [79] Borah AJ, Agarwal M, Goyal A, Moholkar VS. Physical insights of ultrasound-assisted ethanol production from composite feedstock of invasive weeds. *Ultrason Sonochem* 2019;51:378–85.
- [80] Neel PI, Gedanken A, Schwarz R, Sendersky E. Mild sonication accelerates ethanol production by yeast fermentation. *Energy Fuels* 2012;26(4):2352–6.
- [81] Sulaiman AZ, Ajit A, Yunus RM, Chisti Y. Ultrasound-assisted fermentation enhances bio-ethanol productivity. *Biochem Eng J* 2011;54(3):141–50.
- [82] Stobienia M, Kalschne DL, Peron-Schlosser B, Colla LM, Baraldi IJ, Colla E. Evaluation of ultrasound waves on *S. cerevisiae* stimulation in the bio-ethanol production from rice bran. *Bioenergy Res* 2020;10:1–11.
- [83] Buzzi CA, Santos D, Sieben TC, Motta GV, Mello PA, Flores EMM. Furfural production from lignocellulosic biomass by ultrasound-assisted acid hydrolysis. *Ultrason Sonochem* 2019;51:332–9.
- [84] Marullo S, Rizzo C, Meli A, D'Anna F. Ionic liquid binary mixtures, zeolites, and ultrasound irradiation: a combination to promote carbohydrate conversion into 5-Hydroxymethylfurfural. *ACS Sustainable Chem Eng* 2019;7(6):5818–26.
- [85] Nomura S, Wakida K, Mukasa S, Toyota H. Catalytic effect on ultrasonic decomposition of cellulose. *Jpn J Appl Phys* 2018;57(7).
- [86] Wang S, Tao X, Zhang G, Zhang P, Wang H, Ye J, Li F, Zhang Q, Nabi M. Benefit of solid-liquid separation on volatile fatty acid production from grass clipping with ultrasound-calcium hydroxide pretreatment. *Bioresour Technol* 2019;97:104.
- [87] Chowdhury ZZ, Hamid SBA. Preparation and characterization of nanocrystalline cellulose using ultrasonication combined with a microwave-assisted pretreatment process. *BioResources* 2016;11(2):3397–415.
- [88] Cui S, Zhang S, Ge S, Xiong L, Sun Q. Green preparation and characterization of size-controlled nanocrystalline cellulose via ultrasonic-assisted enzymatic hydrolysis. *Ind Crop Prod* 2016;83:346–52.
- [89] Lama-Muñoz A, Del Mar Contreras M, Espínola F, Moya M, Romero I, Castro E. Optimization of oleuropein and luteolin-7-o-glucoside extraction from olive leaves by ultrasound-assisted technology. *Energies* 2019;12(13).
- [90] Corrales M, Toepfl S, Butz P, Knorr D, Tauscher B. Extraction of anthocyanins from grape by-products assisted by ultrasonics, high hydrostatic pressure or pulsed electric fields: a comparison. *Innovat Food Sci Emerg Technol* 2008;9(1):85–91.
- [91] Zhou CH, Xia X, Lin C-X, Tong D-S, Beltramini J. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem Soc Rev* 2011;40(11): 5588–617.
- [92] Bussemaker MJ, Day K, Drage G, Cecelja F. Supply chain optimisation for an ultrasound-organosolv lignocellulosic biorefinery: impact of technology choices. *Waste Biomass Valori* 2017;8(7):2247–61.
- [93] Bussemaker MJ, Zhang D. Effect of ultrasound on lignocellulosic biomass as a pretreatment for biorefinery and biofuel applications. *Ind Eng Chem Res* 2013;52 (10):3563–80.
- [94] Santos DT, Veggi PC, Meireles MAA. Extraction of antioxidant compounds from Jabuticaba (*Myrciaria cauliflora*) skins: yield, composition and economical evaluation. *J Food Eng* 2010;101(1):23–31.
- [95] Zhao L, Zhang X, Xu J, Ou X, Chang S, Wu M. Techno-economic analysis of bio-ethanol production from lignocellulosic biomass in China: dilute-acid pretreatment and enzymatic hydrolysis of Corn Stover. *Energies* 2015;8:4096–117.
- [96] Kandasamy MK, Hamawand I, Bowtell L, Seneweera S, Chakrabarty S, Yusaf TF, Shakor Z, Algayyim S, Eberhard F. Investigation of ethanol production potential from lignocellulosic material without enzymatic hydrolysis using the ultrasound technique. *Energies* 2017;10.
- [97] Van Dael M, Kuppens T, Lizin S, Passel SV. Techno-economic assessment methodology for ultrasonic production of biofuels. In: Fang Z, Smith Jr R, Qi X, editors. Production of biofuels and chemicals with ultrasound. Dordrecht: Springer; 2014. p. 317–45.